Influence of defect structure and external pressure on optical properties of ions with d$^3$ type electronic structure (Cr$^{3+}$ and Mn$^{4+}$) in selected oxide crystals

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A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Physics

Thesis supervisor: Prof. Dr. hab. Andrzej Suchocki

December 2007
Dedication

This work is dedicated to my family.

To my parents for their unconditional support during my postgraduate studying and confidence in my abilities.

To my wife Liuba for tolerance, patience and love.

To my little daughter Julia. May this work serve as an encouragement in her efforts, whatever the goals would be.
Acknowledgements

I would like to express my deepest respect and most sincere gratitude to my supervisor, Prof. Andrzej Suchocki, for his guidance and encouragement at all stages of my work. His constructive criticism and comments from the beginning to the end of this work is highly appreciated. His careful editing contributed enormously to the production of this thesis.

I am very grateful to Prof. L. Arizmendi and Prof. F. Jaque for their kind cooperation and the samples of lithium niobate.

My deep appreciation goes to Dr. Agata Kamińska who helped me to obtain practical skills in high-pressure measurements using DAC and for assistance in experimental work.

I thank Dr. D. Galančiak for cooperation in research work on GGG:Mn, YAG:Nd and YAlO₃:Mn materials.

I also wish to thank all my colleagues, both past and present, from the ON 4 division of Institute of Physics, PAS, for their assistance, which was very helpful during work on this thesis.

Serhiy Kobyakov
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Chapter 1

Thesis layout

The subject of this work is a study of some properties of d^3 type dopants in popular optical crystals: gallium gadolinium garnet (Gd$_3$Ga$_5$O$_{12}$), yttrium aluminium perovskite (YAlO$_3$) and lithium niobate (LiNbO$_3$). These crystals are used extensively in many optical applications in modern industry.

The gallium gadolinium garnet (often abbreviate as GGG) is a colourless synthetic material with good thermal, mechanical and optical properties. It is used as a substrate for magneto-optical films and as a diamond simulant. The GGG is also a good material for magnetic bubble memory [1]. Another perspective application of the GGG is an active medium for solid-state lasers [2, 3, 4]. Rare earth doped (Nd and Er) garnets show good laser generation characteristics [5, 2, 6]. Nd, Cr-doped GGG crystals are characterized by improved laser efficiency and perform as a self-Q-switched laser material [4, 7]. Manganese doped GGG is a suitable material for tunable lasers [8].

Yttrium orthoaluminate, often called yttrium aluminium perovskite (YAP), is a synthetic material with excellent optical, magnetic, electric and piezoelectric properties. The most important application of YAP is the solid-state laser host material [9, 3, 4]. Cerium doped YAP is a fast scintillator material used in X-ray and synchrotron experiments [10, 11]. Manganese doped YAP has been shown to be suitable material for holographic data storage at elevated temperatures [12, 13, 14], laser light optical limiters [15] and a good thermoluminescence dosimetry phosphor for a high-dose dosimetry of ionizing radiation [16, 17]. It was also shown recently that the YAlO$_3$:Mn is a good phosphor for fibre optic fluorescence thermometers [18].

The dopants with d^3 structure of the outer shell create optically active centers in these crystals. When substituted for cations, surrounded by coordinated ligands, the centers energy structure is described by Tanabe-Sugano diagrams [19], and depends on symmetry of the cation site, number of the ligands and strength of the established bonds. For the same dopant, these parameters would vary from host to host, therefore created optical centers would also vary in their properties.

Very powerful method in investigation of the centers properties is the high-pressure measurements, because the application of external pressure change the interatomic di-
tances, which in turn change the properties of optical centers. With the use of Diamond 
Anvil Cell (DAC), it is possible to observe changes in the centers energy structure in situ. 
This method is also very helpful in identification of optical centers.

The first aim of this work is to obtain new information about properties of the Mn$^{4+}$ 
centers in GGG and YAP under application of external pressure.

The Mn$^{4+}$ centers in the YAP produce luminescence in the same spectral region where 
the ruby R-lines are observed. Since the ruby is used as a pressure sensor in high-pressure 
measurements, a new sensor, namely YAG:Nd, has been proposed for pressure estimation.

The lithium niobate is a very popular material in non-linear optics. It possesses an 
excellent optical transmission along with unique combination of electro-optical, acoustic, 
piezoelectric, pyroelectric and non-linear optical properties making it an extremely versa-
tile non-linear crystal material. It is the material of choice for the manufacture of the 
number of acoustic, electro-optical and non-linear optical devices. Owing to cheap pro-
duction of big crystals and easy tailoring their properties to the wide range of photonic 
applications, lithium niobate is one of the most used dielectric materials today [20]. Since 
then, the thorough information about the defect chemistry of lithium niobate is essential 
for tailoring the properties of this crystal to different optical applications.

It was published recently that some of the optical centers, created by chromium in 
lithium niobate, are bleachable under laser illumination whereas the rest of the chromium 
centers are stable [21]. These preliminary results shown that the photobleachable cen-
ters are related to the chromium substituted for niobium ions with (possibly) another 
perturbing defect in close proximity [22].

Further study of photobleachable chromium centers, obtaining detailed information 
about the bleaching process and its correlation with the niobium polarons is the second 
aim of this work.

A number of different optical experiments, including photoluminescence, light-induced 
optical absorption, thermoluminescence and paramagnetic resonance, have been planned 
and carried out to solve the stated problems. While the results of lithium niobate in-
vestigation are in preparation for publication, the rest are published in:

1. Ya. Zhydachevskii, D. Galanciak, S. Kobyakov, M. Berkowski, A. Kamińska, A. Su-
   chocki, Ya. Zakharko, A. Durygin Photoluminescence studies of Mn$^{4+}$ ions in YAlO$_3$ 
crystals at ambient and high pressure J. Phys.: Condens. Matter 18 (49), 11385 
(2006);

2. S. Kobyakov, D. Galanciak, A. Kamińska, A. Suchocki, M. Malinowski Nd$^{3+}$-doped 
Yttrium Aluminium Garnet crystal as a near-infrared pressure sensor for diamond 
anvil cells Appl. Phys. Lett. 88, 234102 (2006);

3. D. Galanciak, M. Grinberg, W. Gryk, S. Kobyakov, A. Suchocki, G. Boulon, A. Bre-
nier Influence of high pressure on the luminescence transitions of Mn$^{4+}$-doped gadolin-
ium gallium garnet J. Phys.: Condens. Matter 17, 7185-7197 (2005);
Chapter 2

Fundamentals

2.1 Transition metal ions in solids

Transition metals are the group of elements situated between the s- and p-elements in the periodic table. They have incomplete d subshell along with partially or completely filled higher s subshell, which defines their peculiar properties such as ferromagnetism, paramagnetism, and an ability to form metal complexes.

In ionic solids the transition metals of iron group loose the outer 4s electrons and possibly some 3d electrons when forming ionic bonds, and as a result, their outer shell configuration becomes 3d\textsuperscript{n} [23]. The valence electrons in transition metals are present in more than one subshell, so such elements can (and actually do) exhibit several oxidation states. Some common ionic states of the transition metal ions are presented in table 2.1.

Table 2.1: Commonly found ionic states of the iron group transition metals and the corresponding number of electrons in the 3d subshell [23].

<table>
<thead>
<tr>
<th>Ions</th>
<th>Number of electrons in the 3d subshell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti\textsuperscript{3+}</td>
<td>V\textsuperscript{4+}</td>
</tr>
<tr>
<td>V\textsuperscript{3+}</td>
<td>Cr\textsuperscript{4+}</td>
</tr>
<tr>
<td>V\textsuperscript{2+}</td>
<td>Cr\textsuperscript{3+}</td>
</tr>
<tr>
<td>Cr\textsuperscript{2+}</td>
<td>Mn\textsuperscript{3+}</td>
</tr>
<tr>
<td>Mn\textsuperscript{2+}</td>
<td>Fe\textsuperscript{3+}</td>
</tr>
<tr>
<td>Fe\textsuperscript{2+}</td>
<td>Co\textsuperscript{3+}</td>
</tr>
<tr>
<td>Fe\textsuperscript{+}</td>
<td>Co\textsuperscript{2+}</td>
</tr>
<tr>
<td>Co\textsuperscript{+}</td>
<td>Ni\textsuperscript{2+}</td>
</tr>
<tr>
<td>Ni\textsuperscript{+}</td>
<td>Cu\textsuperscript{2+}</td>
</tr>
</tbody>
</table>

The ions with incomplete 3d subshells have a number of low-energy levels, between which optical transitions can occur. The energies of the optical transitions lay in the visible and near infrared optical regions. Owing to this, the transition metals form optically active
centers in semiconductors and wide bandgap crystals.

The 3d electrons of the transition metals in solids do not form a complete electronic subshell and are coupled strongly with the nearby ions via Coulomb interaction. This usually leads to a strong influence of the crystal field on their optical properties in comparison with a weak influence experienced by rare-earth ions [23].

The charge transfer (CT) transitions of the 3d ions, in which an electron is transferred between the cation and a neighbouring ligand, occur in the ultraviolet region and give rise to very strong absorption bands.

The only properties of the 3d$^3$ ions, in particular Cr$^{3+}$ and Mn$^{4+}$, in octahedral crystal field symmetry would be considered in this work.

### 2.1.1 d$^3$ ions in octahedral crystal field

Spectral lines of free ions (can be observed in ionized gas) correspond to transitions between discrete energy levels of the ions. The energy structure in Russel-Saunders coupling approximation is described by distinct electronic configurations called "terms". In this theory, the Coulomb interaction between the valence electrons is assumed to be greater than the spin-orbit interaction, which is an adequate approximation for light transition metals of the iron group. Each term is then noted by the symbol $^{2S+1}L$ where $S$ is the resultant spin quantum number of a valence electrons system, $L$ is the total orbital angular momentum quantum number and $2S + 1$ is the multiplicity of the term.

For example, chromium has electronic configuration [Ar]3d$^5$4s$^1$. The commonly found ionized chromium has the 3d$^3$ configuration of the outer electronic subshell. The lower-energy terms of this ion and their energies are presented in table 2.2.

<table>
<thead>
<tr>
<th>Terms</th>
<th>Energy (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2$F</td>
<td>$\sim36,700$</td>
</tr>
<tr>
<td>$^2$H</td>
<td>$\sim21,200$</td>
</tr>
<tr>
<td>$^2$D</td>
<td>$\sim20,400$</td>
</tr>
<tr>
<td>$^2$G</td>
<td>$\sim15,200$</td>
</tr>
<tr>
<td>$^2$P</td>
<td>$\sim14,200$</td>
</tr>
<tr>
<td>$^4$P</td>
<td>$\sim14,200$</td>
</tr>
<tr>
<td>$^4$F</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.2: The lower-energy terms of the free Cr$^{3+}$ ion and their energies [19].

When ion is embedded in a solid, its energy structure is modified by the non-spherical electric field (crystal field) of the neighbouring ions (ligands). Arrangement of ligands defines symmetry of crystal field. The 3d$^3$ ions are mostly found in octahedral crystal field symmetry [19].

The energy structure of ion in certain symmetry of crystal field is also described by
set of terms, but these terms, of cause, differ from those of a free ion. The crystal field
strength and its symmetry must be considered when deriving the ion energy structure.

The crystal field theory was the first attempt to describe some properties of the coordi-
nation complexes. It was developed by applying group theory and quantum mechanics
to the electrostatic interaction between the central ion and the ligands [24]. This theory
gives a satisfactory picture of chemical, kinetic and some magnetic properties of the
complexes as well as the energy structure of the central ion.

In the ligand field theory, the basics of the crystal field theory are combined with
the theory of the molecular orbitals. Therefore, the ligand field theory can in addition
describe the bonding properties between the central ion and the ligands and more ade-
quately describes energy structure of the central ions in complexes [25]. Though the ligand
field theory is more adequate than the crystal field one, some simplifications have been
made nevertheless. Frequently, no spin-orbit or electron-lattice interaction are considered,
therefore the theory show limited agreement in some experimental aspects.

The table 2.3 illustrates the terms energy of a free 3d\(^3\) ion as a function of the Racah
parameters and splitting of the terms in the octahedral crystal field. The new terms are
classified by irreducible representations of the \(O_h\) symmetry group [23].

Table 2.3: The Russell-Saunders term energies for d\(^3\) configuration and splitting of the
free-ion levels in an octahedral crystal field [23].

<table>
<thead>
<tr>
<th>LS term energies</th>
<th>Splitting into octahedral field terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^2\text{F} = 3A + 9B + 3C)</td>
<td>(^2\text{A}_2 + ^2\text{T}_1 + ^2\text{T}_2)</td>
</tr>
<tr>
<td>(^2\text{H} = 3A - 6B + 3C)</td>
<td>(^2\text{E} + ^2\text{T}_1 + ^2\text{T}_2)</td>
</tr>
<tr>
<td>(a^2\text{D} = 3A + 5B + 5C + \alpha)</td>
<td>(^2\text{E} + ^2\text{T}_2)</td>
</tr>
<tr>
<td>(b^2\text{D} = 3A + 5B + 5C - \alpha)</td>
<td>(^2\text{E} + ^2\text{T}_2)</td>
</tr>
<tr>
<td>(^2\text{G} = 3A - 11B + 3C)</td>
<td>(^2\text{A}_1 + ^2\text{E} + ^2\text{T}_1 + ^2\text{T}_2)</td>
</tr>
<tr>
<td>(^2\text{P} = 3A - 6B + 3C)</td>
<td>(^2\text{T}_1)</td>
</tr>
<tr>
<td>(4\text{P} - 3A)</td>
<td>(^4\text{T}_1)</td>
</tr>
<tr>
<td>(4\text{F} = 3A - 15B)</td>
<td>(4\text{A}_2 + 4\text{T}_1 + 4\text{T}_2)</td>
</tr>
</tbody>
</table>

where \(\alpha = (193B^2 + 8BC + 4C^2)^{1/2}\)

The only energy differences between terms are obtained in experimental studies. Thus,
the common summand 3A is ignored and the only \(B\) and \(C\) Racah parameters are of
interest [23].

Diagrams of the d\(^n\) ions energy structure in octahedral symmetry as a function of
the crystal field have been obtained by Tanabe and Sugano [19]. In the diagrams,
the energy of the ground term is set to zero and the energies of all other terms are shown
with respect to the ground term. Each intersection with a vertical line for a given value
of the crystal field \(Dq\) gives the energy of a particular term. This way the diagrams
predict the absorption and luminescence properties of d\(^n\) ions using purely theoretical
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Figure 2.1: The energy diagram of a 3\textsuperscript{d} ion in the octahedral crystal field, assuming that C/B = 4,8 (appropriate for Cr\textsuperscript{3+} in Al\textsubscript{2}O\textsubscript{3}) [23].

...considerations, and allow to estimate the strength of the crystal field, experienced by an ion, from experimental results.

The diagram for d\textsuperscript{3} ions in octahedral symmetry is shown in Fig. 2.1. The C/B ratio is usually around 4,5 for the valence electrons of d\textsuperscript{3} ions in octahedral crystal field [23].

The 4\textsuperscript{T}_1, 4\textsuperscript{T}_2 \leftrightarrow 4\textsuperscript{A}_2 transitions are allowed and strongly phonon-coupled. In absorption and luminescence they produce rather wide bands with FWHM in order of a few thousands cm\textsuperscript{-1}.

The 2\textsuperscript{E} \leftrightarrow 4\textsuperscript{A}_2 transitions are spin-forbidden and can only occur due to spin-orbit interaction. They are weakly phonon-coupled and therefore seen in absorption and luminescence as a very narrow lines with FWHM in order of a few or a few tens cm\textsuperscript{-1}.

If the ligand’s octahedron is distorted from its ideal shape, the 2\textsuperscript{E} term can be further splitted into two sublevels 2\textsuperscript{A} and 2\textsuperscript{E} due to combined effect of spin-orbit coupling and trigonal field. Accordingly, two narrow lines are seen in the absorption and luminescence. They were first observed in luminescence of ruby, and therefore labelled as R\textsubscript{1} and R\textsubscript{2} (the 2\textsuperscript{A} \leftrightarrow 4\textsuperscript{A}_2 and 2\textsuperscript{E} \leftrightarrow 4\textsuperscript{A}_2 transitions respectively). Usually, only the R\textsubscript{1} line is observed at liquid helium (LH) temperatures. The R\textsubscript{2} line becomes visible at elevated temperatures owing to thermal population of the 2\textsuperscript{A} level. The value of 2\textsuperscript{E} level splitting is usually equal to a few tens cm\textsuperscript{-1}. The FWHM of the ruby R-lines are less than 2 cm\textsuperscript{-1} at LH temperatures [23].

The combination of spin-orbit coupling and trigonal field also cause the splitting of 4\textsuperscript{A}_2 ground term, but this splitting is much lower than that of 2\textsuperscript{E} level, and usually is less than one cm\textsuperscript{-1}.

On the basis of the diagram, d\textsuperscript{3} centers can be classified to the weak-crystal-field and...
strong-crystal-field ones. The weak-crystal-field centers have the $^4T_2$ as the first excited level, and the strong-crystal-field ones – the $^2E$ level. Therefore, the two types of d$^3$ optical centers are differ in experimental studies by wide or narrow spectral bands, respectively.

It was shown in [26] that the d$^3$ terms energies can be calculated using the formulas:

$$E (^4A_2 \to ^4T_2) = 10Dq$$

$$x = \frac{[E (^4A_2 \to ^4T_2) - E (^4A_2 \to ^4T_1)]}{Dq}$$

$$Dq/B = 15(x - 8)/(x^2 - 10x)$$

$$E (^4A_2 \to ^2E) = 3.05C + 7.9B - 1,8B^2/Dq$$

### 2.1.2 Nephelauxetic effect

Under application of external pressure the distances between ligands and the central ion decrease and the crystal field is increased in its magnitude. The Racah parameters of the central ion are decreased due to increase of overlap of the central ion and ligands wave functions. The decrease of the Racah parameters in comparison with their free-ion values due to increased covalency of interatomic bonds is called nephelauxetic effect [27].

The nephelauxetic effect reveals itself as a redshift of the R-lines luminescence with increase of external pressure instead of the blueshift predicted by the Tanabe-Sugano diagram (see Fig. 2.1).

The quantitative model of the nephelauxetic effect, based on the Harrison theory of bonding [28], has been recently published in [29] and [30]. A short description of the model is given below.

The wave function of the central ion is reduced due to mixing with ligands wave functions, thus giving $\psi_d = (1 - a)\psi_{3d}/2$, where $a$ is the polarity parameter and $\psi_{3d}$ is the wave function of unperturbed ion. The $a$ is given by:

$$a = \frac{V_3}{\sqrt{V_2^2 + V_3^2}}$$

where $V_2 = \eta h^2/m_e R_0^2$ is the covalent energy, $\eta$ is a dimensionless coefficient, $m_e$ is the electron mass, $R_0$ is the distance between the central ion and ligands, $V_3 = (\epsilon_s - \epsilon_p)/2$ is the polar energy, which is a function of the Herman-Skillman potentials $\epsilon$ [31] for the appropriate atoms participating in the bonds. The coefficient $\eta$ is used as an adjustable parameter in calculations.

The covalent energy $V_2$ increases with the applied pressure due to decrease of the interatomic distances. The dependence of the distances on the applied pressure is described by the Murnaghan equation of state [32]:

$$\frac{R_0}{R_p} = \left( \frac{pB'_0}{B_0} + 1 \right)^{1/3}$$
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where $B_0$, $B'_0$ is the bulk modulus and its pressure derivative of the solid and $p$ is the applied pressure.

Since the $B$ Racah parameter is the average over $\psi_d$ of the two electron repulsion energy operator, it scales with pressure as

$$B_p = B \left( \frac{1 + a_p}{1 + a} \right)^2 \tag{2.4}$$

where $a$ and $a_p$ is the polar coefficients for ambient and a given pressures respectively.

It is supposed that the $B/C$ ratio does not change with pressure, therefore the $C$ Racah parameter is scaled with pressure in the same manner.

The crystal field parameter $Dq$ is given by

$$Dq = \frac{\langle r^4 \rangle Z e^2}{3 R_0^5} \tag{2.5}$$

where $e$ is the elementary charge, $Z$ is the charge number, $\langle r^4 \rangle$ is the expected value of the $r^4$ orbital radius operator.

The average $\langle r^4 \rangle$ is scaled as

$$\langle r^4 \rangle_p = \langle r^4 \rangle \left( \frac{1 + a_p}{1 + a} \right) \tag{2.6}$$

The quadratic dependence of the $B$ and $C$ on the $(1 + a_p)$ comes from the fact that they are proportional to the Slater integrals $P^k$, which are, in turn, proportional to the fourth power of d wave functions, in contrast to the $\langle r^m \rangle$ values that are proportional to the square of d wave functions $[19]$.

The values of the parameter $\eta$ for $sp$, $sp^2$ and $sp^3$ bonds are expected to be around 3.2 $[28]$. It is then possible to apply the theory to the experimental data, using the equations 2.1.

This model has been successfully applied for interpretation of the experimental high-pressure studies of LiNbO$_3$:Cr$^{3+}$ $[29]$ and YAG:Cr$^{3+}$ $[30]$ crystals.
2.2 Polarons

2.2.1 Introduction

A slowly moving electron in polarizable medium induces its local deformation by the Coulomb interaction (Fig. 2.2). This local arrangement, caused by the electron, in turn forms a potential well around it. The potential well hampers carrier movement changing its mobility. Moving through the crystal, the electron “drags” the polarization with it and this can be considered as a cloud of phonons accompanying the carrier.

Such self-consistent system is treated in physics as a single entity – a quasiparticle named polaron. The possibility of self-trapped carrier state was first mentioned by L. D. Landau in 1933 in attempt to explain the optical properties of alkali halides [33]. Further development of the concept was made by S. I. Pekar in 1951 [34], and the term ”polaron” was proposed by him in 1946 [35].

Owing to the interaction with phonons, the physical properties of self-trapped electron differ from those of the free electron. As the result of polaron creation, the total energy of the electron-lattice system is reduced, and this energy gain is considered as the energy of the polaron creation (stabilization, dissociation energy or self-energy). Since the lattice deformation must move for polaron to move, a polaron’s effective mass is in general greater than that of a free electron.

Polarons have spin just as electrons do. Two interacting polarons are spinless, and such arrangement is treated as a single entity named bipolaron.

There are two types of polarons depending on their spatial extension of lattice polarization: large and small. Large polarons are spread to several or several tenth of lattice constants. They are created when long-range Coulomb interaction (sometimes called Fröhlich interaction, see next subchapter) between the carrier and lattice plays important role in formation of the quasiparticle. Small polarons are confined within only a single lattice site and formed due to short-range electron-lattice interaction.

Fundamental differences between the large and small polarons result in optical spectra with distinguishing features. The transport properties also differ markedly. These differences permit large and small polarons absorption bands to be distinguished from one another. Here only the basic features of large and small polarons are presented.
2.2.2 Large polarons

The general model of the large polaron was elaborated by Herbert Fröhlich in 1954 [36]. He introduced Hamiltonian, describing interaction between a charge carrier and the long-wavelength optical phonons:

\[ H = \frac{p^2}{2m_b} + \sum_k \hbar \omega_{LO} a_k^\dagger a_k + \sum_k (V_k a_k e^{ikr} + h.c.) \]  

(2.7)

where \( p \) is a canonical momentum operator, \( m_b \) is a band mass of the carrier, \( a_k^\dagger \) and \( a_k \) are the creation and annihilation operators for LO optical phonons of wave vector \( k \) and energy \( \hbar \omega_{LO} \), \( V_k \) are the Fourier components of the electron-phonon interaction and \( h.c. \) is the Hermitian conjugate of the first term inside the round brackets. The first summand represents kinetic energy of a free electron, second – the energy of phonons and the third describes the electron-phonon interaction.

This model describes so-called large polarons because of the large spatial extension of carrier-phonon interaction. Such polarons are also seen in the literature as Fröhlich polarons or Landau-Fröhlich polarons.

The \( V_k \) are given by

\[ V_k = -i \frac{\hbar \omega_{LO}}{k} \left( \frac{4 \pi \alpha}{V} \right)^{\frac{1}{2}} \left( \frac{\hbar}{2m_b \omega_{LO}} \right)^{\frac{1}{4}} \]  

(2.8)

\[ \alpha = \frac{e^2}{\hbar c} \left( \frac{m_b c^2}{2 \hbar \omega_{LO}} \right)^{\frac{1}{2}} \left( \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0} \right) \]  

(2.9)

where \( \alpha \) is the Fröhlich coupling constant (dimensionless), \( \varepsilon_\infty \) and \( \varepsilon_0 \) are the electronic and static dielectric constants of the continuum respectively.

The coupling constant \( \alpha \) describes the strength of the electron-phonon interaction. Two carrier-phonon coupling regimes are distinguished, leading to the different calculation of the ground state energy of the polaron. In weak coupling regime (\( \alpha \ll 1 \)) charge carrier interacts weakly with the phonons. In strong coupling regime (\( \alpha \gg 1 \)) charge carrier is bonded strongly to the phonons, which theoretically can even lead to its localization. Both approximations were examined by Pekar [34] and Fröhlich [36].

The Fröhlich coupling constants for selected materials are given in table 2.4.

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha )</th>
<th>Material</th>
<th>( \alpha )</th>
<th>Material</th>
<th>( \alpha )</th>
<th>Material</th>
<th>( \alpha )</th>
</tr>
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<tbody>
<tr>
<td>InSb</td>
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<td>ZnSe</td>
<td>0,43</td>
<td>KI</td>
<td>2,5</td>
<td>CdF(_2)</td>
<td>3,2</td>
</tr>
<tr>
<td>InAs</td>
<td>0,052</td>
<td>CdS</td>
<td>0,53</td>
<td>TiBr</td>
<td>2,55</td>
<td>KCl</td>
<td>3,44</td>
</tr>
<tr>
<td>GaAs</td>
<td>0,068</td>
<td>AgBr</td>
<td>1,53</td>
<td>KBr</td>
<td>3,05</td>
<td>CsI</td>
<td>3,67</td>
</tr>
<tr>
<td>GaP</td>
<td>0,20</td>
<td>AgCl</td>
<td>1,84</td>
<td>RbI</td>
<td>3,16</td>
<td>SrTi(_3)</td>
<td>3,77</td>
</tr>
<tr>
<td>CdTe</td>
<td>0,29</td>
<td>Al(_2)O(_3)</td>
<td>2,40</td>
<td>Bi(<em>{12})SiO(</em>{20})</td>
<td>3,18</td>
<td>RbCl</td>
<td>3,81</td>
</tr>
</tbody>
</table>

Table 2.4: Fröhlich coupling constants for selected materials [37].
In strong coupling regime the stabilization energy and the effective mass of large polaron are given by

\[ E_0 = -\frac{\alpha^2}{9\pi} \hbar \omega_{LO} = -0.0354\alpha^2 \hbar \omega_{LO} \quad m^* = m_b \left( 1 + 0.0200\alpha^4 \right) \] (2.10)

In weak coupling regime

\[ E_0 = -\alpha \hbar \omega_{LO} \quad m^* = \frac{m_b}{1 - \alpha/6} \] (2.11)

The more sophisticated treatment of the large polaron was given by Feynman in [38], where he described the polaron problem using path integral. In this approach, the polaron model was formulated as equivalent one-particle problem, eliminating the phonon field. Applying the variation principle for path integrals, Feynman obtained a smooth interpolation between weak and strong coupling regimes. This model of the polaron remains the most successful approach to the polaron problem in theoretical physics.

A free large polaron generally moves coherently. Since the electron-lattice interaction is extended over several lattice sites, the self-trapped electron can continuously adjust to alterations of the atomic positions and thereby move between sites. Thus, the coherent motion of a free large polaron is associated with classical motion of atoms. The large polarons move in the crystal with relatively high mobilities \( \mu > 1 \text{ cm}^2/\text{Vs} \) that fall with increasing temperature [39].

The photoionization of a large polaron is considered as an excitation of a self-trapped carrier from the ground state in the potential well to the continuum of unbound states (see Fig. 2.3). After that, the carrier can move to the next lattice site and relax again with the formation of the polaron.

The large polaron absorption coefficient [39] is given by

\[ \alpha = \frac{128 \pi e^2}{3 m \omega_c} \left( \frac{k R}{1 + (k R)^2} \right)^4 \] (2.12)

where \( k \) is a wave vector of photoionized carrier: \( k \equiv \sqrt{2m(\hbar \omega - 3E_p)}/\hbar \), \( R \) is the radius of the polaron, \( E_p \) is the polaron stabilization energy and \( \omega \) – photon frequency.

Photoionization of the large polarons produce temperature-independent absorption band that begins when the photon energy exceeds three times the large polaron stabilization energy (Fig. 2.4) [39]. This band is asymmetric with more broad high-energy side. As the size of the large polaron is reduced, the peak of its absorption band shifts to the higher energies.
Figure 2.4: The frequency dependence of the absorption coefficient for photoionization of a large polaron plotted against photon energy, assuming that $T = 0 \, \text{K}$ [39].

It should be noted that by absorbing a phonon the trapped carrier could rise to excited bound state (such states are shown as dashed lines in Fig. 2.3). This intrapolaron transitions are not as intense as the photoionization ones due to the selection rules [39].

### 2.2.3 Small polarons

For some materials, the Fröhlich model is not appropriate since the lattice polarization, induced by carrier, is extended to the length of the lattice constant only. To describe the situation, Holstein proposed the molecular crystal model in which the energy of a charge carrier depends only on the deformation of the molecule that it occupies [40, 41]. Distinctly from the large polaron, the carrier forming small polaron tends to be localized at only one lattice site.

Holstein showed that both thermal and optical transport properties of the small polarons could be explained considering only two of the equivalent localization sites [41]. A very nice interpretation of this model was given by Bogomolov et al. in [42] and Faust et al. in [43].

The interaction energy of a carrier with crystal lattice can be approximated by $E_{\text{int}} = -Fq$ where $q$ is a coordinate representing the distortion of near surroundings and $F$ is the force that the carrier exerts on the lattice. The elastic energy is given by $E_{\text{elast}} = \frac{1}{2}Kq^2$. From this, the small polaron stabilization energy is derived as $E_{P}(q_{\text{min}}) = -\frac{F^2}{2K}$.

The polaron stabilization energy is also called "formation" or "dissociation" energy or the self-energy of the polaron. The total energy of the electron-lattice system is lowered
by $E_P$ owing to the formation of a polaron, or in other words, $E_P$ is the energy necessary to take a self-trapped electron off the potential well to the infinity.

Considering only two of the equivalent localization sites, namely 1 and 2, the total energy of the system can be written as

$$E_{tot} = E_1 + E_2 = \frac{K}{2} (q_1^2 + q_2^2) - F(n_1 q_1 + n_2 q_2)$$

(2.13)

where $n_1 = 1$ and $n_2 = 0$ if the carrier is localised at site 1 and vice versa if it is at the site 2. Taking into account that $n_1 + n_2 = 1$ and after introduction $q = q_1 - q_2$ and $Q = q_1 + q_2$ the equation 2.13 is transformed to

$$E_{tot} = \frac{K}{4} (q^2 + Q^2) - (n_1 - n_2) \frac{F}{2} q - \frac{F}{2} Q$$

(2.14)

Under charge transfer from one site to another the terms containing $Q$ do not change, therefore the energy in these two possibilities is given by

$$\bar{E}_1 = \frac{K}{4} q^2 - \frac{F}{2} q \quad \text{and} \quad \bar{E}_2 = \frac{K}{4} q^2 + \frac{F}{2} q$$

(2.15)

This result is graphically illustrated in Fig. 2.5.

Figure 2.5: Configurational coordinate illustration of the small polaron model [43].

The transport of small polarons takes place due to thermally activated jumps of the polarons from site to site. Such motion of the polarons is called hopping. Therefore, the conductivity of small polarons $\sigma = enf \mu$ is characterized by a thermally activated mobility $\mu = \mu_0 \exp(E_a/k_B T)$. The hopping transport occurs over the barrier $E_a$ at $q = 0$. It is seen from the Fig. 2.5 that $E_a = E_P/2$. Owing to thermal activation, the small polaron
transport differs fundamentally from the transport of the large polarons. The Arrhenius-type behaviour of the mobility is used as a fingerprint to identify small polaron behaviour in solids [44].

The small polarons move with extremely low mobilities $\mu \ll 1 \text{ cm}^2/\text{Vs}$ that increase with increasing temperature.

![Schematic illustration of the photoionization of a small polaron](image)

The process of small polarons photoionization differs from large polarons one. During the photoionization of a small polaron, a self-trapped carrier is excited from its localized state to a neighbouring localized state (Fig. 2.5 a).

The small polaron absorption arises when the self-trapped carrier is induced to transfer from its initial localized state to a localized state at next equivalent lattice site.

According to the Franck-Condon principle, the optically induced transitions between equivalent sites occur with the absorbing of the photon with energy $E_{opt} = \hbar \omega = 4E_a$ (see Fig. 2.5). Taking this into account, the small polaron absorption band is peaked at $4E_a$ and broadened due to the phonons dispersion. The broadening $\Delta$ can be derived as $\Delta = \sqrt{8E_a E_{vib}}$ where $E_{vib}$ is the energy of phonons. At low temperature the $E_{vib}$ is zero-point vibrational energy $E_{vib} = \hbar \omega_{ph}/2$ and at high temperatures it can be treated classically as $E_{vib} = k_b T$.

The small polaron absorption coefficient [39] is given by

$$\alpha = \frac{2\pi^2 e^2}{m' \omega c} \frac{t'}{\Delta} \exp \left( -\frac{(4E_a - \hbar \omega)^2}{\Delta^2} \right)$$

(2.16)

where $t'$ is the intersite electronic transfer energy, $m'$ is the electron effective mass, $e$ - charge of the electron, $c$ - speed of light and $\omega$ - photon frequency.

The absorption band of small polarons is broadened due to phonons, and become broader at higher temperatures. The band is asymmetric, having broader low-energy side (Fig. 2.7).

The small polarons are called free if their stabilization is caused only by self-induced lattice distortion. Bound small polarons are additionally trapped by near lattice defect. Because of trapping, the optical transitions occur at $4E_a + E_d$ and potential barrier for hopping is raised by $\sim E_d/2$ [45].
2.2.4 Bipolarons

When two charge carriers interact with each other simultaneously through the Coulomb force and via carrier-phonon-carrier interaction, either two independent polarons can occur or a bound state of two polarons – a bipolaron – can arise. Whether bipolarons are created or not depends on the competition between the repulsive forces (direct Coulomb interaction) and the attractive forces (charge-phonon interaction) [44].

The bipolarons can be free or localized, as well as the polarons. The free bipolarons are usually spread in some lattice sites, and therefore called large. The small bipolarons are localized and their spread is characterized by a radius of the lattice constant order. Small bipolaron can be confined to only one lattice site (intrasite bipolaron) or two neighbouring sites (intersite bipolaron) [46].

For the intrasite bipolarons, the direct Coulomb repulsion is described by the potential energy of the carriers interaction (also called Hubbard energy). The effective potential \( U_{eff} \) resulted in the competition of Coulomb repulsion and charge-phonon interaction determines whether the two charge carriers occupy the same lattice site or not. If the polaron interaction dominates the Coulomb repulsion (\( U_{eff} < 0 \), negative-\( U \)), the charge carriers would occupy the same site.

The stabilization energy of bipolarons is doubled with respect to the stabilization energy of the polarons. The optical spectra of large and small bipolarons are similar to those for large and small polarons, respectively. The only difference is that peaks of the bipolaron absorption tend to have higher energies than that of the polarons [39].
2.3 Gallium Gadolinium Garnet

2.3.1 Crystal structure

Garnets crystallize in slightly distorted body centered cubic structure (space group \( Ia3d - O_h^{10} \)) [47, 48]. There are 160 atoms in the unit cell, 96 of which are oxygens [47]. The primitive cell contains eight formula units \( \text{C}_3\text{A}_2\text{D}_3\text{O}_{12} \) where C is dodecahedral, A - octahedral, D - tetrahedral crystallographic sites (see Fig. 2.8) [49, 50]. Dodecahedral sites (local symmetry \( D_2 \)) are occupied by large trivalent rare earth ions such as \( \text{Y}^{3+}, \text{Gd}^{3+}, \text{La}^{3+}, \text{Lu}^{3+} \). Octahedral (C\(_a\)) and tetrahedral (S\(_4\)) sites are occupied by medium size trivalent ions - \( \text{Fe}^{3+}, \text{Al}^{3+} \) or \( \text{Ga}^{3+} \) [48]. The octahedral sites are trigonally distorted.

Figure 2.8: Oxygen polyhedra in garnet structure and their mutual orientation [49].

The oxygens do not form a close packed array. Their arrangement forms three distinct intrinsic sites mentioned above. Each oxygen ion is at the corner of four polyhedra: one tetrahedron, one octahedron and two dodecahedra [50].

Garnets with chemical formula \( \text{C}_3\text{B}_5\text{O}_{12} \), where A and D sites are occupied by the same ions denoted B, exhibit slight deviations from cubic symmetry due to partial exchange of sites between C and B atoms [51].

Bulk GGG crystals are grown by Czochralski technique [52].

2.3.2 Mn-doped GGG

Manganese enters the GGG crystal preferentially substituting for \( \text{Ga}^{3+} \) ions in octahedral sites. To compensate the charge excess, introduced by non-isovalent \( \text{Mn}^{4+} \) ions,
the crystals are additionally doped by Ca$^{2+}$ ions that enter the dodecahedral sites (substituting for Gd$^{3+}$ ions).

The photoluminescence (PL) spectrum of GGG:Mn,Ca crystal at low temperatures consists of two sharp lines peaked at 663.5 and 668 nm and a broader structure at 681 nm (see Fig. 2.9 a). The first two lines are the R$_1$ lines ($^2$E $\rightarrow$ $^4$A$_2$ transitions) of two different strong-crystal-field manganese centers labelled "A" and "B" respectively. These two lines will be noted as R$_A$ and R$_B$ later in the text. The broader structure is produced to vibronic transitions coupled to center A (see Fig. 2.10 a) [53].

At the higher temperatures, when the R$_2$ lines of both A and B centers are observed, the R-lines overlap, making the luminescence spectra more complicated. The R-lines of both A and B manganese centers in GGG host are significantly broadened (FWHM is about 60 cm$^{-1}$) due to relatively large disorder caused by codoping the GGG crystal with Ca$^{2+}$ ions [53]. The absorption and photoluminescence excitation (PLE) spectra of the R$_A$ and R$_B$ lines are presented at Fig. 2.9 b. The 500 nm absorption band is a convolution of $^4$A$_2$ $\rightarrow$ $^4$T$_2$ transitions of the two Mn$^{4+}$ centers.

Another minor strong-crystal-field Mn$^{4+}$ center, not visible in Fig. 2.9 due to the low intensity, has been detected under selective excitation experiments. This center, labelled "C", shows $^2$E $\rightarrow$ $^4$A$_2$ emission peaked at 671 nm. The summary of the Mn$^{4+}$ centers is shown in table 2.5.

The three octahedral Mn$^{4+}$ sites reveal different properties due to different local environments in the GGG host. Ionic radii of Mn$^{4+}$ and substitutional Ga$^{3+}$ ions are comparable and equal to 62 and 60 pm respectively. The similar ionic radii have also the Ca$^{2+}$ and Gd$^{3+}$ ions (99 and 94 pm respectively), so the GGG lattice does not deform significantly.

Figure 2.9: a) Temperature dependence of the luminescence spectra of GGG:Mn,Ca crystal excited by 514.5 nm laser line and b) Absorption and PLE spectra in the region of the intrashell transitions at T = 10 K [53].
Table 2.5: Properties of the Mn$^{4+}$ centers in the GGG:Mn,Ca crystal (T = 10 K) [53].

<table>
<thead>
<tr>
<th>Parameters \ Centers</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitation peak, nm</td>
<td>660.5</td>
<td>667</td>
<td>670</td>
</tr>
<tr>
<td>Emission peak, nm</td>
<td>663.5</td>
<td>668</td>
<td>671</td>
</tr>
<tr>
<td>Stokes shift, cm$^{-1}$</td>
<td>68</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>$^2$E level splitting, cm$^{-1}$</td>
<td>80</td>
<td>170</td>
<td>40</td>
</tr>
<tr>
<td>Decay time, $\mu$s</td>
<td>1280 ± 90</td>
<td>445 ± 30</td>
<td>370 ± 10</td>
</tr>
</tbody>
</table>

Figure 2.10: a) PLE spectra of GGG:Mn,Ca crystal measured at A and B centers zero-phonon emission at T = 8 K. b) Azimuthal dependence of the polarization degree of A and B centers. The experimental setup is sketched in the right bottom corner: L is a xenon lamp, P – polarizer, S – sample, F – filter and PMT is a photomultiplier [53].

Therefore, the Mn$^{4+}$ sites differ by the different distances to the charge-compensating Ca$^{2+}$ ions [54].

Taking into account longer radiative lifetime of the A center, it was supposed that the B and C centers have shorter distances to the Ca$^{2+}$ ions, thus their octahedra are perturbed more strongly. This way the center of inversion is destroyed and zero-phonon $^2$E $\rightarrow ^4$A$_2$ transitions of B and C centers become electric-dipole-allowed and stronger than their phonon sidebands. This is supported by more intense phonon sideband of the A center in PLE spectra (presented in Fig. 2.10 a) and lack of azimuthal dependence of polarized emission measurements (Fig. 2.10 b). The degree of polarization was defined as $(I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the emission intensities parallel and perpendicular to the polarization of excited light, respectively [53].

The shortest distance between dodecahedral and octahedral sites (3.47 Å) is almost two times smaller than the distance between two neighbouring octahedral sites (5.36 Å). Thus, the Mn$^{4+}$ centers can be strongly affected by the presence of charge-compensating Ca$^{2+}$ ions. Considering this, the B and C centers are attributed to the Mn$^{4+}$ ions having the charge-compensating Ca$^{2+}$ ions as a first neighbours. The A centers have Ca$^{2+}$ ions as the second neighbours or farther [53].
2.4 Yttrium orthoaluminate

2.4.1 Crystal structure

The perovskite structure is very common in oxides, characterized by chemical formula \( \text{ABO}_3 \). In the ideal perovskite structure the A cations along with oxygens form close packed array, where the B ions occupy 25% of the octahedral sites. Each A cation is coordinated to twelve oxygens, thus occupy dodecahedral sites. The cubic primitive cell of the ideal perovskite lattice is shown in Fig. 2.11. The A cations are placed at the body-centered positions, the oxygens are at the edge-centered positions and the B cations are at the corners of the cubic cell. The perovskite structure can be also visualized as \( \text{BO}_6 \) octahedra connected by their tops (Fig. 2.11 b). Then the gaps between the octahedra represent the dodecahedra filled with the A cations [55].

![Perovskite structure diagram](image)

**Figure 2.11:** The primitive cell of the ideal perovskite structure (a) and arrangement of the \( \text{BO}_6 \) octahedra (b) [55].

Usually the ionic radii of the A and B cations are different (the A one being larger), therefore the lattice structure of the real perovskites is deformed. The most common distortion is the tilting of the \( \text{BO}_6 \) octahedron along one or more axes.

YAP has a distorted perovskite structure that belongs to the orthorhombic centrosymmetric \( \text{Pbnm} \) space group with four formula units in the primitive cell [56, 57]. The lattice constants are \( a = 5.179 \, \text{Å} \), \( b = 5.329 \, \text{Å} \) and \( c = 7.370 \, \text{Å} \) [58]. The \( \text{YO}_{12} \) dodecahedra are strongly distorted, whereas the \( \text{AlO}_6 \) octahedra are almost ideal [56, 58]. The oxygens occupy two non-equivalent positions denoted as \( 4e \) and \( 8d \).

Pure and doped bulk YAP crystals are grown by the Czochralski technique [59, 60].
2.4.2 Mn-doped YAP

The schematic picture of the YAP:Mn\textsuperscript{4+} perovskite structure is given in Fig. 2.12. Recent studies show that manganese enters the YAP crystal as the Mn\textsuperscript{4+} and Mn\textsuperscript{5+} ions, substituting for aluminium in octahedral sites and as the Mn\textsuperscript{2+} ions substituting for yttrium in dodecahedral sites [12, 61, 62, 63, 64]. The luminescence properties of the Mn\textsuperscript{4+} ions in octahedral sites will be considered in this work.

![Figure 2.12: The projection of the YAP:Mn\textsuperscript{4+} crystal structure to the xz-plane [65].](image)

Absorption spectra of manganese doped YAP crystals are presented in Fig. 2.13. The band peaked at around 21 000 cm\textsuperscript{-1} is caused by $^4A_2 \rightarrow ^4T_2$ transitions of Mn\textsuperscript{4+} ions [66, 63]. The Mn\textsuperscript{5+} ions produce absorption bands at 12 000, 15 000, 18 000 and 26 000 cm\textsuperscript{-1} (transitions $^3T_1(^3F) \rightarrow ^3T_2(^3F)$, $^3T_1(^3F) \rightarrow ^3T_1(^3P)$ and $^3T_1(^3F) \rightarrow ^3A_2(^3F)$) [64]. Very intense absorption above 26 000 cm\textsuperscript{-1} is caused by the O-Mn charge transfer bands [63, 67].

The Mn\textsuperscript{4+} ions reveal themselves also in PL experiments showing characteristic spectra at around 700 nm. The room temperature and the LH temperature spectra of manganese luminescence are presented in Fig. 2.14. The two sharp lines at 691.3 and 692.7 nm, which become apparent at low temperature, are the zero-phonon $R_2$ and $R_1$ lines of Mn\textsuperscript{4+} ions. The broad structure at lower energies is a phonon sideband of zero-phonon Mn\textsuperscript{4+} transitions. The $R$-lines are very small in comparison with their phonon sideband, and their splitting is equal to 30 cm\textsuperscript{-1} [18].

It was shown in [68] and [66] that under $\gamma$ and laser (488 nm) irradiation of YAO\textsubscript{3}:Mn crystal at room temperature the Mn\textsuperscript{4+} and Mn\textsuperscript{2+} ions are further ionized to Mn\textsuperscript{5+} and Mn\textsuperscript{3+} states respectively. The electrons, released under the irradiation, are trapped on deep traps available in the host. The trapped electrons are seen to recombine with the
manganese ions when heating the crystal up to 500 K. Strong thermoluminescence signal, related to Mn$^{4+}$ and Mn$^{2+}$ ions, is observed under the heating.

The beam coupling effect was observed in YAlO$_3$:Cr [69] and YAlO$_3$:Mn [12] crystals in holographic diffraction experiments.

A strong photorefractive effect was observed in YAlO$_3$:Mn crystal. This effect has been explained by the distortion of crystal lattice induced by manganese. The crystal become non-centrosymmetric owing to the manganese, in contrary to essentially centrosymmetric undoped YAP [12].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{absorption_spectra.png}
\caption{Absorption spectra of the YAP:Mn$^{4+}$ crystals at room temperature: (1) – 0,1 mol\%, (2) – 0,2 mol\% of Mn (with respect to the aluminium content) [66].}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{photoluminescence_spectra.png}
\caption{Photoluminescence spectra of the YAP:Mn$^{4+}$(0,2 mol\%) crystal at room (2) and 10 K (1) temperatures. The spectra were excited by 514,5 nm laser line [66].}
\end{figure}
2.5 Lithium Niobate

2.5.1 Crystal structure

Oxygens form tight-packed, slightly distorted hexagonal structure in lithium niobate. Tetrahedral sites are empty and 1/3 of octahedral sites are filled by lithium cations, 1/3 by niobium cations and 1/3 are empty. Along the Z axis cations are placed in following order: Li, Nb, □, Li, Nb, □... where □ denote structural vacancy. Figure 2.15 shows the sequence of octahedra along the polar Z axis. Oxygen octahedra in the Z direction have common facets and are deformed so the oxygen atoms do not form columns parallel to the trigonal axis, as in ideal hexagonal close packing, but are staggered instead (see Fig. 2.16). Lithium octahedra are slightly larger than the niobium ones.

![Diagram of crystal structure](image)

Figure 2.15: Fragments of the lithium niobate crystal structure in the ferroelectric and paraelectric phases and the ion positions with respect to the oxygen layers [70, 71].

Relative positions of oxygen octahedra and their next neighbours for one type of cation are not the same, therefore it would be more precisely to describe the sequence as Li_L, Nb_L, □_L, Li_R, Nb_R, □_R where indices L and R denote "Left" and "Right" sites. These two kinds of sites (of the same entity) can be transformed between themselves by a reflection x → -x and a shift by c/2 [72].

The lithium niobate exists in ferroelectric phase below Curie temperature. In this phase cations are shifted from centers of the oxygen octahedrons. There are two possible
arrangements of the ions with respect to oxygen frame, corresponding to opposite electric domains. The positive direction of Z axis is defined as a direction from negative to positive end of the domain.

It is necessary to move the lithium ions through oxygen layers to change the polarization (to "squeeze" the ions through oxygen triangle). This can be done near or above the Curie temperature for bulk material, applying small electric field while growing the crystal. The polarization reversal in waveguides or thin layers can be done by applying high electric field or electron beam bombardment [74]. Lithium niobate sometimes called "frozen" displacement ferroelectric [75] because of the high electric fields necessary to repolarize the crystal at ambient temperature. Ferroelectricity in this crystal was discovered by Matthias and Remeika in 1949 [76].

Heating the crystal above Curie temperature induces second-order phase transition. Average positions of the Li ions in the paraelectric phase lie in oxygen layers, and the Nb ions are centered between planar oxygen layers (see Fig. 2.15 b). This arrangement makes the paraelectric phase non-polar [70]. The rest of this work will consider only the ferroelectric phase.

Lithium niobate is a member of the trigonal crystal system. Its crystal structure belongs to 3m point group [77]. It also belongs to R3c space group in ferroelectric phase [73]. In the trigonal system two different unit cells can be chosen: hexagonal (a = 5,1483 Å, c = 13,863 Å [78]) and rhombohedral (a = 5,4944 Å, α = 55°52′ [78]). The conventional hexagonal cell in lithium niobate contains six formula units, and the rhombohedral cell contains only two [70].

The lithium niobate crystals grow non-stoichiometrically with [Li]/[Nb] < 1 because of the disbalanced solubility of Li₂O and Nb₂O₅ at the temperature of crystal growth [79]. Different growth conditions (Czochralski method) do not produce stoichiometric crystals, there is always an excess of niobium and deficiency of lithium. The best crystals for optical applications (among non-stoichiometric compositions) are the congruent ones with [Li]/[Nb] = 0,942 – at this composition the crystal has the same [Li]/[Nb] ratio as it was in the melt. Congruent crystals have a very high concentration of intrinsic defects.

Stoichiometric crystals contain much less intrinsic defects than the congruent ones.
Such crystals can be produced by Top-Seeded Solution Growth (TSSG) with addition of K$_2$O [80, 81]. Addition of K$_2$O to the melt lower the growth temperature, thus reaching balanced solubility of Li$_2$O and Nb$_2$O$_5$ (see phase diagram of lithium niobate, for example in [82]). Potassium practically does not enter the crystal under growth, it only helps to lower the crystallization temperature [81]. Stoichiometric lithium niobate can be produced also by Vapour Transport Equilibration (VTE) treatment of congruent crystals [83] and double crucible Czochralski method [84].

Physical properties of lithium niobate depend on crystal composition. A good indicator of crystal’s stoichiometry is its Curie temperature (1020°C for congruent crystals and 1180°C for stoichiometric ones) that uniquely determines the chemical composition of the sample [82]. In fact, the other parameters, such as refractive index and fundamental absorption edge, can be also used for stoichiometry characterization [85].

### 2.5.2 Intrinsic defects

Lithium niobate crystals, especially congruent ones, contain a large number of intrinsic defects. Therefore the charge compensation, which is necessary for non-univalent impurity incorporation, can be easily obtained. In general, lithium niobate can be easily doped with non-univalent impurities in large concentrations. The charge compensation with intrinsic defects leads to the creation of families of electrically non-equivalent centers. Such centers have different relative locations of the impurity ions with respect to their charge compensators. This fact makes investigation of defects in lithium niobate a complicated task [72].

There are several non-equivalent positions in the lithium niobate lattice. The most important ones are the sites along optical z axis: Li site, Nb site and structural vacancy. All these sites have point group symmetry $C_3$. An isolated defect in such sites creates a center (also called axial center) with corresponding symmetry. All other possible sites in the lattice have symmetry $C_1$ [86].

X-ray analysis of the congruent crystals [87] show that lithium is missing from 5.9% of all relevant sites and they are filled with Nb ions, creating so-called niobium antisites Nb$_{Li}^{5+}$. This defect is charged positively with respect to the lattice – Nb$_{Li}^{\text{Li}}$ in Kröger-Vink notation [88]. The niobium antisite defect influences many properties of lithium niobate, such as fundamental edge of absorption, luminescence quenching and photorefractive effect. This is the main defect created due to non-stoichiometry of the crystals. In order to explain the non-stoichiometry of lithium niobate and charge compensation for antisites two defect models have been proposed: the niobium vacancy model and the lithium vacancy model.

The charge excess created by antisites can be compensated by a correspondent number of Nb vacancies [89], giving

$$[\text{Li}_{1-x}\text{Nb}_{5x}]_{Li}[\text{Nb}_{1-4x}\square_{4z}]_{NbO_3}$$

with $x = 0.0118$. 

26
This is so-called niobium vacancy model of antisite defects, which was supported by a single-crystal X-ray structure analysis [87]. It is necessary to notice that Donnerberg in [90] on the basis of computer simulation show that Nb vacancies are very unfavourable energetically. To resolve this discrepancy it was proposed that regular cation stacking sequence in lithium niobate in some regions is changed to ilmenite-like stacking sequence (Fig. 2.17) [91]. It was shown in [92] that the ilmenite sequence is only slightly less favourable than the regular LiNbO₃ structure.

\[
\text{ABO}_3: \quad \text{B A } \square \quad \text{B A } \square \quad \text{B A } \square \quad \text{B A } \square
\]

Ilmenite: \quad \text{B A } \square \quad \text{A B } \square \quad \text{B A } \square \quad \text{A B } \square

Figure 2.17: Cation stacking sequence of ABO₃ oxides and ilmenite structure.

There is opposite model of charge compensation, which claims that all niobium sites are filled with niobium and the charge compensation is realized by lithium vacancies according to the formula:

\[
[\text{Li}_{1-5x}\text{Nb}_x\square_{4z}][\text{Li}\text{Nb}]\text{O}_3
\]

This model was proposed in [93] and supported by X-ray diffraction, neutron diffraction [94, 95, 96], NMR [97] and Raman scattering experiments [98, 99]. According to theoretical calculations [90, 100, 101] the lithium vacancies model is more favourable energetically.

The lithium vacancies model is more popular due to a solid experimental attestation. The lithium vacancies are believed to be created in the lithium niobate due to its non-stoichiometry. They are charged negatively with respect to the lattice – \( \square'_{Li} \) in Kröger-Vink notation. The local charge compensation can be obtained by removing an electron from one of the neighbouring \( O^{2-} \) ions under ionizing radiation. This leads to creation of holes, captured at the oxygen ions (\( O^- \) hole polarons, see below).

### 2.5.3 Polarons

**Nb⁴⁺ small polarons**

It has been reported recently that in MgO and ZnO doped lithium niobate the electron traps are associated with the Nb ions and not with divalent impurities [102, 43]. The electron, captured at niobium ion, forms Nb⁴⁺ complex, which can be considered as a small polaron [103]. Since the niobium ions are found in both Li and Nb sites, two kinds of small polarons are found in lithium niobate: niobium small polaron in lithium site denoted as \( \text{Nb}_{Li}^{4+} \), and niobium small polaron in niobium site \( \text{Nb}_{Nb}^{4+} \).

The niobium polarons are observed by both EPR and optical absorption measurements [105, 106]. In EPR, the Nb⁴⁺ polarons are seen as a characteristic 10-line pattern due to interaction with \( ^{93}\text{Nb} \) nucleus, the only stable isotope of niobium (Fig. 2.18 1) [105].
2.5. LITHIUM NIOBATE

Figure 2.18:
1) ESR of Nb$^{4+}$ in congruent LiNbO$_3$ [104]. a – crystal reduced and illuminated. The strong extra line at 0,35 T belongs to Ti$^{3+}$. b – after X-irradiation at low temperature, wide absorption around 0,34 T is due to O$^-$.
2) Optical absorption of congruent LiNbO$_3$ [104]. a – reduced sample before illumination (2,5 eV band, bipolarons). b – after illumination (1,6 eV band, Nb$^{4+}_{Li}$ small polaron). c – unreduced sample.

Figure 2.19: Absorption of lithium niobate doped with 7,25 mol% ZnO. Solid line – 295 K, dashed line – 6 K. The band, peaked at around 1 eV, is due to Nb$^{4+}_{Nb}$ small polarons [43].
In absorption the Nb$^{4+}_{Li}$ small polarons show broad band peaked at 780 nm [107, 108, 104] (fig. 2.18 2). The stabilization energy is equal to 0,8 eV (obtained from the absorption spectrum) [104].

In above-threshold magnesium or zinc doped lithium niobate a broad absorption band, peaked at 1200 nm, was shown to emerge due to Nb$^{4+}_{Nb}$ small polarons [43] (Fig. 2.19). The activation energy, obtained from absorption and conductivity measurements in temperature range 150 - 296 K, is found to be equal to 0,24 eV. Corresponding stabilization energy is equal to 0,48 eV. In such crystals the Nb$^{4+}_{Nb}$ polarons are additionally bound at low temperatures to unknown defect with the bonding energy equal to 0,13 eV [43].

The interesting feature has been detected in absorption studies of the small polarons in lithium niobate at room temperature. The relaxation kinetics of the light-induced absorption was shown to be stretched-exponential instead of single-exponential, predicted by the standard rate equations [109, 110, 111, 112, 113, 114, 115, 116, 117, 118]. The empirical stretched-exponential function (also known as Kohlrausch-Williams-Watts function) differs from the exponential one by the additional parameter $\beta$:

$$F(t) = \exp \left[ - \left( \frac{t}{\tau_{KWW}} \right)^{\beta} \right]$$  \hspace{1cm} (2.17)

where $\tau_{KWW}$ is the characteristic relaxation time and $\beta$ is the stretching parameter that depends on distribution width ($0 < \beta < 1$). With $\beta = 1$ the Kohlrausch-Williams-Watts function is reduced to standard exponential law.

It should be noted that $\tau_{KWW}$ is not the time, necessary for decay intensity to decrease by the factor of $e$ as it is in exponential decay. The $\tau_{KWW}$ is just a characteristic time of the stretched exponential decay process. The average relaxation time of stretched exponential decay can be calculated using

$$\langle \tau \rangle = \frac{\tau_{KWW}}{\beta} \Gamma \left( \frac{1}{\beta} \right)$$  \hspace{1cm} (2.18)

where $\Gamma$ is the gamma function.

Higher moments of the relaxation time are given by

$$\langle \tau^n \rangle = \frac{\tau_{KWW}^n}{\beta} \frac{\Gamma \left( \frac{n}{\beta} \right)}{\Gamma(n)}$$  \hspace{1cm} (2.19)

Using the formulas $\langle (\tau - \langle \tau \rangle)^2 \rangle = \langle \tau^2 \rangle - \langle \tau \rangle^2$ and 2.19, the standard deviation of the relaxation times from their average value $\langle \tau \rangle$ can be found as

$$\sigma = \sqrt{\frac{\tau_{KWW}^2}{\beta} \left[ \Gamma \left( \frac{2}{\beta} \right) - \frac{1}{\beta} \Gamma^2 \left( \frac{1}{\beta} \right) \right]}$$  \hspace{1cm} (2.20)

The $\sigma$ depends strongly on $\beta$.
\[ \sigma = \begin{cases} 
0, & \text{if } \beta = 1 \\
\infty, & \text{if } \beta = 0 
\end{cases} \quad (2.21) \]

This dependence originates from the distribution of the relaxation times, which also depends strongly on \( \beta \) (the larger is \( \beta \), the broader is the distribution). As a result, at certain values of \( \beta \) the standard deviation is larger than the average decay time:

\[ \sigma < \langle \tau \rangle \quad \text{if } 1 \geq \beta > 0, 605 \]
\[ \sigma > \langle \tau \rangle \quad \text{if } 0, 605 > \beta \geq 0 \quad (2.22) \]

The stretched-exponential relaxation of the light-induced polarons absorption has been explained by the dependence of the individual polaron lifetime on the distance from it to the recombination center [109]. The statistical model of polarons recombination, described in [119], as well as computer simulations [109, 114], illustrate that the stretched exponential relaxation kinetics are produced if the diffusive hopping transport of polarons takes place.

**Niobium bipolarons**

Niobium bipolarons are formed by trapping of two electrons at neighboring niobium ions, located in lithium and niobium sites – \( \text{Nb}^{4+}_{\text{Li}}:\text{Nb}^{4+}_{\text{Nb}} \). They are the lowest-energy electron traps in lithium niobate, described in literature.

While no EPR signal is observed (the niobium bipolarons are diamagnetic), reduced pure lithium niobate samples show absorption band at 530 nm (2.5 eV), ascribed to the bipolarons [104] (see Fig. 2.18 b). The niobium bipolarons dissociate to the antisite small polarons and free electrons with temperature [120], and are also seen to be bleachable under visible light [104].

**O\(^-\) hole polarons**

Oxygen octahedra at lithium vacancies are approximately symmetric, containing six nearly equivalent oxygen ions. The valence band holes tend to be localized at one of the oxygen ions, forming the O\(^-\) small hole polarons. In such clusters, the hole polarons are capable to change the localization between equivalent oxygen ligands, remaining bound to the vacancy.

The O\(^-\) small hole polarons are found to be created along with \( \text{Nb}^{4+}_{\text{Li}} \) small polarons. Presence of both of the polarons was confirmed by EPR measurements in [105, 121] (Fig. 2.18 a). Holes on the oxygen ions are detected by EPR as a single line around \( 2,002 < g < 2,047 \) [104]. The O\(^-\) small hole polarons produce strong and wide absorption band at around 530 nm (2.5 eV), which is shown in Fig. 2.20.

On the basis of theoretical considerations it was shown in [122] that such polarons would produce absorption bands that satisfy the condition:
Figure 2.20: Optical absorption of congruent LiNbO$_3$ at $T = 77$ K: a) as-grown, b) after irradiation with 1,7 MeV electrons. The band, peaked at 2,5 eV is due to the O$^-$ small hole polarons [121].

$$\frac{W^2}{M} = 2\ln(2)\hbar\omega_0 \approx 0.14 \text{ eV} \quad (2.23)$$

where $W$ – half width at half maximum of the peak, $M$ – peak energy, $\hbar\omega_0$ – LO phonon energy (typically around 0.1 eV [122]).

This relation between absorption peak position and its width can be useful in experimental studies. However, this indirect evidence of the hole polarons is only valid when the presence of holes at oxygen sites is proved and there are no other charge carriers able to localize at other equivalent ions. The stabilization energy of the O$^-$ hole polarons can be found from absorption as a half of the peak energy [122].

Another absorption band at around 3,1 eV (400 nm) has been discussed in [105, 107, 123, 124, 125, 126] to originate due to hole polarons. Both 2,5 and 3,1 eV bands are shown to disappear simultaneously along with niobium polarons band under heating of the crystal [107].

2.5.4 Mg-doped lithium niobate

Photorefractive effect, which is useful in holographic data storage, is undesirable in some other applications since a high-power laser beam can induce a local change of refractive index in the crystal. Photorefractive effect therefore sometimes called photorefractive damage (optical damage).

Photorefractive effect is a combination of two effects: charge migration followed by electro-optic effect. In lithium niobate, the dominant charge migration mechanism is the
bulk photovoltaic effect and the dominant electro-optic effect is the linear (Pockels) effect. In all available range of compositions, the stoichiometric crystals are the most resistant to the photorefractive damage. Nevertheless, the powers of laser light, to which such crystals are restricted, are still not high enough to use them as Q-switches and high-power electro-optical modulators.

Another way to improve the resistance to optical damage is to dope the crystal with divalent ions – magnesium, zinc, indium or scandium [127, 128, 129, 130, 131]. The most popular optical damage inhibitor is magnesium.

Magnesium enters the crystal to the lithium sites as $\text{Mg}^{2+}_{\text{Li}}$ ions, preferably substituting for niobium antisite defects [132, 133]. With increase of Mg concentration, the number of the antisite defects is reduced, until the moment there would be no antisites at all. Because of such selectivity, doping with Mg influences the crystal properties in the threshold way. Decrease of the antisite defects concentration in consequence increases the crystal’s photoconductivity, since the niobium antisites are known as an effective electron traps in the congruent crystals. Improved resistance to the photorefractive damage in such crystals is connected with increased photoconductivity [128, 134]. Magnesium ions do not contribute directly to the photorefractive process.

The magnesium doping threshold for the congruent crystals was estimated as around 4.5 mol% of MgO in the melt [128]. For the near stoichiometric crystals, where the total number of internal defects is expected to be much lower, the magnesium doping threshold is smaller, around 1 – 2 mol% (depending on the Li/Nb ratio in the crystal) [135, 136, 137].

### 2.5.5 Cr-doped lithium niobate

The congruent crystals, doped with $\text{Cr}^{3+}$ ions, are green in colour because of the position of two chromium optical absorption bands ($^{4}A_2 \rightarrow ^{4}T_1$ and $^{4}A_2 \rightarrow ^{4}T_2$ transitions) in the visible region (more precisely by the position of the dip between them that is situated exactly at the green light wavelength – 555 nm, see Fig. 2.21 a).

Chromium substitutes for lithium (Cr$\text{Li}$) and niobium (Cr$\text{Nb}$) in lithium niobate. In crystals, doped only with chromium, the Cr$^{3+}$ ions prefer Li sites, therefore in such crystals there is much more Cr$\text{Li}$ centers than Cr$\text{Nb}$ ones. EPR, ENDOR and optical spectroscopy measurements suggest that the major part of Cr$^{3+}$ ions is substituted for the Li$^{+}$ ions [22, 138, 139]. Several Cr$^{3+}_{\text{Li}}$ centers are detected (see table 2.6).

Photoluminescence spectrum of congruent lithium niobate doped with chromium is shown in Fig. 2.23 (the solid line). The broad luminescence, peaked near 910 nm (11 000 cm$^{-1}$), corresponds to $^{4}T_2 \rightarrow ^{4}A_2$ transition of the dominant unperturbed $\gamma$-Cr$\text{Li}$ center (using Macfarlane’s notation [22]). This is a weak-crystal-field center, which has $^{4}T_2$ as a first excited level. The $^{4}T_2 \rightarrow ^{4}A_2$ transition is strongly phonon-coupled and allowed, with decay time of a few microseconds [140]. It is also possible to detect the R-lines of the $\gamma$-Cr$\text{Li}$ center, but only in relatively high temperatures (> 50 K), when the $^{2}E$ level of this center is thermally populated [141, 139].
Figure 2.21: Optical absorption of LiNbO$_3$:Cr (a) and LiNbO$_3$:Cr,Mg (b) crystals [142].

On the high-energy side of broad $\gamma$-Cr$_{Li}$ luminescence there are several narrow R-lines from minor strong-crystal-field chromium centers (relative integrated intensity to the $\gamma$-Cr$_{Li}$ broad-band is 1/100 [23]). They correspond to the $^2E \rightarrow ^4A_2$ transitions, peculiar to the strong-crystal-field configuration, where the first excited level is $^2E$. Such transitions are spin-forbidden (the spin-orbit coupling partially releases them) and weakly phonon-coupled (this is why they are so narrow in comparison with the broad luminescence of the weak-crystal-field centers). Two strong-crystal-field centers are detected in photoluminescence: $\alpha$- and $\beta$-Cr$_{Li}$. Most probably, the strong-crystal-field chromium centers are perturbed by intrinsic crystal defects. The energy levels of discussed centers are given in table 2.6.

The chromium R-lines are very broad in lithium niobate. They typically have FWHM of $\sim 40 - 50$ cm$^{-1}$ in congruent crystals [143, 144] and $\sim 20$ cm$^{-1}$ in the near-stoichiometric crystals [140, 137]. In contrast, the chromium R-lines halfwidths in Al$_2$O$_3$ are less than 2 cm$^{-1}$ [23]. It was shown in [145] that the R-lines are broadened owing to distribution of the Racah parameters, which in turn are distributed due to influence of the internal defects to Cr$^{3+}$–O$^{2-}$ covalent bonds. Such situation is in contrast to the broadening of luminescence due to distribution in crystal field strength in glasses and disordered oxides [23].

2.5.6 Cr,Mg-doped lithium niobate

The congruent crystals, doped with Cr and Mg below the threshold, are green in colour and EPR and ENDOR measurements suggest that all Cr$^{3+}$ ions are substituted for the Li$^+$ site [146, 147, 139]. Optical experiments show similar spectra to the chromium only doped lithium niobate.

The crystals are pink for concentrations above the threshold. The colour change is
Figure 2.22: EPR spectra of lithium niobate doped with chromium and magnesium at room temperature. The upper spectrum corresponds to the above-threshold Mg-doped sample, the lower – to the pre-threshold Mg-doped one [147].

Figure 2.23: Photoluminescence of LiNbO$_3$:Cr (solid line) and LiNbO$_3$:Cr,Mg (dashed line). $T = 20$ K, Ar$^+$-ion laser 514 nm line was used as an excitation source [142].

induced by the shift of the dip in chromium intrashell absorption to the longer wavelength and lowering of the $^4T_2 \rightarrow ^4A_2$ absorption band (see Fig. 2.21 b). The absorption change in pink samples has been explained by the coexistence of two types of Cr$^{3+}$ centers: Cr$_{Li}^{3+}$ and Cr$_{Nb}^{3+}$ [142, 147, 136].

EPR and ENDOR also showed that a new isotropic chromium center appears located in the niobium sites (see Fig. 2.22) [148, 146, 147]. The high-pressure PL measurements were also helpful in identification of the chromium centers in double doped lithium niobate. It was shown in [140] that in above-threshold Mg-doped sample the broad luminescence band ascribed to the weak-crystal-field $\delta$-Cr$_{Nb}^{3+}$ center is visible at 93 kbar, whereas at the
similar pressure in pre-threshold crystal no broad bands are detected (all weak-crystal field Cr$^{3+}_{Li}$ centers are transformed to high-crystal field ones at these pressures).

Photoluminescence of such crystals (shown in Fig. 2.23b) have two new R-lines associated with the Cr$^{3+}_{Nb}$ strong-crystal-field centers. Broad luminescence is shifted to the lower energies, which is explained by overlap of the broad bands of the weak-crystal-field Cr$^{3+}_{Nb}$ and Cr$^{3+}_{Li}$ centers [142] (see Fig. 2.23a, dashed line).

The presence of two kinds of Cr$^{3+}$ centers is explained by the incorporation peculiarities of Mg ions. For concentrations below the threshold, manganese substitutes for the niobium antisite defects and chromium substitutes for lithium ions. After the threshold magnesium substitutes for lithium only, therefore the chromium enters both lithium and niobium sites [147].

A summary of detected chromium centers is given in table 2.6. By now, we can distinguish between Cr$^{3+}_{Li}$ and Cr$^{3+}_{Nb}$ centers, but little is known about perturbing defects of the strong-crystal-field chromium centers.

Table 2.6: Chromium centers in lithium niobate [22]

<table>
<thead>
<tr>
<th>Center</th>
<th>$^2$E energy, cm$^{-1}$</th>
<th>$^2$E splitting, cm$^{-1}$</th>
<th>PL Broad-band, cm$^{-1}$</th>
<th>Occupation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>13 640</td>
<td>95</td>
<td>n/a</td>
<td>Li (distorted)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>13 720</td>
<td>64</td>
<td>n/a</td>
<td>Li (distorted)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>13 790</td>
<td>38</td>
<td>11 100</td>
<td>Li</td>
</tr>
<tr>
<td>$\delta$</td>
<td>not observed</td>
<td>not observed</td>
<td>10 500</td>
<td>Nb</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>13 532</td>
<td>55</td>
<td>n/a</td>
<td>Nb (distorted)</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental

3.1 Optical absorption

Cary 5000 double-beam spectrophotometer was used to measure absorption in visible and near-infrared regions (a photomultiplier was used in the visible region as a detector, and the PbS detector for the near infrared). It was equipped with helium continuous flow cryostat Oxford CF 104 for low-temperature measurements. Temperature in cryostat was controlled by Oxford ITC4 temperature controller. Baseline correction of spectrophotometer was performed before each measurement.

Results of optical absorption measurements are shown as an optical density of samples:

\[ OD(\lambda) = \frac{1}{d} \log_{10} \left( \frac{I_0}{T} \right) \]  \hspace{1cm} (3.1)

where \( I \) is the intensity of transmitted light, \( I_0 \) is the intensity of incident light, \( d \) is the sample thickness.

3.2 Laser-induced optical absorption

Laser-induced absorption was treated as a difference between absorptions after and before laser illumination of a sample. The 325 nm line of He-Cd laser and the 514.5 nm line of Ar\(^+\)-ion laser were used as an excitation sources.

This experiment was carried out in several steps. Sample was cooled to 4 K and the reference absorption spectrum was measured. Then the sample was exposed to the laser for 30 minutes. Finally second absorption scan was performed giving absorption spectra after laser excitation. Difference between these two absorption spectra gives the absorption spectrum induced by laser illumination.

Since Cary 5000 does not have second double monochromator between sample chamber and optical detector, a fragment of Si wafer was used as an optical filter to cut off dispersed laser radiation (Fig. 3.1). This simple setup improvement gave a possibility to measure near infrared absorption under laser irradiation of the sample.
3.3 PHOTOLUMINESCENCE

However in the visible region, where the absorption signal was measured by photomultiplier, the simultaneous absorption measurements and laser illumination of a sample was not possible due to high distortions of the signal, introduced by the laser light. Different optical filters placed between cryostat and the detector did not help to solve this problem.

Figure 3.1: Setup for absorption measurements under laser illumination.

3.3 Photoluminescence

The photoluminescence setups are shown in Fig. 3.2 a.

Lines of Ar+ ion Innova 400 laser were used as an excitation. To avoid the effect of heating the samples by the laser beam usually small incident light powers were applied (below 10 mW at the sample). Laser beam was dispersed by Pellin-Broca prism to cut off laser plasma lines from the main generation line. Next, the beam was modulated by New Focus 3501 optical chopper. To carry out low temperature experiments Oxford Optistat CF LT continuous flow helium cryostat was used, equipped with Oxford ITC503s temperature controller. Light, emitted by sample, was dispersed using GDM 1000 double grating monochromator. Two types of photomultiplier tubes were used depending on spectral range and time response: S20-type EMI 9816QB for visible region and S1-type EMI 9684B (photon counter) for visible and near infrared regions.
Figure 3.2: Photoluminescence setups.

The setup (Fig. 3.2 a) gives a possibility to measure luminescence decay kinetics using SR430 multichannel scaler instead of lock-in and S1-type EMI 9684B photomultiplier tube in photon counting mode. For fast PL scans and for a very low PL signals another setup was used equipped LN-cooled CCD camera and Jobin Yvon – Spex TRIAX 320 monochromator (Fig. 3.2 b). Optical filter, shown in both setups was used to cut off laser radiation from sample’s photoluminescence.

All data were normalized to the detector spectral sensitivity.

3.4 High-pressure measurements

The most popular tool for study the properties of matter under high pressures is the Diamond Anvil Cell (DAC). The DAC is a device capable of generating static pressures almost as great as those in the centre of the Earth. This is a simple but very powerful tool in high-pressure measurements.

DAC consists of two diamonds with small flat surfaces (culets) on their tips and a thin metal gasket (Fig. 3.3). The diamonds are placed opposite to each other, culet to culet, squeezing the gasket. Small hole is drilled in the gasket precisely at the center of the place diamonds touch it. The hole and culets outline the high-pressure cell. Sample and a pressure sensor are placed into the cell, and then it is filled with pressure-transmitting medium and closed by diamonds. Application of external force to the diamonds results in increase of static pressure in the cell.

The DAC allows to carry out experiments in wide range of temperatures – from liquid helium (placing the DAC in a cryostat) to a few hundreds kelvins (direct heating of sample by laser light).
Owing to small sizes of the high-pressure cell (a few hundred microns) and high force applied to the anvils (around 1000 kg or even more) the sample is subject to very high pressures. Naturally, the diamond is the most appropriate material for anvils since it is the hardest known substance. In addition, different kinds of experimental studies can be carried out including direct observation of the sample due to transparency of diamond in a very broad range of light from infrared to the near-ultraviolet ($\leq 5$ eV) and also in the region of hard x-rays ($\geq 10$ keV).

The smaller the size of the culet, the higher pressures can be obtained. In practice, the culet size is selected depending on the required pressure range. An empirical relation connects the culet size and maximum pressure that can be achieved by using such anvils [149]:

$$d = \sqrt{\frac{125}{P_{\text{max}}}}$$

(3.2)

where $d$ is the culet diameter in mm and $P_{\text{max}}$ is the maximum pressure in kbar that can be safely achieved.

The critical issue in DAC operation is precise axial and parallel alignment of the diamonds so the culets are touching each other with their full area. This is usually done by observing them through one of the diamonds under the microscope, illuminating the DAC from the other side by white light. The axial alignment is corrected by achieving the round shape of resulting culets overlap, and the parallel misalignment is easily detected by interference fringes that appear between culets surface. Misalignment results in diamonds failure under the experiment already at low starting forces applied to the DAC [150]. Therefore, a skilled operator is required to perform the high-pressure experiments using the DAC.

Figure 3.3: Cross-section of the diamond anvil cell.

Before drilling the hole and loading the sample, the gasket must be preindented to a certain thickness. This is done using a high force, almost as high as will be used during experiment. When the gasket is squeezed between the anvils, it deforms plastically and extrudes outwards. The extrusion results in creation of thick belt of material around the culets that support the diamonds preventing their unaxial movement during experiment (Fig. 3.4).

Typical plot of gasket thickness between anvils versus applied pressure is shown in Fig. 3.5. Initially the gasket thickness change drastically with applied pressure. After
some value, the thickness does not change a lot with pressure rise, and this is called the thin gasket regime. In this regime, material almost does not extrude from under the anvils providing that the sample hole does not collapse or expand before necessary pressure in DAC is obtained. The necessary thickness of the gasket is reached after several preindentations with increasing force, pointing the moment when its thickness does not change much between last two runs [151].

The proper operation of the DAC implies the size relations between starting gasket thickness, culet diameter, hole diameter and preindented gasket thickness as 10:10:3:1 [151]. Using other size relation than recommended result in achieving lower pressures than expected or even diamonds failure. After drilling the hole in the gasket, the DAC is ready for loading a sample and a pressure sensor.

The last step in preparation the DAC to experiment is filling the high-pressure cell with pressure-transmitting medium. This is necessary to assure that the pressure would be hydrostatically applied to the sample.

![Cross-section of a preindented gasket with sample hole](image)

Figure 3.4: Cross-section of a preindented gasket with sample hole [150].

![Graph showing gasket thickness](image)

Figure 3.5: The gasket thickness $t$, normalized to the radius of the culet $r_0$ in function of the pressure under diamonds $P$, normalized to the compressive strength of gasket material. The dashed line points the border, below which the DAC is operated in the thin gasket regime [151].

Several pressure-transmitting media are known, such as methanol/ethanol mixture, special oils and noble gases [152]. Unlike the noble gases, the alcohol mixtures and oils glassify in LH temperatures. The most suitable medium for low-temperature studies is argon [150], though filling the DAC with argon require special apparatus (Fig. 3.6).

The DAC, loaded with sample and pressure sensor, is placed into the tube (external
force is not applied to the diamonds at this moment). The tube is then sealed and air is replaced by argon through several pumping out – argon filling iterations. Then argon is delivered into the tube under pressure around 5 bar and the dewar is slowly filled with liquid nitrogen. Since argon in this pressure and temperature start to condense, the tube is filled with liquid argon to the level of liquid nitrogen. When the level of liquid argon is above the DAC, the force is applied to the diamonds using external hydraulic system, thus sealing the high-pressure cell.

The standard method of pressure estimation inside DAC is the ruby luminescence scale [153, 154, 155]. The pressure is evaluated from redshift of the $R_1$ ruby line (14 406 cm$^{-1}$ at ambient pressure and LH temperature) measured after each pressure increase during experiment. Up to 195 kbar, the shift of $R_1$ ruby line with pressure can be considered as linear with coefficient $-0.77\pm0.03$ cm$^{-1}$/kbar [153], and at higher pressures, where non-linearity of ruby lines shift is sufficient, the pressure can be estimated using equation:

$$P[\text{kbar}] = 3808 \left[ \left( \frac{\lambda_0}{\lambda} \right)^5 - 1 \right]$$

where $\lambda$ – position of ruby $R_1$ line under pressure, $\lambda_0$ – position of the $R_1$ line at ambient pressure (in cm$^{-1}$) [155].

Pressure in DAC can be considered as hydrostatic or very close to hydrostatic using proper size relations of the culets, sample hole, gasket thickness, samples and proper pressure-transmitting medium. Deviation from hydrostaticity can be easily detected by broadening of the ruby $R_1$ line. The FWHM of $R_1$ line at ambient pressure is approximately 2.5 cm$^{-1}$. In the experiments, shown in this work, it was less than 6 cm$^{-1}$ at highest pressures, which indicates that deviations from the hydrostaticity were rather weak.

Owing to high sensitivity of this method to the experimental conditions (alignment of the diamonds, size relations of elements etc.), great care was taken to fulfil all necessary requirements of DAC operation.

Diacell Products MCDAC-1 with 500 $\mu$m culets (in diameter) was used to study low-temperature PL of samples under high pressure. Argon was used as pressure-transmitting medium. To perform a low temperature experiments DAC was placed into Oxford CF Figure 3.6: Apparatus for loading condensed gases into the DAC [150].
LT continuous flow helium cryostat. Temperature was controlled by Oxford ITC503s temperature controller. Photoluminescence setups are shown in Fig. 3.2.

The gaskets were preindented to 50 μm and 150 μm holes were drilled in it. The samples were prepared by polishing to 20 – 25 μm and loaded manually in DAC, chopping a piece of appropriate size. Ruby balls of 5 μm in diameter were used as pressure sensors. To automate the routine algorithm of pressure evaluation, simple program was designed to process experimental data of ruby R-lines luminescence (see page 108).

3.5 Thermoluminescence[156], [157]

Thermoluminescence (strictly speaking Thermally Stimulated Luminescence, TSL) is the emission of light from an insulator or semiconductor when it is heated after excitation at low temperature. In contrast to incandescence, under thermoluminescence light is emitted due to carriers recombination. Heating serves only as a trigger that helps in releasing charge carriers from local defects where they are "trapped" (this is why such defects are called "traps").

In this short review two possibilities will be distinguished: when the same kind of traps has strictly defined energy of activation, and when they are distributed in energy.

**Systems with single-level energy traps**

Simple model of thermoluminescence is shown in Fig. 3.7. There are two energy levels in the band gap. One serves as an electron trap, another as a hole trap.

At low temperatures, when $k_B T < E_a$, electrons from valence band absorb photons $h\nu_{ex}$ from external source of radiation and rise to conduction band (transition 1), where they are free to move through the sample. After that, they are captured by electron traps (transition 2) and localized, since thermal energy is too low to excite them back to conduction band. Holes, which left in the valence band, are captured by another level that acts as a hole trap (transition 5). The carriers can stay trapped at these levels for a very long time in low temperatures.

Next, the sample is being heated. When $k_B T \approx E_a$ electrons start to rise from traps to the conduction band (transition 3). Here two processes are possible: electrons can be captured back by traps (retrapping) or can recombine with holes (transition 4). The level, on which recombination occur, is called the recombination level. Recombination of
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charge carriers leads to the detectable luminescence $h\nu_{TSL}$ if the probability of radiative recombination prevails over non-radiative for this level.

Rate equations can be written as follow:

$$\frac{dn_c}{dt} = ns \exp \left(- \frac{E_t}{k_BT} \right) - n_c (N - n) A_n - n_c m A_{mn} \quad (3.4)$$

$$\frac{dn}{dt} = n_c (N - n) A_n - ns \exp \left(- \frac{E_t}{k_BT} \right) \quad (3.5)$$

$$\frac{dm}{dt} = -n_c m A_{mn} \quad (3.6)$$

where $N$ is the concentration of the traps, $n_c$ is the concentration of free electrons in conduction band, $n$ is the concentration of trapped electrons, $m$ is the concentration of holes in recombination level, $s$ is pre-exponential factor (attempt-to-escape frequency), $k_B$ is the Boltzmann constant, $A_n = \mu_n \sigma_n$ is the retrapping probability and $A_{mn} = \mu_n \sigma_{mn}$ is the recombination probability, $\mu_n$ is the electron thermal velocity.

From the Fig. 3.7 it is clear that $\frac{dn_c}{dt} = \frac{dm}{dt} - \frac{dn}{dt}$ and charge neutrality gives $n_c + n = m$.

Intensity of thermoluminescence is given as:

$$I_{TL} = -\eta \frac{dm}{dt} \quad (3.7)$$

where $\eta$ is a radiative efficiency (if all recombination events produce photons and all photons are detected then $\eta = 1$).

Equations 3.4 – 3.6 are both time and temperature dependent and analytically insoluble. Therefore to acquire analytical relationship between intensity of thermoluminescence and the temperature $I_{TL}(T)$ it is necessary to make several simplifying assumptions and consider two general approximations: with and without retrapping.

The two assumptions, usually employed to simplify resulting equations, are the quasi-equilibrium assumptions: free electrons concentration is always much smaller than the trapped electrons concentration ($n_c \ll n$) and the rate of change of the free electrons concentration is always very much less than the rate of change of the trapped electrons concentration ($\left| \frac{dn_c}{dt} \right| \ll \left| \frac{dn}{dt} \right|, \left| \frac{dm}{dt} \right|$). It means that the free electron lifetime is much shorter than the trapped electron lifetime, once electron is excited to conduction band it quickly recombines with a hole on recombination center. It leads to

$$-\frac{dn}{dt} \simeq -\frac{dm}{dt} = I_{TL} \quad (3.8)$$

and thus

$$I_{TL} = ns \exp \left(- \frac{E_t}{k_BT} \right) \left[ 1 - \frac{(N - n)\sigma_n}{(N - n)\sigma_n + m\sigma_{mn}} \right] \quad (3.9)$$

Another assumption is that the probability of retrapping the carrier is negligible: $m\sigma_{mn} \gg (N - n)\sigma_n$. Then equation 3.9 becomes

$\eta$
\[ I_{TL}(t) = -\frac{dn}{dt} = sn \exp \left( -\frac{E_l}{k_BT} \right) \]  
\hspace{1cm} (3.10)

where \( s \) is a frequency factor, \( n \) is a electron concentration in the trap, \( E_l \) is the activation energy of the trap. Solution of this differential equation is:

\[ n(t) = n_0 \exp \left( -s \int_{T_0}^{T} \exp \left( -\frac{E_l}{k_BT} \right) dt \right) \]  
\hspace{1cm} (3.11)

Using linear heating function \( T = T_0 + \beta t \), where \( T_0 \) is a starting temperature and \( \beta \) is a heating rate, we get:

\[ n(T) = n_0 \exp \left[ -\frac{s}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E_l}{k_BT} \right) dT \right] \]  
\hspace{1cm} (3.12)

Inserting this into equation 3.10 yields the Randall-Wilkins first-order equation:

\[ I_{TL}(T) = sn_0 \exp \left( -\frac{E_l}{k_BT} \right) \exp \left[ -\frac{s}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E_l}{k_BT} \right) dT \right] \]  
\hspace{1cm} (3.13)

Another possibility is that retrapping dominates, or \( m\sigma_{nn} \ll (N - n)\sigma_n \). Then applying it to 3.9 gives:

\[ I_{TL}(t) = -\frac{dn}{dt} = s \left( \frac{\sigma_n}{N\sigma_{mn}} \right) n^2 \exp \left( -\frac{E_l}{k_BT} \right) \]  
\hspace{1cm} (3.14)

Now \( \frac{dn}{dt} \propto n^2 \), so this is the second-order process. With the additional assumption that \( \sigma_n = \sigma_{mn} \), integration of equation 3.14 gives the Garlick-Gibson thermoluminescence equation for second-order processes:

\[ I_{TL}(T) = \left( \frac{n_0^2}{N} \right) s \exp \left( -\frac{E_l}{k_BT} \right) \left[ 1 + \left( \frac{n_0 s}{\beta N} \right) \int_{T_0}^{T} \exp \left( -\frac{E_l}{k_BT} \right) d\theta \right]^{-2} \]  
\hspace{1cm} (3.15)

For different relative magnitudes of retrapping and recombination probabilities May and Partridge wrote an empirical expression for general-order process:

\[ I_{TL}(t) = n^b s' \exp \left( -\frac{E_l}{k_BT} \right) \]  
\hspace{1cm} (3.16)

where \( s' \) has the dimensions of \( m^{3(b-1)} s^{-1} \) and \( b \) is defined as general-order parameter and not necessarily 1 or 2. Integration of equation 3.16 for \( b \neq 1 \) gives:

\[ I_{TL}(T) = s'' n_0 \exp \left( -\frac{E_l}{k_BT} \right) \left[ 1 + \left( \frac{b-1}{\beta} \right) \int_{T_0}^{T} \exp \left( -\frac{E_l}{k_BT} \right) d\theta \right]^{-\frac{1}{b-1}} \]  
\hspace{1cm} (3.17)

where \( s'' = s' n_0^{(b-1)} \).

If \( b = 1 \) and \( b = 2 \) equation 3.17 reduces to equations 3.9 and 3.15, respectively.
Methods of analysis

The simplest and most applicable method for evaluating the activation energy $E_t$ from experimental data is the initial rise method. The common feature of the both theoretical equations 3.13 and 3.15 is the exponential rise of the beginning of glow curves. If $\ln(I_{TL})$ is plotted as a function of $1/T$, a straight line is produced in the initial rise range with slope of $-\frac{E_t}{k_B}$ (Arrhenius plot), from which the activation energy of the trap $E_t$ can be readily found.

Halperin et al. [158] proposed an extension of initial rise method by plotting $\ln(I_{TLn^{-b}})$ versus $1/T$. Whereas the plot of $I_{TL}$ vs. $1/T$ normally yields a straight line only up to ~ 5% of the maximum intensity, Halperin method extends this range substantially. It allows to determine activation energy from the slope $(-\frac{E_t}{k_B})$ and pre-exponential factor from intersection of the line with Y axis $(s'/\beta)$. Another advantage is that straight line will only emerge when $b$ is correct. This method is restricted only to single isolated peaks. When thermoluminescence peaks overlap, this method can give accurate values only for the low-temperature peak. Parameters obtained for other peaks would not be accurate, though straight lines corresponding to the peaks are produced.

Another way to obtain glow curve parameters is to fit the experimental data to the appropriate analytical expressions 3.13, 3.15 or 3.17.

When TSL peaks overlap, partial annealing technique is useful in obtaining peaks parameters. Partial annealing means preheating the sample to the particular temperature after excitation, then cooling the sample back to the initial temperature, and after that thermoluminescence is measured.

When it is hard to get the peaks positions straight from glow curve, several annealing-
measuring cycles performed in the temperature range where detectable signal is measured. After excitation, the sample is annealed to the particular $T_{stop}$ temperature, cooled back to the beginning, and then the glow curve is recorded. In order to improve the accuracy of the experiment, step between annealing temperatures of 3 – 5 K is usually accepted.

If one makes the plot of first peak maximum versus annealing temperature (so-called $T_m$-$T_{stop}$ plot, Fig. 3.9), horizontal sections of the curve would show the peaks maxima [159]. This method is very effective in pinpointing peaks positions, though smaller peaks are sometimes masked by their more prominent neighbours. It is also possible to say of what order the peaks are (Fig. 3.9).

![Figure 3.9: Schematic $T_m$-$T_{stop}$ curves for first-order (line B) and second-order (line C) thermoluminescence. Column (a) represents the case of a single glow peak, (b) – overlapped peaks, (c) – quasi-continuous distribution of peaks [159].](image)

From the data, obtained this way, one can also plot activation energy versus annealing temperature (so-called $E_a$-$T_{stop}$ plot), in which staircase-shaped curve is produced [160]. However, this method is restricted to the situation when each next peak possesses greater activation energy than previous one, which is not always true.

**Systems with distributed traps**

Previous section described thermoluminescence, assuming that all traps have the same energy of activation. In fact, it is true in most cases for crystalline materials, where surrounding of the particular defect is strictly defined. It results in equal, discrete activation
Figure 3.10: Annealing of samples: a and b – 1st and 2nd order kinetics, both are theoretical curves (numbers denote subsequent decrease of the initial filling of traps) [156], c – ZnIn$_2$S$_4$ [161], d – polystyrene [162].

energy for such traps. However, the activation energy of traps in polymeric compounds, amorphous materials and crystals with deviations from stoichiometry can produce bands rather than discrete levels.

Thermoluminescence is sensitive to the traps distributed in energy or frequency factor. Under annealing cycles first-order thermoluminescence peak remain in the same position, in second-order TSL it slightly shifts to higher temperatures (Fig. 3.10 a, b). For the energy-distributed traps the peak shifts continuously to higher temperatures with increase of annealing temperature (Fig. 3.10 c, d) [159]. The spread of activation energies in distribution can be estimated from initial rise method applied to glow curves obtained by several annealing experiments [156].

Tunnelling [156]

The carriers transport via conduction or valence band is not the only way by which the carriers can be transferred from the traps to the recombination centers. Very important channel of the carriers transport in solids is the tunnelling. This effect is shown to be responsible for the afterglow effect in LH temperatures in some materials [163, 164, 165].
The afterglow was shown to follow a hyperbolic law, namely, \( I \propto t^{-1} \), and therefore does not produce any peaks in thermoluminescence because of its essential temperature-independent character.

The model of the carriers tunnelling in solids was proposed by Mikhailov in [166]. In this model (see Fig. 3.11), an electron in a trap of depth \( E_1 \) is separated by a distance \( r \) from a positively charged center. After tunnelling through the potential barrier the electron can recombine with the positive charge of the recombination center, emitting a luminescence photon.

The tunnelling rate \( K \) is given by

\[
K = \nu \exp(-\phi r) \quad (3.18)
\]

where \( \nu \) is a frequency factor, \( r \) is the electron-hole separation and \( \phi \) is given by

\[
\phi = \frac{2\sqrt{2mE_1}}{h} \quad (3.19)
\]

where \( m \) is the mass of the electron.

If no reverse transfer is assumed, the luminescence intensity is proportional to the tunnelling rate:

\[
I = -\frac{dn}{dt} = Kn = Kn_0 \exp(-Kt) \quad (3.20)
\]

where \( n_0 \) is the initial density of trapped charge.

The time dependence of the luminescence is then given by

\[
I(t) = \int_0^t Kn_0 \exp(-Kt) dr \quad (3.21)
\]

From equation 3.18, \( dK = -(K/\phi)dr \), then

\[
I(t) = \int_0^t -\left[ \frac{Kn_0 \exp(-Kt)}{K} \right] dK = -\frac{n_0 \phi \exp(-Kt)}{t} \quad (3.22)
\]

For large \( r \), when \( K \approx 0 \) and \( \exp(-Kt) \approx 1 \), the luminescence would obey the hyperbolic law:

\[
I(t) \approx -\frac{n_0 \phi}{t} \quad (3.23)
\]

Since luminescence was measured in arbitrary units (the photon counting technique was not used in the PL measurements in this work), and the frequency factor \( \nu \) remains
unknown, this model would be used only qualitatively in the interpretation of experimental results.

**Thermally assisted tunnelling**

The electron in quantum well can be thermally excited to the higher energy state \((E_2\) in the Fig. 3.11) within the well before tunnelling takes place. In this case, it still does not have enough energy to escape from the well, and still the only way to do it is the tunnelling. This mechanism is often referred as "thermally assisted tunnelling". The probability of the electron release for the thermally assisted tunnelling depends on temperature, therefore this mechanism produce peaks in thermoluminescence. At low temperatures the probability may be lower than that for tunnelling, but become much larger at higher temperatures.

**Experimental setup**

Setup for thermoluminescence measurements is shown in Fig. 3.2 b. Samples were placed in cryogenerator Leybold RW2. The He-Cd laser Plasma HCCL-15UM with 325 nm generation line was used as an excitation source. Leybold temperature controller LTC 60 provides the possibility of linear heating. To ensure a good temperature control of the experiment, temperature sensor was placed very close to the sample. Sample’s luminescence was collimated on the slit of the Triax 320 monochromator equipped with LN-cooled Spectrum One CCD-3000 camera. The same heating rate equal to 0.1 K/s was used in all experiments.

### 3.6 EPR

Low-temperature EPR measurements were performed in Bruker 300 and Bruker EMX X-band spectrometers equipped with continuous flow Oxford ESR910 and ESR900 cryostats respectively. Temperature in the cryostats was observed using Oxford ITC4 and ITC5s temperature controllers.

A sample was illuminated by 514.5 nm laser light through optical window in the resonator or quartz holder.
Chapter 4

Results and discussions

4.1 Gallium gadolinium garnet

4.1.1 Sample

The GGG:Mn$^{4+}$ crystal was grown by the Czochralski technique at Claude Bernard Lyon I University. The growth was performed under nitrogen (480 l/h) and oxygen (4,8 l/h) flow in order to decrease gallium oxide decomposition [52]. Manganese has been added in the form of MnO$_2$. The crystal was also doped with equal quantity of calcium by adding CaCO$_3$ to the melt. The composition of the melt was

$$\{\text{Gd}_{3-x}\text{Ca}_x\}|\text{Ga}_{1.95-x}\text{Mn}_x\text{Gd}_{0.5}|(\text{Ga}_3)\text{O}_{12}$$

where $x = 4.85 \times 10^{-3}$. The contents of dodecahedral, octahedral and tetrahedral sites are shown by the brackets {}, || and () respectively.

4.1.2 Experimental results

The luminescence spectrum of the GGG:Mn,Ca crystal in the region of the R-lines is presented in Fig. 4.1. The spectrum shows two narrow lines at 663.5 nm (15 072 cm$^{-1}$) and 668.7 nm (14 955 cm$^{-1}$) denoted as A and B respectively, and the broader structure peaked at 681 nm (14 684 cm$^{-1}$) labelled SA. The A and B lines are the zero-phonon R$_1$ lines of two different strong-crystal-field manganese centers. The SA structure is mostly associated to the vibronic sideband of the A manganese center [53].

The third minor manganese center C is not observed in the luminescence spectra because of its very low intensity [53]. Nevertheless, it has been checked that this minor center cause a redshift of the R$_B$ line position for about 20 cm$^{-1}$ (compared with the position of the B center emission under selective excitation, given in [53]).

The shape of the emission spectrum depends on the excitation wavelength, especially at high pressures. In Fig. 4.2, the emission spectra for different laser excitation are shown at pressure equal to 124 kbar. Taking this into account the R-lines luminescence was
Figure 4.1: The R-lines luminescence spectrum of GGG:Mn,Ca crystal at ambient pressure, excited by 514,5 nm laser line. T = 15 K.

Figure 4.2: The luminescence spectra at different excitations of GGG:Mn,Ca crystal. T = 15 K, P = 124 kbar.

investigated using the 514,5 and 488 nm excitation wavelength in the pressure range from ambient to 150 kbar.

The pressure dependence of the emission is shown in Fig. 4.3 a and b. For the 488 nm excitation, the R_A line becomes dominant with pressure, but its sideband becomes weaker. This result suggests that the A manganese center is more affected by the Ca^{2+} ions at higher pressures. In contrary, for the 514,5 nm excitation the R_B line increase in its intensity and the R_A line decrease. Relative changes in intensity of the R_A and R_B lines can be caused by two effects: changes of the excitation efficiency at given excitation.
Figure 4.3: The influence of hydrostatic pressure on the R₁ lines of A and B manganese centers at T = 15 K. The spectra excited by (a) - 488 nm and (b) - 514.5 nm laser lines.

wavelength due to the pressure shift of the ⁴T₂ bands to the higher energy, and increased contribution of electric-dipole-allowed transitions. Lack of the information about pressure dependence of the ⁴T₂ bands does not allow to distinguish between these two possibilities.

The pressure dependences of the relative integrated intensities of the A, B and SA lines to the total luminescence intensity are presented in Fig. 4.4.

The pressure dependences of the Rₐ and Rₜ lines positions are presented in Fig. 4.5. In the investigated pressure range, the lines are shifted linearly to the lower energies with pressure coefficients dE/dP equal to -1.87 and -1.49 cm⁻¹/kbar respectively (red lines). The experimental data was also fit to the nephelauxetic effect model (blue lines), giving the model parameter η equal to 2.31 and 2.81 for the A and B centers respectively.
4.1. GGG

CHAPTER 4. RESULTS AND DISCUSSIONS

Figure 4.4: The pressure dependences of the integrated intensities of the A, B and SA lines to the total luminescence intensity. The spectra are excited by 514.5 nm line at T = 15 K.

4.1.3 Discussion

The shape of the R-lines emission spectrum of the GGG:Mn,Ca crystal is strongly affected by excitation energy and applied hydrostatic pressure. This is caused by the strong shift of the absorption spectra, related to the manganese centers, with pressure. It is consistent with the $d^3$ ion energy structure in octahedral symmetry, predicted by the Tanabe-Sugano diagram (see Fig. 2.1), where the energies of the $^4A_2 \rightarrow ^4T_1$ and $^4A_2 \rightarrow ^4T_2$ transitions increase strongly with pressure. The pressure dependence of the R-lines intensities (Fig. 4.4) supports this conclusion.

At ambient pressure the vibronic sideband of the A center is more intense than its zero-phonon transitions [53]. With increase of pressure, the zero-phonon $R_A$ line becomes more intense relative to its sideband (Fig. 4.4). Taking this into account, the A site environments become more strongly perturbed with the pressure increase. This way the center of inversion is destroyed and the zero-phonon transitions become electric-dipole allowed and stronger than their phonon sideband.

The redshift of the R-lines with pressure, presented in Fig. 4.5, is due to the nephelauxetic effect. The R-lines shift linearly to the lower energies with pressure, showing coefficients $dE/dP$ equal to -1.87 and -1.49 cm$^{-1}$/kbar for the $R_A$ and $R_B$ lines respectively. The experimental data was fit (blue lines in Fig. 4.5) to the nephelauxetic effect model, which gave the parameter $\eta$ equal to 2.31 and 2.81 for the A and B manganese centers respectively.

The $^2E$ level pressure coefficients of the manganese centers in GGG host are about three times larger than those for Cr$^{3+}$ centers [167], which have the same $d^3$ electronic structure. This can be explained by the stronger Coulomb interaction between Mn$^{4+}$ and O$^{2-}$ ions, which results in larger covalency of the bonds, in contrast to the bonds between bonds.
Figure 4.5: The pressure shift of the of the R₁ lines of A and B manganese centers at T = 15 K. Red lines are linear fits, blue lines are fits to the nephelauxetic effect model (see page 9).

the Cr³⁺ and O²⁻ ions. In addition, stronger interaction between Mn⁴⁺ and Gd³⁺ ions (mediated through oxygen) can also increase the value of the pressure coefficients. The Hartree-Fock energies of the neutral atoms are: Mn – 1,27 (3d), Cr – 1,13 (3d), Gd – 1,51 (4f), O – 1,26 (2p) Ry [168]. In the GGG crystal the 2p levels of oxygen ions are split into a broad p band due to interaction with Gd and Ga atoms. Since manganese enters the crystal in a higher oxidation state than chromium does, its 3d levels are additionally lowered by the Coulomb attraction, therefore they have comparable values with the 4f levels of gadolinium. Having similar energies, the 4f electrons of gadolinium and 3d electrons of manganese interact electrostatically, being in resonance with oxygen valence 2p band.
4.2 Yttrium orthoaluminate

4.2.1 Sample

YAP:Mn crystal was grown in a pure nitrogen atmosphere using Czochralski technique in Institute of Physics, Polish Academy of Sciences. The melt contained 4 mol% more yttrium than aluminium oxide in comparison with the stoichiometric composition. The manganese has been added to the melt in the form of MnO₂ and its concentration was 0,2 mol% with respect to the aluminium content.

This sample distinguished from the others investigated earlier by the lower photochromic sensitivity related to the Mn⁴⁺ ions. Owing to the fact that the Mn⁴⁺ ions do not completely recharge under laser illumination, the high-pressure PL measurements (which require very small size samples) becomes possible. The sample has been annealed in hydrogen for 1 h at 1300 K in order to increase the luminescence intensity of non-intentional Cr³⁺ dopant. The chromium is present in the crystal as an uncontrolled impurity.

4.2.2 Experimental results

The PL spectra in the R-line region of the as-grown and annealed samples are shown in Fig. 4.6. The sharp lines at 691,3 and 692,7 nm are due to R₂ and R₁ lines of the Mn⁴⁺ ions respectively. The sharp line at 721,1 and 723,4 nm are related to the R₂ and R₁ lines of the Cr³⁺ center.

It is seen from the Fig. 4.6 that the chromium R-lines and the broad structure at 735

![Figure 4.6: The photoluminescence spectra of the YAlO₃:Mn,Cr sample in the region of the R-lines at T = 10 K, (a) as-grown crystal and (b) after annealing in hydrogen. The spectra were excited by 514,5 nm laser line.](image-url)
Figure 4.7: The photoluminescence spectra of the manganese R-lines at different temperatures in YAlO$_3$:Mn,Cr sample. The spectra were excited by 514.5 nm laser line.

- 760 nm become more intense after annealing of the sample. The broad structure is ascribed to the vibronic sideband of the strong-crystal-field Cr$^{3+}$ centers. Increase of the Cr$^{3+}$ center luminescence is the only difference induced by the annealing treatment – the Mn$^{4+}$ luminescence remains unchanged. The increase of the Cr$^{3+}$ luminescence is due to increase of the Cr$^{3+}$ ions concentration because of valence state change of the Cr$^{4+}$ centers (Cr$^{4+} \rightarrow$ Cr$^{3+}$). The same effect was observed in EPR measurements after annealing the YAlO$_3$:Cr samples in reducing atmosphere [169].

The manganese R-lines luminescence spectra at different temperatures are shown in Fig. 4.7. The spectral separation of the two R-lines (i.e. the splitting of the $^2E$ level) is equal to 30 cm$^{-1}$. Such splitting for Mn$^{4+}$ is about 80 and 60 cm$^{-1}$ in Al$_2$O$_3$ [170] and Y$_3$Al$_5$O$_{12}$ [171] respectively. The smaller value of the $^2E$ level splitting show that the oxygen octahedron, hosting the Mn$^{4+}$ ions, is less distorted in YAlO$_3$ than it is in Al$_2$O$_3$ and Y$_3$Al$_5$O$_{12}$.

Some complications raised in the high-pressure measurements. Owing to very low intensity of the manganese R-lines and their spectral positions, they overlap with the ruby luminescence that is used for pressure calibration in DAC. Therefore, another pressure sensor, which does not exhibit luminescence in this spectral region, was necessary for such measurements. A new pressure sensor – YAG:Nd$^{3+}$ – has been found to meet all the requirements. Detailed information is given on page 103.

The pressure dependence of the annealed YAlO$_3$:Mn,Cr sample luminescence is shown in Fig. 4.8. The spectral resolution of these results is slightly worse than of those presented in Fig. 4.6. This is because the setup parameters have been optimized to measure a very
small intensity signal originated from the tiny sample inside the DAC. It was checked that the R-lines are not widened due to the lower spectral resolution of the measurements.

All lines in the luminescence spectra undergo a redshift. The pressure coefficients of the Mn$^{4+}$ and Cr$^{3+}$ R$_1$ lines are equal to -1.16 and -1.08 cm$^{-1}$/kbar respectively. The pressure coefficients for the vibronic sideband lines are in the region from -1.2 to -1.3 cm$^{-1}$/kbar, except for the line peaked at 732 nm (at ambient pressure), for which the pressure coefficient is equal to -2.0 cm$^{-1}$/kbar. The pressure dependence of the lines positions are presented in Fig. 4.9.

The experimental results were also fit with the nephelauxetic model described in page 9. The parameter $\eta$ is found to be equal to 1.87 for the Mn$^{4+}$ centers.

4.2.3 Discussion

The pressure coefficient of the Cr$^{3+}$ R-lines in YAP is slightly larger than that of Cr$^{3+}$ in the ruby. This is in agreement with the difference in experimentally obtained bulk moduli of those materials: $B_0$(YAP) = 192 GPa [172] and $B_0$(ruby) = 253 GPa [173]. The pressure coefficients of the vibronic sideband lines are slightly larger than the pressure coefficients of the zero-phonon lines, which is in agreement with the typical pressure dependence of phonon energies in crystals.

The pressure coefficients of the Mn$^{4+}$ and Cr$^{3+}$ R$_1$ lines are similar. This is surprising since the larger valence state of the Mn$^{4+}$ ion should induce stronger overlap between the
Figure 4.9: The pressure-induced spectral dependence of the YAlO₃:Mn,Cr sample sharp photoluminescence lines measured at T = 10 K. The 514.5 nm laser line was used as an excitation. Filled symbols are used for Mn⁴⁺ and Cr³⁺ R₁ lines, open symbols represent vibronic sideband lines. Red lines are linear fits, blue line – the nephelauxetic model approximation (see page 9).

cation and the ligands, thus having larger degree of chemical bonds covalency. Owing to this, the pressure coefficients of the Mn⁴⁺ ions are larger than that of the Cr³⁺ ions, when substituted the same host sites [54]. Indeed, it is not occur in the YAP crystal. The similarity of the pressure coefficients for both cations may occur due to the influence of some other defect on the one of the dopant ions, altering its properties. In fact, it has been shown that annealing in hydrogen atmosphere increases the intensities ratio of Cr³⁺/Mn⁴⁺ luminescence, which implies that annealing affects the point defect system of YAP crystals.
4.3 Lithium niobate

4.3.1 Samples

Four samples of lithium niobate, doped with chromium and magnesium, have been chosen to study the crystal’s defect structure in this work. Different concentrations of magnesium result in differences in the defect structure. Chromium is used as an optical probe of those changes. Detailed information about the samples is given in table 4.1.

Table 4.1: Composition of the samples and dopant concentrations in the melt.

<table>
<thead>
<tr>
<th>Notation</th>
<th>Composition</th>
<th>Li content, mol%</th>
<th>Dopants in the melt, mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>S1</td>
<td>near stoich.</td>
<td>49,7</td>
<td>0,2</td>
</tr>
<tr>
<td>C1</td>
<td>congruent</td>
<td>48,6</td>
<td>0,1</td>
</tr>
<tr>
<td>C2</td>
<td>congruent</td>
<td>48,6</td>
<td>0,1</td>
</tr>
<tr>
<td>C3</td>
<td>congruent</td>
<td>48,6</td>
<td>0,1</td>
</tr>
</tbody>
</table>

First two samples S1 and C1 are doped with Mg above the threshold (see page 31 for details), two other – C2 and C3 – are the pre-threshold Mg-doped ones.

Congruent crystals were grown in air using Czochralski technique from a congruent melt (Li/Nb = 0,945) at the Universidad Autónoma de Madrid, Spain. The pre-threshold Mg-doped samples C2 and C3 are green in colour. The above-threshold Mg-doped sample C1 is pink. For all congruent crystals, the Cr/Nb ratio of ~0,25 mol% was measured by total x-ray fluorescence, because of high effective segregation coefficient for the chromium in LiNbO₃ (κeff ~ 2 [174]).

The near stoichiometric crystal S1 was grown by the top-seeded solution growth method [81] at the Universidad Autónoma de Madrid, Spain. The crystal shows a uniform pink colour along the whole length. As it was mentioned above, potassium does not enter the crystal during its growth, it only causes the crystal to grow very close to stoichiometric composition [175].

All samples were cut perpendicular to the c axis and the faces were polished to spectroscopic quality.

4.3.2 Experimental results

Photoluminescence

It was published recently in [21] that two of the chromium R-lines, detected in near stoichiometric double doped lithium niobate, are bleachable under 514,5 nm Ar⁺-ion CW laser excitation (2,41 eV).

Figure 4.10 illustrates the observed photobleaching. The R-lines, originated from the strong-crystal-field Cr³⁺ centers, are seen on the high-energy shoulder of broad ⁴T₂ → ⁴A₂
luminescence associated with the weak-crystal-field $\gamma$- and $\delta$-$\text{Cr}^{3+}$ centers. The lines at 731 and 734.9 nm are attributed to the $R_1$ lines of $\beta$- and $\alpha$-$\text{Cr}^{3+}_{\text{Li}}$ centers respectively [22, 140]. The $R$-lines of the weak-crystal-field $\gamma$-$\text{Cr}^{3+}_{\text{Li}}$ center are seen only in the temperatures above 50 K, when the $^2\text{E}$ level is thermally populated [141, 139].

The lines at 740.3 and 738.0 nm were also observed in [22], and have been attributed to the $R$-lines of the strong-crystal-field $\varepsilon$-$\text{Cr}^{3+}_{\text{Nb}}$ center, perturbed by a nearby vacancy or antisite. The $^2\text{E}$ level splitting of this center was indicated to be 55 cm$^{-1}$ in [22] and 42 cm$^{-1}$ observed in this work. However, it can be shown using the Maxwell-Boltzmann distribution that at such $^2\text{E}$ level splitting and low temperatures (11 K) the population of upper level $2\Sigma$ would be three orders lower than that of the level $\Sigma$. Since the intensities
ratio of the observed lines is approximately $1/5$, they must be attributed to the $R_1$ lines of two different strong-crystal-field $\text{Cr}^{3+}_{Nb}$ centers, which would be noted further as $\varepsilon$ and $\varepsilon'$. Initially the $R_1$ lines of the $\varepsilon$- and $\varepsilon'$-$\text{Cr}_{Nb}$ centers are more intense than the $\alpha$- and $\beta$-$\text{Cr}_{Li}$ ones. They slowly fade with laser illumination, whereas the $\alpha$- and $\beta$-$\text{Cr}_{Li}$ $R$-lines remain of the same intensity. The intensities ratio of the $\varepsilon$- and $\varepsilon'$-$\text{Cr}^{3+}_{Nb}$ $R_1$ lines stays constant as they decrease under laser illumination. These experiments show that a selective optical bleaching mechanism takes place in the crystals and it is related only to the strong-crystal-field $\varepsilon$- and $\varepsilon'$-$\text{Cr}^{3+}_{Nb}$ centers.

Once the illumination is switched off, the intensities of the bleached $R_1$ lines remain diminished, and only little percent recovery has been observed at low temperatures. The original intensities of the lines were found to recover after heating the sample up to 160 K. This result suggests that a stable electron trap is involved in the process.

In order to check the thermal stability of the trap, the thermal recovery of the bleached $\varepsilon$- and $\varepsilon'$-$\text{Cr}_{Nb}$ $R_1$ lines intensities was measured as a function of annealing temperature. The experiment was carried out in three steps. First of all the initial photoluminescence spectrum was measured at low temperature after freezing the sample and bleaching the $R$-lines to the 20% of their initial intensities. Next, the sample was annealed to desired temperature and instantly quenched back. The luminescence was recorded again. The ratio of the bleached $R$-lines intensity to the intensity after annealing is shown in Fig. 4.11 as a function of annealing temperature. The bleaching was performed using 1 W of 514.5 nm laser light, the photoluminescence was measured using only 1 mW of the same laser line. The recovery of the intensity of the bleached lines starts from approximately

![Graph showing thermal recovery of Cr lines intensity versus annealing temperature for Mg-doped congruent sample C1. The graph includes a line equation $E_a = 0.13 \pm 0.02$ eV.](image-url)
110 K and the full recovery is observed after heating the sample up to 160 K. Similar results have been also obtained for the $\varepsilon$- and $\varepsilon'$-Cr$_{Nb}$$^{3+}$ centers in congruent and near-stoichiometric samples in [176]. The thermal stabilities of the both lines are equal. Activation energy, obtained from the Arrhenius plot, is equal to 0.13 ± 0.02 eV.

It was proposed in [21] and [177] that the bleaching of the R-lines is caused by photoionization of the $\varepsilon$- and $\varepsilon'$-Cr$_{Nb}$ centers under laser illumination. Free electrons, released because of the photoionization, are then trapped at niobium ions creating Nb$^{4+}$ small polaron. The ionized chromium centers remain in the 4$^+$ charge state.

Taking this into account the simple model of the bleaching process was introduced in [21]. The $\varepsilon$- and $\varepsilon'$-Cr$_{Nb}$ centers concentration $N$ under laser illumination must be time-dependent according to:

$$\frac{dN(t)}{dt} = -\sigma(\lambda)I(\lambda)DN(t) + kN'(t)$$  \hspace{1cm} (4.1)

where $\sigma(\lambda)$ – the absorption cross section of the bleachable centers, $I(\lambda)$ – the light intensity, $D$ – coefficient proportional to the decay time of the chromium $^4T_1 \rightarrow ^4A_2$ radiative transitions, $k$ – the Nb$^{4+}$ thermal ionization coefficient and $N'(t)$ – concentration of the Nb$^{4+}$ polarons, taking into account that $N_0 = N(t) + N'(t)$ where $N_0$ is the initial concentration of the bleachable centers, $N(t)$ is their time-dependent concentration.

The solution of the equation (4.1) is:

$$N = A + B\exp\left(\frac{-t}{\tau_0}\right)$$  \hspace{1cm} (4.2)

where

$$A = kN_0/(\sigma DI + k),$$

$$B = I\sigma D N_0/(\sigma DI + k),$$

$$1/\tau_0 = \sigma DI + k.$$  

The luminescence intensity is then written as:

$$L(t) = I\sigma(\lambda)N(t) = A_0 + B_0\exp\left(\frac{-t}{\tau_0}\right)$$  \hspace{1cm} (4.3)

where

$$A_0 = \sigma I k N_0 / (\sigma DI + k),$$

$$B_0 = I^2 \sigma^2 D N_0 / (\sigma DI + k).$$

According to this model, the PL kinetics of the $\varepsilon$- and $\varepsilon'$-Cr$_{Nb}$ centers must have single-exponential form, which was successfully illustrated in [21] (see Fig. 4.12).

Fig. 4.13 and 4.14 show the intensity kinetics of the prominent $\varepsilon'$-Cr$_{Nb}$$^{3+}$$^1R_1$ line in near stoichiometric and congruent crystals, measured in more extended time interval than it
Figure 4.12: Photoluminescence bleaching kinetics of the $\varepsilon'$-Cr$_{Nb}^{3+}$ R$_1$ line under different laser lines in double doped near stoichiometric sample [21]. Solid lines are the experimental data, dashed lines - single-exponential fits using equation 4.3. $T = 10$ K.

Figure 4.13: Kinetics of the $\varepsilon'$-Cr$_{Nb}^{3+}$ R$_1$ line under 514.5 nm laser excitation (black line) and stretched-exponential fit (red line) for the near-stoichiometric sample S1. $T = 10$ K. The values of parameters of the stretched-exponential fit are given in the graph.

was done in [21, 177]. It is not possible to obtain a satisfactory single-exponential fit of this data using the model introduced in [21, 177]. Only stretched-exponential function gives good results. This can be explained by the fact that the model does not take into account some additional factors, which will be discussed in detail later.

The broad luminescence, ascribed to the $^4T_2 \rightarrow ^4A_2$ transitions of the weak-crystal-field Cr$_{Li}$ and Cr$_{Nb}$ centers, was also checked for being photobleachable. As it is seen from
Fig. 4.14: Kinetics of the \( \varepsilon' \)-\( \text{Cr}^{3+} \) \( \text{Nb} \) line under 514,5 nm laser excitation (black line) and stretched-exponential fit (red line) for the congruent sample C1. \( T = 10 \) K. The values of parameters of the stretched-exponential fit are given in the graph.

Fig. 4.15, the broad band does not show any as slow kinetics as the bleachable R-lines do under the 514,5 nm laser illumination. It was detected instead that at the very beginning of the laser illumination the PL signal shows a fast decay, stabilizing after that on some level. After the fast initial decay, the PL signal is stable for a very long time. It was checked that the fast decay is originated from the sample, and it is not related to some experimental setup peculiarities.

The fast decay is very intense only for the first time the laser strikes the sample. Subsequent repetitions do not produce decays of the same intensity. Very small intensity decays are detected instead.

The thermal quenching of the fast decay intensity has been measured in the following way: the sample was cooled from the room to certain temperature in the dark and luminescence was measured as a function of time. The ratio of the decay intensity at certain temperature to the decay intensity at 4 K is shown in Fig. 4.16 as a function of temperature. The fast decay intensity becomes smaller starting from 100 K and almost disappears at 180 K, which resembles the thermal behaviour of the optical bleaching of the \( \varepsilon \)- and \( \varepsilon' \)-\( \text{Cr}_{\text{Nb}} \) centers (Fig. 4.11).

The observed fast decay may be connected with \( \text{Cr}^{3+}_{\text{Li}} \) centers since the PL measurements were carried out in the region of broad luminescence, originated from weak-crystal-field \( \text{Cr}^{3+}_{\text{Li}} \) and \( \text{Cr}^{3+}_{\text{Nb}} \) centers. Light-induced EPR measurements of the \( \text{Cr}^{3+}_{\text{Li}} \) line, which have been expected to correlate with the fast decay, were not successful because of low intensity of the \( \text{Cr}^{3+}_{\text{Li}} \) line (i.e. very low signal/noise ratio of the measurements) in \( \text{Cr} \) and above-threshold Mg-doped lithium niobate. Further studies are necessary to reveal the origin of the fast PL decay.
Figure 4.15: Photoluminescence kinetics of the $^4T_2 \rightarrow ^4A_2$ broadband measured at 1000 nm using the 514.5 nm line of Ar$^+$-ion laser at $T = 4$ K.

Figure 4.16: Thermal quenching of the fast decay intensity, observed in photoluminescence of the $^4T_2 \rightarrow ^4A_2$ broadband at $\lambda = 1000$ nm and $T = 4$ K. Arrhenius plot of the data and obtained activation energy are shown in the inset.
Light-induced absorption

In [21] the Nb$^{5+}_{Nb}$ ions are presumably mentioned as the electron traps involved in the bleaching process of the ε- and ε’-Cr$_{Nb}$ centers. This assignment has been made based on the absorption measurements, where 1200 nm broad band was detected after laser illumination. This absorption band is connected with the Nb$^{4+}_{Nb}$ small polarons according to [43].

Light-induced absorption experiments were carried out to study the niobium small polarons absorption and their kinetics in the above-threshold magnesium doped samples. The 325 nm of He-Cd laser (~15 mW) and 514,5 nm Ar$^+$-ion laser (~1 W) lines were used as an excitation sources.

![Graph showing optical absorption of the above-threshold Mg-doped LiNbO$_3$:Cr,Mg samples.](image)

Figure 4.17: Optical absorption of the above-threshold Mg-doped LiNbO$_3$:Cr,Mg samples. T = 4 K.

The transmissions of both above-threshold Mg-doped samples are limited at shorter wavelength (see Fig. 4.17) due to the strong charge transfer (CT) transitions related to the Cr$^{3+}$ ions [147, 178]. It should be noted that for congruent and near stoichiometric samples the absorption edge is reported to be at slightly lower wavelength than 325 nm, i.e. at 319 and 303 nm respectively for absorption coefficient equal to 20 cm$^{-1}$ [81]. Therefore the 325 nm light is close to the maximum of the charge transfer band, and penetrates into the samples deeper than the light with energy above the bandgap.

The He-Cd laser was used since it induces stronger absorption changes in the samples than the 514,5 nm Ar$^+$-ion laser line with less power of the light. The beam was not focused on sample and the power of 325 nm line was estimated to be equal to 0,88 kW/m$^2$. The high power of 514,5 nm line, necessary to induce the polarons absorption, also caused heating of the samples, which was considered as an undesirable effect.

Two absorption bands peaked at 1200 and 530 nm are detected after 30 min of the He-Cd laser illumination (Fig. 4.18). It should be noted that the light-induced absorp-
Figure 4.18: Light-induced absorption of the above-threshold Mg-doped LiNbO$_3$:Cr,Mg samples at liquid helium temperature after 30 minutes of the 325 nm (blue line) and 514.5 nm (green line) laser excitations. T = 4 K.

Absorption is treated as a difference between the sample absorption after and before the laser illumination.

The 530 and 1200 nm absorption bands of the congruent sample C1 seem to be superimposed over additional absorption of the unknown origin, growing from smaller energies to the absorption edge of the sample.

An additional small absorption peak is visible near 780 nm after 514.5 nm excitation in the congruent C1 sample and barely detectable in near stoichiometric S1 one. This peak is connected with Nb$^{1+}$ small polarons absorption [104]. This fact leads to the conclusion that there is still a small amount of niobium antisite defects in both above-threshold Mg-doped samples despite of the high Mg content.

There are differences in absorptions induced by 325 and 514.5 nm laser excitations.
For the C1 sample the 1200 nm broad band is present under 325 nm excitation and absent for 514.5 nm one. The 780 nm absorption band is seen only under 514.5 nm excitation and is not visible under 325 nm one. However, the shift of the broad near-infrared band in C1 sample (in comparison with the S1 sample) can be explained by overlapping the broad 1200 nm absorption structure with 780 nm Nb$_{Li}$$_{2}$± band.

Sequence of annealing experiments was performed to check the thermal stability of both absorption bands (Fig. 4.19). The samples were cooled down to 4 K and then the reference absorption was measured (the absorption was measured in ranges 400 - 700 nm to capture the whole 530 nm peak and in 1150 - 1250 nm to obtain the intensity of the 1200 nm peak maximum). After that, the samples were excited by the He-Cd laser for 30 minutes and the absorption was measured again. The difference between absorption after and before the laser illumination gives the reference intensity of the light-induced absorption bands. Next, the samples were heated up to a certain annealing temperature and cooled down. The absorption was measured again. The difference between the "annealed" absorption and the reference one gives the intensity of the "annealed" light-induced absorption bands. Plot of the intensities ratio annealed to initial versus annealing temperature is shown in Fig. 4.19. It should be noted that background, caused by 1200 nm band, was carefully subtracted when peaking the 530 nm band intensity. It is seen that both bands bleach simultaneously with temperature, extinguishing completely near 100 K.

It was mentioned earlier that the broad band peaked at 1200 nm is described in the literature as a Nb$_{Li}$$_{2}$± small polarons absorption in lithium niobate crystals doped with MgO and ZnO [43]. Very similar absorption band was also detected in 1 mol% Mg-doped near stoichiometric samples after excitation by 325 nm laser [179].

The high-energy band, peaked at 530 nm, is fortuitously similar in shape and placed in the same position as the absorption bands of three different defects detected in lithium niobate.

The 530 nm band is very similar in shape and placed in the same position as the Cr$_{Ni}$$_{3}$±, 4A$_{2}$ → 4T$_{1}$ intrashell absorption, shown in [142] (Fig. 5). The intensity of absorption due to photobleachable centers can be estimated to check this assumption. It was shown in [23] that the integrated luminescence intensity of all chromium R-lines is about 1/100 lower than that of the broad 4T$_{2}$ → 4A$_{2}$ radiative transitions. Two of four R-lines are shown to be photobleachable. If the concentration of the only bleachable ε- and ε'-Cr$_{Ni}$ centers is about 1/200 lower than the whole chromium content, and the chromium 4A$_{2}$ → 4T$_{1}$ and 4A$_{2}$ → 4T$_{2}$ absorption bands intensities are about 1.5 cm$^{-1}$, the expected absorption change due to bleaching would be around 0.005 cm$^{-1}$, assuming the same absorption cross-section for all chromium centers and that the 2/3 of the bleachable centers are ionized. Such low magnitudes are smaller than observed polarons absorptions, and therefore can be barely visible in light-induced absorption spectra. In addition, increase of chromium absorption under laser illumination is in disagreement with observed R-lines bleaching. Owing to small amount of the bleachable centers, it is also not very likely to detect
Figure 4.19: Thermal stabilities of the Nb\textsuperscript{4+} and O\textsuperscript{-} polaronic absorption bands after 325 nm excitation. Arrhenius plots of the data and obtained activation energies are shown in the insets.

the Cr\textsuperscript{4+} absorption and, in fact, no additional absorption bands were detected in these measurements.

The 530 nm band is also very similar to Nb\textsuperscript{4+}:Nb\textsubscript{Li}\textsuperscript{4+} bipolarons absorption [120]. In the above-threshold Mg-doped samples the amount of Nb\textsubscript{Li} antisites is strongly reduced, so detection of the bipolarons absorption is very unlikely. However, their creation, at least in trace amounts, cannot be entirely discarded especially for congruent C1 sample. For this sample the Nb\textsuperscript{4+}:Li antisites absorption was detected under 514,5 nm excitation (see below) and some other evidences of the antisites have been also found in thermoluminescence experiments (see next chapter for detail).

It was shown in [179] that holes bound to lithium vacancies are produced under 325 nm
Figure 4.20: Intensity of the light-induced absorption, measured at 1200 nm as a function of 514.5 nm excitation power for the S1 sample. T = 4 K.

Laser light in near stoichiometric Mg-doped lithium niobate. A similar absorption band peaked at 530 nm was shown to be peculiar to $O^-$ hole small polarons in congruent lithium niobate [107, 122]. Taking this into account the 530 nm band is believed to be connected with $O^-$ hole small polarons. In addition, the 530 nm band has been checked to satisfy the hole polaron condition $W^2/M \approx 0.14$ eV [122]. For this band (both samples), the relation was estimated to be 0.136 eV. The stabilization energy of the $O^-$ hole small polaron is equal to 1.2 eV.

Identical thermal stabilities of both $Nb_{Nb}^{4+}$ and $O^-$ small polarons absorption bands (Fig. 4.19) point to their mutual recombination.

Despite of high power of the 514,5 nm excitation, it produces smaller absorption changes than the 325 nm line. It was shown in [105] and [111] that the $O^-$ hole polarons and associated with them $Nb_{Li}^{4+}$ small polarons can be produced by 532 nm pulsed laser light by two-photon ionization in undoped congruent lithium niobate. To check if the light-induced absorption of samples is produced by 514,5 nm excitation by two-photon process a plot of the broad $Nb_{Nb}^{4+}$ absorption intensity as a function of excitation power has been made (Fig. 4.20). It is seen from this plot that the dependence is not parabolic, which means that the 514,5 nm light does not excite the samples via two-photon absorption process. It should be noted that the non-linear excitation dependence of the absorption could be connected with the heating of sample by the laser light.

Taking into account the high power of the 514,5 nm excitation light, necessary to produce the light-induced absorption, it is assumed that this light hits the tail of the CT band. Thus, both laser lines induce the same excitation process, but the 325 nm line is more efficient since it is much closer to the peak of the CT band.

Build-up and decay kinetics of the light-induced $Nb_{Nb}^{4+}$ small polarons absorption are detected under 325 nm laser excitation (Fig. 4.21). Absorption kinetics under the 514,5 nm
Figure 4.21: Light-induced absorption kinetics of Nb$_{3+}$ small polarons, taken at 1220 nm, $T = 4$ K. Build-up and decay of the absorption kinetics are fit with stretched-exponential function (red and blue lines). The values of parameters of the stretched-exponential fits are given in the graph.

excitation was rather weak and highly perturbed by noise. Therefore, they are not shown in this work. Surprisingly, no relaxation of laser-induced absorption has been detected for the near-stoichiometric sample S1.

Same as in the R-line bleaching kinetics (Fig. 4.14), fitting the absorption kinetics with one or two exponential function does not produce acceptable results. Both rise and fall of the light-induced absorption in both above-threshold Mg-doped samples can be approximated with stretched-exponential function with reasonable accuracy.

Some parameters of the stretched-exponential approximation, such as $\beta$, $\langle \tau \rangle$ and $\sigma$, depend strongly on the parameter $y_0$ that corresponds to the background intensity. Since
the stretched exponential function decay very slowly after the time \( \tau_{KWW} \) (much slower than the standard exponential function with the same decay time \( \tau_{KWW} \)), it is necessary to continue the measurement for a very long time to obtain the parameter \( y_0 \) experimentally. The lower is \( \beta \) the slower is the decay. Owing to difficulties in precise determination of the \( y_0 \), the rest of the parameters, obtained from experimental data approximation, may contain significant uncertainty. Therefore, the stretched-exponential approximation is used to show the non-exponential character of the polarons kinetics in absorption and bleaching of the Cr\(^{3+}\) Nb R-lines. In fact, the stretched-exponential function is widely used in approximation of kinetics of small polarons in lithium niobate [109, 110, 111, 112, 113, 114, 115, 116, 117, 118].

The \( O^- \) small polaron absorption kinetics was not measured due to the experimental setup restrictions (see page 37 for more detail).

**EPR**

It has been published recently in [180] that the almost isotropic EPR line, ascribed to the Cr\(^{3+}\) Nb centers [148], is bleachable under the 514,5 nm laser illumination. The intensity of the line diminishes for several percents under the laser light, depending on the illumination intensity. Almost total recovery of the signal intensity is observed after switching off the illumination. In both diminish and recovery of the signal two different kinetics occur, one almost instantaneous and second one with characteristic time in the order of minutes. After laser illumination the EPR signal does not recur to the initial intensity (see Fig. 4.22). It should be noted that the only change of the EPR signal is shown, which is about several percent of the whole line intensity. This effect seems to correlate with the optical bleaching of the \( \varepsilon^- \) and \( \varepsilon'\)-Cr\(_{\text{Nb}}\) centers described above, assuming that the both strong-crystal-field and weak-crystal-field Cr\(_{\text{Nb}}\) centers produce identical EPR lines.

Recent experiments, which have been made on modern Bruker EMX X-band spectrometer, did not succeed to repeat these results. No slow kinetics has been observed. The only fast change of the EPR signal is detected after switching the laser illumination on and off. It has been also observed that the temperature does not return to its initial value after laser illumination. Small deviations equal to \( 0,05 - 0,2 \) degree (at 3,8 K) have been always observed, which most probably induced by heating of cryostat internals by laser light. The temperature rises by \( 1 - 2 \) K under the laser illumination (0,6 W of 532 nm line, frequency-doubled YAG:Nd CW laser). It should be noted that this is not the temperature of the sample itself, but the temperature of helium gas that flows around the sample. Since the sample absorb light at 532 nm (see Fig. 4.17), the laser heats the sample, which in turn heats the helium gas. Small changes of the EPR signal intensity correlate very well with the measured temperature. After laser illumination of the sample and adjusting the temperature to its precise pre-illumination value, the EPR signal intensity returns to its initial magnitude (taking into account the experimental accuracy).
4.3. LITHIUM NIOBATE

CHAPTER 4. RESULTS AND DISCUSSIONS

Figure 4.22: Influence of 514.5 nm laser illumination on the EPR signal of Cr$^{3+}_{\text{Nb}}$ center in near stoichiometric above-threshold Mg-doped LiNbO$_3$:Cr$_x$Mg crystal, T = 3 K. The only change of the EPR signal is shown, which constitute a few percent of the whole line intensity.

Figure 4.23: Intensity of the Cr$^{3+}_{\text{Nb}}$ EPR signal as a function of temperature. Black squares – experimental data, red line – analytical Curie-Weiss approximation. The region of the experimental temperatures is shown in the inset.

The temperature dependence of the Cr$_x$Nb EPR line intensity is shown in Fig. 4.23. In the low temperatures region the EPR signal intensity is governed by Curie-Weiss law. It is shown in the inset that the change of the temperature for only 0.1 K (at LH temperatures) reduces the EPR signal intensity for 1.4%. Taking this into account, the fast kinetics observed in [180] at switching the laser on/off is due to heating the sample by the laser light. The slow kinetics are related to the temperature changes due to setting the thermal balance inside cryostat after switching on/off the laser.
**Thermoluminescence**

Thermoluminescence was used for further investigation of the charge traps in the lithium niobate crystals.

Samples were excited by 325 nm line of He-Cd laser (≈15 mW) at 10 K. The samples were exposed to the excitation for 30 minutes since it was observed that after this time the TSL signal intensity is saturated, and further illumination does not lead to increase of the signal. Thermoluminescence glow curves are taken near 875 nm (averaging in the range 850 – 900 nm that corresponds to the maximum of the luminescence prior to the detector spectral sensitivity normalization) in the temperature interval 15 – 315 K. Heating rate for all measurements was 0.1 K/s. After subtracting of background (caused by dark signal of the detector), all glow curves were normalized to the \(\text{Cr}^{3+}\) thermal quenching of luminescence, individually measured for each sample (Fig. 4.25).

Thermoluminescence glow curves for all four samples are shown in figure 4.24.

As it is seen from Fig. 4.24, there are different sets of TSL peaks in the pre- and above-

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<th>C2</th>
<th>C3</th>
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<tr>
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<td>280 K</td>
<td>275 K</td>
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Table 4.2: TSL peaks positions of the investigated samples.

![Graph showing TSL signal intensity vs. Temperature](image_url)

Figure 4.24: Thermoluminescence glow curves of the LiNbO₃ samples.
Figure 4.25: Thermal quenching of Cr$^{3+}$ luminescence in LiNbO$_3$ samples. 514.5 nm laser line was used as an excitation.

Figure 4.26: Thermoluminescence signal after 325 nm excitation (red line) and photoluminescence of Cr$^{3+}$ taken under 532 nm excitation (black line) for the congruent sample C1. Both spectra are normalized to the detector spectral sensitivity and reduced to equal intensity.

threshold Mg-doped samples. The pre-threshold samples show peaks at temperatures 156 and 211 K (221 K), whereas above-threshold ones show peaks clearly at lower and higher temperatures. Peaks positions obtained from annealing experiments are shown in table 4.2.

As it is seen from Fig. 4.25, the thermal quenching of the Cr$^{3+}$ luminescence for all
samples is different. The pre-threshold samples produce almost similar glow curves where the luminescence quenching starts from approximately 150 K, whereas the above-threshold samples show the luminescence quenching at lower temperatures.

It should be noted that the data, presented in the Fig. 4.25, have not been integrated in the entire spectral range of the chromium broadband luminescence, which then would be proportional to the quantum efficiency of the Cr$^{3+}$ radiative transitions. The integration has been performed in the same spectral range of 850 – 900 nm, where the thermoluminescence signal was measured. Thus, these data serve only to normalize the raw thermoluminescence measurements to the quantum efficiency of the Cr$^{3+}$ luminescence.

The wavelength dependence of the thermoluminescence for all four samples coincides with PL of the Cr$^{3+}$ $^4T_2 \rightarrow ^4A_2$ intrashell transitions, well described in the literature [22, 140]. An example is presented in Fig. 4.26. No other thermoluminescence signal was detected in the visible and near-infrared region in the investigated temperature interval.

**Pre-threshold Mg-doped samples**

Fig. 4.27 shows the glow curves of the pre-threshold samples C2 and C3. These samples have one common peak at around 220 K, Mg undoped sample C3 additionally have a prominent peak at 156 K. As it is shown in inset, the C2 sample produce barely detectable peak at around 95 K. Another small peak at 275 K, overlapped with more intense 221 K one, was detected owing to the plot of the first peak position versus annealing temperature (Fig. 4.28, bottom part).

The annealing spectra of C2 sample, shown in Fig. 4.28 (upper part), resemble the spectra from traps, distributed in energy or frequency factor. The glow curve could not be approximated by first- or second-order TSL equations with reasonable accuracy.

Annealing spectra of the C3 sample is not shown because it was not easy to obtain a clear thermoluminescence signal. First, the TSL signal of this sample is very weak in comparison with the C2 one. Second reason is sparks that appear at different temperatures during heating of the sample. The sparks were caused by the pyroelectric effect. Two of them (smallest ones among all experiments) are seen in Fig. 4.27 and 4.24 at around 175 K. This is, most probably, the result of lower sample conductivity (in comparison with the other samples), since this sample does not contain any Mg at all [127].

Fig. 4.29 show plot of the activation energy versus annealing temperature for the C2 sample. Growth of the activation energy, instead of its distribution around certain value in the peak region, illustrates that the traps are distributed in energy. The evaluated energy distribution range is equal to 0.55 – 0.85 eV.

The experimental data for C3 sample are less clear. A large error bars originated from a very weak thermoluminescence signal does not allow to perform concise analysis.
Figure 4.27: Thermoluminescence glow curves of the pre-threshold samples.
Figure 4.28: Partial annealing the C2 sample and first peak position as a function of annealing temperature.
Figure 4.29: Activation energies, evaluated using the initial rise method versus annealing temperature, for C2 sample are shown in upper plot. In lower part, the initial rise regions of the thermoluminescence are shown for different annealing temperatures.
Figure 4.30: Activation energies, evaluated using the initial rise method versus annealing temperature for C3 sample, are shown in upper plot. Initial rise slopes are presented in lower plot, annealing temperatures indicated.
Above-threshold Mg-doped samples

An afterglow was detected in LH temperatures after 325 nm excitation of the above-threshold samples (Fig. 4.31). This effect has been also seen for Mg-doped near-stoichiometric lithium niobate in [181] and [179], producing similar elevated beginning of the thermoluminescence glow curves. After annealing the sample up to a few tenth degrees or hold it at low temperature for three hours the effect disappear. Isothermal annealing was performed at 11 K to obtain more information about the effect (Fig. 4.32).

![Graph showing TSL signal intensity versus temperature](image)

**Figure 4.31:** Initial rise of the thermoluminescence for the near-stoichiometric S1 sample. It should be noted that background was extracted for both glow curves.

The afterglow effect correlates with relaxation of Nb$_{Nb}$$^{4+}$ small polarons absorption (Fig. 4.21), therefore it is supposed to come from Nb$_{Nb}$$^{4+}$ and O$^-$ small polarons recombination. However, the difference between afterglow intensities suggests that the antisite Nb$_{Li}$$^{4+}$ polarons, localized as the nearest-cation-neighbours to Cr$_{Nb}$$^{3+}$ ions, are responsible for the signal, since larger concentration of the antisites is expected in the congruent C1 sample in comparison with their concentration in the near stoichiometric S1 sample.

The polarons recombination at low temperatures is quite unexpected since it was shown that hopping of the niobium polarons in such crystals starts at approximately 120 K [178]. The only possibility for the polarons to recombine is the charge transport via tunnelling.

The equation 3.22, which describes such effect, fits perfectly the experimental data of the isothermal decays, shown in Fig. 4.32.

The above-threshold congruent C1 and near stoichiometric S1 samples show most prominent peaks at low temperatures (see Fig. 4.33). The congruent sample has the highest peak at 104 K. Position of another peak at 156 K was determined from the annealing experiments (Fig. 4.34). The near stoichiometric sample S1 exhibits two peaks at 76 and 114 K. Both samples also show single thermoluminescence peaks at higher
temperatures, which are described in detail at page 83.

The low-temperature peaks show characteristic pattern of the annealing spectra peculiar to the charge traps, distributed in energy or frequency factors. Fig. 4.35 shows constant increase of the activation energy with annealing temperature, which points to the energy distribution of the traps. The energy distribution is evaluated to be equal to 0.015 – 0.4 eV. No 76 K peak is detected for the congruent C1 sample, and the energy distribution of the 104 K peak is shown to be 0.03 – 0.25 eV.

Both low-temperature peaks in both samples are originated from the traps, distributed in energy. Correlation of the peaks with thermal stability of the small polaron absorption bands, shown in Fig. 4.19, persuades to assign these peaks to the recombination of the \( \text{Nb}^{4+} \) and \( O^- \) small polarons. Since the \( O^- \) small polarons were shown to be stable at these temperatures in [107], they are assigned to be the recombination centers and the \( \text{Nb}^{4+} \) small polarons act as the electron traps. Appearance of the two peaks in the near-stoichiometric S1 sample points to some differences in the niobium polarons involved, which will be discussed in detail later.

The high-temperature wing of the 104 K peak is overlapped with less intense 156 K peak, which is the origin of sudden change of activation energy trend in upper part of the Fig. 4.36. Since the obtained activation energies for this peak are very similar, it is concluded that the peak have single activation energy equal to 0.67 ± 0.11 eV.

Fig. 4.37 presents the annealing spectra for the high-temperature peaks. The pattern of the annealing spectra is characteristic to the traps distributed in energy or frequency factor. The annealing spectra for S1 sample is clipped on the right end due to the restrictions from temperature range of the cryogenerator. The high-temperature peak of
the S1 sample shows no distribution in activation energy, which is found to be equal to 0,79 ± 0,04 eV. The high-temperature peak of the C1 sample also shows no distribution in activation energy, which is equal to 0,71 ± 0,04 eV.

The above-threshold Mg-doped samples S1 and C1 produce barely detectable thermoluminescence peaks after 514,5 nm excitation (Ar⁺-laser, ∼1 W at the sample, shown in Fig. 4.41). This can be explained by the fact that the 514,5 nm line is far from the peak of the CT band, thus it is less efficient in the electron-hole pairs creation than the 325 nm
Figure 4.34: Temperature of the first maximum versus annealing temperature for the low-temperature peaks of above-threshold Mg-doped samples.

line. No high-temperature peaks were detected after 514.5 nm excitation. In fact, the noise grows very strongly at higher temperatures due to lower quantum efficiency of Cr$^{3+}$ luminescence (see Fig. 4.25). Owing to this, the intensities of the high-temperature peaks must be lower than the noise, taking into account the intensities of the first thermoluminescence peaks.
Figure 4.35: Activation energies for the low-temperature TSL peaks of the S1 sample as a function of annealing temperature are shown in upper plot. The initial rise slopes are shown in lower plot, annealing temperatures indicated.
Figure 4.36: Activation energies for the low-temperature TSL peaks of the C1 sample as a function of annealing temperature are shown in upper plot. The initial rise slopes are presented in lower plot, annealing temperatures indicated.
Figure 4.37: Annealing spectra of the high-temperature thermoluminescence peaks of the above-threshold Mg-doped samples.
Figure 4.38: Temperature of the first TSL maximum versus annealing temperature for the high-energy peaks.
Figure 4.39: Activation energies, evaluated using the initial rise method, are presented in upper plot for the high-temperature TSL peak of the near stoichiometric S1 sample. Initial rise slopes are shown in lower plot, annealing temperatures indicated.
Figure 4.40: Activation energies for the high-temperature TSL peak of the congruent C1 sample as a function of annealing temperature are presented in upper plot. Initial rise slopes are shown in lower plot, annealing temperatures indicated.
Figure 4.41: Thermoluminescence glow curves of the above-threshold Mg-doped samples after different excitation wavelength.
4.3.3 Discussion

Light-induced absorption

It was published in [147, 178] that the strong charge transfer absorption band, related to the Cr$^{3+}$ ions, is observed near fundamental edge in the above-threshold magnesium and chromium doped lithium niobate. The 325 nm excitation light is much closer to the peak of the charge transfer band than the 514.5 nm one, and this explains why the low power 325 nm laser light is more efficient in producing electron-hole pairs than the high power 514.5 nm laser illumination.

The CT band is shifted to longer wavelengths in the crystals doped with MgO above threshold (Fig. 4.42), which means that the CT band of the Cr$_{Nb}^{3+}$ ions occurs at smaller energies than that of Cr$_{Li}^{3+}$ ones [140].

Electrons are transferred from oxygen to the Cr$^{3+}$ ions under the CT process. The electrons may then recombine with the holes in valence band, thus restoring the original state of the system or escape the chromium, tunnelling to the nearest electron trap. In the latter case, the free electrons are trapped at the niobium ions, creating niobium small polarons, and holes are stabilized on the oxygens adjacent to the lithium vacancies, creating O$^{-}$ small polarons.

Both types of small polarons are then seen in the light-induced absorption (Fig. 4.18) as two bands, peaked at 530 and 1200 nm, respectively. Those bands were already described in the literature [106, 122]. This result illustrates that in the above-threshold double doped lithium niobate these defects are the major electron and hole traps, respectively. It should be noted that the absorption band of the O$^{-}$ small polarons has not been extensively studied in the literature, and was clearly observed only after electron irradiation at 77 K in [121].

In the C1 sample the broad Nb$_{Nb}^{4+}$ small polaron absorption seems to be shifted to the higher energies, but this can be explained by the presence of additional absorption band peaked at 780 nm, connected with the antisite Nb$_{Li}^{4+}$ small polarons. This explanation is plausible since the above-threshold Mg-doped congruent samples contain more intrinsic defects than the near-stoichiometric ones, also doped with Mg above the threshold.

Owing to the low intensities of light-induced absorption bands, emerged under the 514.5 nm excitation, it is possible to distinguish a small 780 nm band, ascribed to small
electron polarons Nb\textsuperscript{4+}\textsubscript{Li} (Fig. 4.18). The light-induced absorption of the C1 sample shows only the Nb\textsuperscript{4+}\textsubscript{Li} polarons band and no trace of the Nb\textsuperscript{4+}\textsubscript{Nb} one after 514.5 nm excitation, which correspond to the situation when the niobium antisites are filled with electrons and no electrons are trapped at the Nb\textsuperscript{5+}\textsubscript{Nb} ions. Such situation can be realized if the number of ionized oxygen and chromium ions is smaller or equal to the concentration of Nb\textsuperscript{5+}\textsubscript{Li} ions. Taking this into account, during the sample excitation the niobium antisites are filled with electrons first as the deepest traps. When all of the Nb antisites are filled, the electrons start to occupy the intrinsic niobium ions. The resulted light-induced absorption would have the Nb\textsuperscript{4+}\textsubscript{Li} band, and after its saturation the broad Nb\textsuperscript{4+}\textsubscript{Nb} band would appear.

The niobium antisites band in the absorption of the near stoichiometric S1 sample is seen to be of lower intensity in comparison with the C1 sample. This is in agreement with the lower antisites concentration in this sample. The presence of the Nb\textsuperscript{4+}\textsubscript{Li} antisites absorption in both samples testifies that the doping with magnesium above the threshold does not completely remove all antisites in lithium niobate.

**Thermoluminescence**

The thermoluminescence glow curves of the pre-threshold Mg-doped samples and the above-threshold ones are different. The pre-threshold samples show main peaks at 156 and 211 K (221 K) whereas the above-threshold ones show peaks at 76 K and at around 110 K at low temperatures and also peaks at around 280 K at higher temperatures. In the thermoluminescence of the pre-threshold congruent sample C2 a barely perceptible features peculiar to the above-threshold samples are present – the peak at 98 K (shown in Fig. 4.27 inset) and the 275 K peak (detected by the peak position versus annealing temperature plot, see Fig. 4.29). Taking this into account it can be suggested that the thermoluminescence of the pre-threshold samples is related to the Nb\textsuperscript{4+}\textsubscript{Li} polarons, and the thermoluminescence of the above-threshold samples is related to the Nb\textsuperscript{4+}\textsubscript{Nb} polarons.

The 156 K peak is supposed to be connected with the Nb\textsuperscript{4+}\textsubscript{Li} small polarons, since it is seen as the most prominent in the Mg undoped C3 sample, barely seen in the above-threshold Mg-doped congruent C1 sample and not visible in the near stoichiometric S1 sample. The 156 K peak is seen to have a lower intensity in comparison with the prominent peaks of the S1, C1 and C2 samples. It is also likely to be present in thermoluminescence of the C2 sample, but due to its low intensity it can be masked by more intense 211 K peak. The changes of peak intensity from sample to sample are in agreement with the decrease of Nb\textsubscript{Li} antisites concentration, which in turn depends on the doping amount of the magnesium. The concentration of the antisite defects extinguish with increase of magnesium concentration until the threshold, and after the threshold there are only trace amounts of them. The stoichiometric crystals, doped with Mg above the threshold, should contain even smaller amount of the niobium antisites in comparison with congruent crystals.

It was shown in [107] by absorption measurements that the Nb\textsuperscript{4+}\textsubscript{Li} small polarons re-
combine with $O^-$ small polarons in pure congruent lithium niobate after x-ray irradiation in temperature interval 100 – 200 K. The temperature interval fits perfectly to the 156 K peak position. Taking this and the low intensity of the peak in Mg-doped samples into account, the 156 K peak is assigned to the Nb$^{4+}_{Li}$ and $O^-$ small polarons recombination.

Similar peaks were detected in C2 and C3 samples at 211 and 221 K, respectively. The C2 peak shows energy distribution in 0.55 – 0.85 eV. The thermoluminescence results, obtained for the C3 sample, are not clear due to very low intensity of thermoluminescence signal. The origin of the 211 K (221 K) peak is not fully understood.

It was shown in [178] that the hopping transport of the Nb$^{4+}_{Nb}$ polarons in Cr and above-threshold Mg-doped lithium niobate starts at approximately 120 K. However, absorption measurements and the afterglow effect account for the polarons recombination. Taking this into account, the only possibility for the Nb$^{4+}_{Nb}$ and $O^-$ small polarons to recombine is the tunnelling of the electron from one polaron to the other. Since then, it is not surprising that the afterglow decay does not fit to the $\sim \exp(-t/\tau)$ dependence of the first-order kinetics or to the $\sim 1/t^n$, $n \neq 1$ dependence of the second-order kinetic.

The afterglow decay fit perfectly with the equation 3.22. In addition, the first few points of the afterglow curve can be approximated by straight line in the $I = \ln(t)$ coordinates (see Fig. 4.32), just as it is shown for some other materials in [156]. The agreement between the afterglow curve and tunnelling model implies that at temperatures, below the hopping transport of the Nb$^{4+}_{Nb}$ polarons, the tunnelling assists the polarons recombination.

The afterglow correlates with decay of the Nb$^{4+}_{Nb}$ small polarons absorption after switching off the laser illumination (Fig. 4.21). However, more intense afterglow is detected in the congruent C1 sample, than in the S1 one, which points to the antisites Nb$^{4+}_{Li}$ polarons since their concentration is larger in the congruent samples. The shortest Nb-Li distance in lithium niobate is equal to 3.01 Å, and the shortest Nb-Nb (Li-Li) distance is equal to 3.76 Å [86]. Taking this into account, the electron tunnelling from Nb$^{4+}_{Li}$ polarons seems to be the most probable source of afterglow. However, since the shortest Nb-Nb (or Li-Li) distance is not much larger than Nb-Li one in this host, the tunnelling from Nb$^{4+}_{Nb}$ polarons may be also considered as the origin of afterglow.

First thermoluminescence peak is observed at 76 K in the S1 sample. Very similar thermoluminescence peaks are also observed in congruent above-threshold Mg-doped lithium niobate [181] and near stoichiometric crystal doped with 1 mol% of Mg [179] (it should be noted that due to a very high heating rate this peak is shifted to 90 K in [179]). In both works, the presence of the peak is explained by recombination of electrons, trapped at niobium ions, with holes trapped at oxygen near lithium vacancy.

It is shown in this work that the 76 K peak correlates with the thermal stability of both polarons absorption (Fig. 4.19). Taking this into account it can be concluded that this peak is produced by Nb$^{4+}_{Li}$ and $O^-$ small polarons recombination. The $O^-$ small hole polarons served here as the recombination centers since in [107] it was shown that they are thermally stable at the temperatures of the Nb$^{4+}_{Li}$ small polarons release.
4.3. LITHIUM NIOBATE  
CHAPTER 4. RESULTS AND DISCUSSIONS

The peaks at around 70 K were observed in magnesium only doped lithium niobate in previous works [181, 179]. The samples, additionally doped with chromium, show new intense peaks at around 110 K (see Fig. 4.33), and therefore these peaks must be connected with chromium. In the near stoichiometric S1 sample the two peaks at 76 and 114 K show continuous energy distribution in 0.015 – 0.4 eV interval. The similar continuous character of the energy distribution of the congruent C1 sample 104 K peak persuade to assign these two peaks to the same recombination process, i.e. $\text{Nb}^{4+}_{\text{Nb}}$ and $\text{O}^-$ small polarons recombination. Considering this, the peaks at around 110 K can be attributed to the recombination of the $\text{Nb}^{4+}_{\text{Nb}}$ and $\text{O}^-$ small polarons, where the $\text{Nb}^{4+}_{\text{Nb}}$ polarons are perturbed by neighbouring chromium ions. The hopping transport of the polarons is not possible at such low temperatures, therefore the low-temperature peaks could be originated owing to thermally assisted tunnelling of carriers between neighbouring polarons.

High-temperature peaks, observed at around 280 K in above-threshold Mg-doped samples, are shown to have activation energies equal to 0.79 ± 0.04 and 0.71 ± 0.04 eV for near-stoichiometric and congruent samples respectively. Since both peaks show thermoluminescence annealing spectra peculiar to distributed traps but single activation energy, they are supposed to originate from traps, distributed in frequency factor.

The activation energies of both peaks are close to hopping activation energy ($\sim 0.78$ eV) of the $\text{O}^-$ small hole polarons, which was reported in [105, 107, 123, 124, 125, 126]. Such hole polarons have absorption band peaked at 3.1 eV (400 nm), which is partially masked in double doped crystals by the CT bands. Owing to this, the detection of such absorption band was not possible. However, the light-induced polaron absorption bands in the congruent C1 sample (Fig. 4.18) are seen on a background, growing from the longer to shorter wavelength. This broad structure can be the wing of the hole polarons, responsible for the high-temperature thermoluminescence peaks. Taking this into account, the high-temperature peaks may be connected with the hopping of the hole polarons, which absorption band is peaked at 3.1 eV. Another possibility for creation of the high-temperature peaks may be non-intentional dopants that release electrons at those temperatures. For example, Cu is shown to release electrons in lithium niobate at around room temperature, which may lead to thermoluminescence [107].

It was shown in [182, 183, 181] that a blue luminescence is produced during electron-hole recombination in pure and Mg-doped lithium niobate. The last and subsequent works [123, 184, 185, 186] show that the blue luminescence is much more intense in stoichiometric and Mg-doped crystals in comparison with undoped congruent ones. Thermoluminescence peak near 440 nm was observed in Mg-doped (1 mol%) stoichiometric crystal after x-ray and laser illumination (325 and 355 nm) [179]. In another work, the thermoluminescence peak of Mg-doped (5 mol%) congruent crystal is also shown to have maximum at around 450 nm. In this work the only thermoluminescence signal comes from the broad near infrared Cr$^{3+}$ luminescence peaked at 900 nm and no intrinsic blue luminescence has been detected. Taking this into account, the energy of the electron-hole recombination is
transferred to the chromium ions. However, the other possibility is that the chromium ions may serve as mediators in small polarons recombination, and further studies are necessary to reveal the details of the nature of the small polarons recombination in chromium doped lithium niobate.

**R-lines bleaching**

As it is seen from Fig. 4.10, the only chromium centers, located at the niobium sites, are bleachable under laser light. The bleaching is considered as the ionization of the chromium ions, which then remain in the 4+ charge state. In fact, the net charge (with respect to the lattice) of the Cr$_{3+}$ centers is 2-, so they could be further ionized by extracting one electron. In contrast, the Cr$_{3+}$ centers have a net charge equal to 2+ and therefore it would need much more energy to take off an electron from them. Under this consideration, the Cr$_{3+}$ centers appear to be more stable than the Cr$_{3+}$ ones, which explain selective nature of the optical bleaching.

Ionization of the ε- and ε'-Cr$_{Nb}$ centers at low temperatures is possible owing to tunnelling of the electron from the chromium to neighbouring electron trap (niobium ion). The tunnelling of electron is much probable if the chromium ion is excited to the $^4T_2$ or $^4T_1$ state, what can be easily achieved using laser illumination (of course, the energy of photons must be in the range of chromium intrashell transitions). This is in analogy with the thermally assisted tunnelling, where the electron on the upper excited level in the potential well has larger probability to tunnel through the well than that at the ground state.

The experimental results, shown in this work, support the model presented in [21]. The only amendment introduced is taking into consideration the tunnelling transport of the electrons, which results in non-exponential kinetics of the bleaching. The fact that the bleaching kinetics cannot be approximated by the equation 3.22 can be explained by different distances between chromium and niobium ions, therefore resulting kinetics correspond to the sum of different decays.

The fact that the R-lines bleaching recovery is observed only under heating of the sample to particular temperatures leads to the conclusion that an electron trap is involved in the process. It is seen from the thermal recovery of the bleachable R-lines (Fig. 4.11), that the electron trap is thermally activated at around 110 K, and at 160 K full recovery of the initial signal intensity is observed. The observed bleaching recovery occur at the same temperatures, at which the photocurrent of such samples increases [178]. The temperature dependence of the photoconductivity shows activation energy equal to 0.13 eV, which matches exactly the energy of binding the Nb$_{Nb}^{4+}$ small polarons by unknown defect in highly Mg-doped lithium niobate [43]. In addition, the Nb$_{Nb}^{4+}$ small polarons are shown to be responsible for the photocurrent. Taking this into account, the observed bleaching recovery occurs due to the hopping transport of the Nb$_{Nb}^{4+}$ small polarons.
Model

Now the processes of excitation and relaxation of the above-threshold Mg-doped samples can be illustrated.

Under laser excitation in the CT band, the electrons are transferred to the Cr$^{3+}$ ions from the delocalized states of the valence band, formed partially of the 2p states of the oxygen ions [187] (Fig. 4.43 a, blue arrow). The electrons may then recombine with the holes produced in the valence band, thus restoring the original state (grey arrow). Another possibility is the tunnelling of the electron to the nearest electron trap (dashed arrow). In the latter case, the electrons are trapped at the electron traps, creating niobium small polarongs. The holes in the valence band, after a process of lattice relaxation, can be stabilized on the oxygen ions adjacent to the lithium vacancies, creating O$^-$ small polarongs.

Along with this, one of the outer shell electrons of the $\varepsilon$- and $\varepsilon'$-Cr$_{Nb}$ centers, when transferred to the upper excited level, can also tunnel to one of the adjacent niobium ions (Fig. 4.43 b, dashed arrows). Owing to this, the chromium ions remain in 4+ charge state, and bleaching of these centers is observed.

![Diagram](image_url)

**Figure 4.43:** a) Creation of the Nb$^{4+}_{\text{Nb}}$ and O$^-$ small polarongs under laser illumination, b) photoionization of the Cr$^{3+}_{\text{Nb}}$ ions. Blue arrow – CT transitions, green arrow – chromium intrashell transition, grey arrow – recombination of the charge carriers, dashed arrows – tunnelling.

At low temperatures a part of niobium and oxygen small polarongs recombine due to tunnelling of the electrons from niobium electron polarongs to oxygen hole polarongs (Fig. 4.44 a, dashed arrows), which result in the low-temperature afterglow (Fig. 4.32).

The other trapped carriers cannot escape the traps at LH temperatures because there is no possibility to find the amount of energy, necessary to transfer them over the trap’s potential barrier and probability to tunnel through the barrier is very low. Below 100 K another type of tunnelling – the thermally assisted tunnelling takes place (also noted by dashed arrows), resulting in the low-temperature thermoluminescence peaks in above-threshold Mg-doped samples (Fig. 4.33).
The recombination energy of the polarons is transferred to the chromium ions (huge grey arrow), and chromium intrashell transitions produce detectable thermoluminescence signal (green arrow).

From approximately 120 K and above, the Nb$_{\text{Nb}}^{4+}$ small polarons become mobile, and bleached $\varepsilon$- and $\varepsilon'$-Cr$_{\text{Nb}}$ centers are filled with electrons due to the hopping transport of the Nb$_{\text{Nb}}^{4+}$ small polarons (Fig. 4.44 b, bent arrows).

Additionally, similar processes can take place in samples C1 and S1 at temperatures close to room temperature, inducing the high-temperature peaks (Fig. 4.37). The signal can be originated due to hopping motion of hole polarons or recombination of the hole polarons with electrons emitted from the deep traps, associated with the non-intentional impurities [107]. The recombination energy is also transferred to chromium ions, which, in consequence, produce the thermoluminescence signal.

![Diagram](image)

Figure 4.44: a) Recombination of the Nb$_{\text{Nb}}^{4+}$ and O$^-$ small polarons and b) thermal recovery of the photoionized Cr$_{\text{Nb}}$ ions. Dashed arrows – tunnelling, huge grey arrow – transfer of the polarons recombination energy to chromium ions, small grey arrow – non-radiative relaxation, green arrow – radiative intrashell transitions.
Chapter 5

Summary

The main conclusions are summarised as follows:

**GGG: Mn$^{4+}$**

The influence of external hydrostatic pressure on luminescence properties of GGG:Mn$^{4+}$ crystal has been studied. Obtained data compared with properties of the isovalent Cr$^{3+}$ ion in the same GGG host. Larger value of the pressure coefficient, observed for the Mn$^{4+}$ ion in GGG in comparison with the Cr$^{3+}$, can be explained by the different strength of coupling of these ions with host.

The nephelauxetic effect is responsible for the redshift of both manganese R$_1$ lines with pressure. The $\eta$ parameter equal to 2,31 and 2,81 for the A and B manganese centers respectively was found from fitting the experimental data with the model described at page 9.

**YAP: Mn$^{4+}$**

The narrow R-line luminescence of the Mn$^{4+}$ and Cr$^{3+}$ centers has been studied in the function of external hydrostatic pressure at low temperature. The measurements show that the pressure coefficients of Mn$^{4+}$ and Cr$^{3+}$ dopant ions are similar, most probably due to the influence of another point defect on one of these ions.

Redshift of the Mn$^{4+}$ R$_1$ line with pressure is due to the nephelauxetic effect. Approximation of the experimental data with the nephelauxetic effect model gives the $\eta$ parameter equal to 1,87.

**LiNbO$_3$: Cr$^{3+}$,Mg**

The defect structure of LiNbO$_3$:Cr$^{3+}$,Mg congruent and near stoichiometric crystals has been studied using light-induced absorption, thermoluminescence and luminescence techniques. The study revealed additional information about Nb$^{4+}_{Nb}$ and O$^-$ small polarons and their behaviour at low temperatures, below those at which hopping of the Nb$^{4+}_{Nb}$ small polarons occurs.
CHAPTER 5. SUMMARY

The Nb$_{Ni}^{4+}$ and O$^-$ small polarons are produced under laser illumination by electron transfer from oxygen to chromium ions and subsequent tunnelling of the electron to the nearest niobium ions that act as electron trap. After the excitation, the small polarons are seen to recombine at low temperatures via tunnelling of the electron between neighbouring niobium and oxygen polarons.

Nb$_{Ni}^{4+}$ polarons are shown to be the major electron traps in the above-threshold Mg doped lithium niobate. The doping of the lithium niobate with magnesium was shown to reduce strongly the concentration of the antisites. The magnesium doping does not extinguish completely the concentration of the antisite defects, as it is stated in the literature. The excitation and relaxation processes are discussed in detail.

Thermoluminescence spectra were found to be very informative in investigation of the LiNbO$_3$:Mg crystals defect structure. This confirms the potential of this method in non-destructive characterisation of the crystals quality, as it was already mentioned in [179].

In the variety of the Cr$^{3+}$ centers in lithium niobate, the photoionization undergo the only two strong-crystal-field ones, located at the niobium sites. The mechanism of the photoionization has been discussed.
Appendices

A. YAG: Nd$^{3+}$ as a pressure sensor

Motivation

The significant part of the DAC operation is the accurate pressure estimation. Only indirect methods are available, and the most popular is the photoluminescence sensors.

The photoluminescence sensor is a crystal doped with transitional metal or rare earth, which photoluminescence lines shift with the pressure. A small chip of the sensor is placed in the high-pressure cell along with the sample, thus the pressure inside the DAC can be easily evaluated by measuring the emission line shift.

The ideal luminescence pressure sensor is a singlet line of small linewidth, high pressure coefficient and small temperature coefficient. Of course, the line must be intense, it must be in the spectral region, covered by most of the available luminescence detectors, and it would be useful if no additional photoluminescence surround the line. Commercial availability and a low price are also important.

Today a several pressure sensors are known, some of them are listed in table 5.1. All the sensors, listed in table 5.1, show luminescence lines in the red-yellow visible region.

The most popular pressure sensor today is ruby (Al$_2$O$_3$:Cr$^{3+}$) owing to its availability and very high luminescence efficiency. In this crystal, chromium shows two very intense and narrow luminescence lines noted as $R_1$ and $R_2$ (694.2 and 692.7 nm respectively). The lines shift to the lower energies with pressure, which was thoroughly studied in the

<table>
<thead>
<tr>
<th>Material</th>
<th>$\lambda$, cm$^{-1}$ at 1 bar</th>
<th>$dE/dP$, cm$^{-1}$/kbar</th>
<th>$dE/dT$, cm$^{-1}$/K</th>
<th>Ref.</th>
</tr>
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<td>Al$_2$O$_3$:Cr$^{3+}$</td>
<td>14405</td>
<td>-0.776</td>
<td>-0.140</td>
<td>[188]</td>
</tr>
<tr>
<td>YAlO$_3$:Cr$^{3+}$</td>
<td>13835</td>
<td>-1.339</td>
<td>-0.144</td>
<td>[188]</td>
</tr>
<tr>
<td>YAG:Eu$^{3+}$</td>
<td>16932</td>
<td>-0.565</td>
<td>0.014</td>
<td>[189]</td>
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<tr>
<td>LaOCl:Eu$^{3+}$</td>
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<td>-0.075</td>
<td>0.015</td>
<td>[190]</td>
</tr>
<tr>
<td>LaOBr:Eu$^{3+}$</td>
<td>17301</td>
<td>-0.898</td>
<td>0.015</td>
<td>[191]</td>
</tr>
<tr>
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<td>-0.780</td>
<td>-0.005</td>
<td>[192]</td>
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<tr>
<td>SrB$_4$O$_7$:Sm$^{2+}$</td>
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<td>-0.543</td>
<td>0.002</td>
<td>[193]</td>
</tr>
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<td>BaFCl:Sm$^{2+}$</td>
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<td>0.034</td>
<td>[194]</td>
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<td>SrFCl:Sm$^{2+}$</td>
<td>14486</td>
<td>-2.305</td>
<td>0.048</td>
<td>[194]</td>
</tr>
</tbody>
</table>

Table 5.1: Parameters of selected photoluminescence pressure sensors.
Figure 5.1: Photoluminescence of ruby, containing 2.1 at.% of chromium [202].

literature [188, 153, 154, 155, 195, 196]. Up to 300 kbar the pressure coefficient of the R-lines can be considered as linear (-0.776 cm\(^{-1}\)/kbar) within 5% accuracy [153]. Shift of the R-lines with temperature has been also well studied [197, 198, 199, 200, 201], and this effect can be easily corrected during calculations.

In spite of the ruby’s popularity and suitability, it has some shortcomings. In luminescence ruby shows not only the R-lines, but also a broad phonon-assisted band and chromium pairs luminescence [202]. As it is seen from the Fig. 5.1, this additional luminescence, though not very intense, covers practically all red wavelength region. Crystals with small chromium concentration are used as the pressure sensors, therefore they show no luminescence from the chromium pairs, but the phonon-assisted band remains visible. This additional broad structure can interfere with the investigated luminescence, especially when it is very weak.
Figure 5.2: Left part: Nd$^{3+}$:YAG near infrared luminescence at different pressures [203], excited by 514.5 nm line at room temperature. Right part: pressure induced changes of the $^4F_{3/2}$ (R) level splitting in YAlO$_3$ and Y$_3$Al$_5$O$_{12}$.

Therefore, another pressure sensor is necessary to carry out luminescence measurements in this wavelength interval. The new sensor must correspond to the pressure sensor requirements, but its luminescence must be well separated from the red spectral region.

Solving the problem

Nd$^{3+}$:YAG was proposed by Hua and Vohra as a pressure sensor, emitting light in near infrared region (see Fig. 5.2) [203]. Authors investigated luminescence in the 850 – 900 nm region, where some of Nd$^{3+}$ lines show non-zero pressure coefficients.

Nd$^{3+}$ ions substitute for dodecahedral Y$^{3+}$ site in yttrium aluminium garnet (YAG, Y$_3$Al$_5$O$_{12}$). Observed by Hua and Vohra luminescence corresponds to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions (see Fig. 5.3, left part). According to the conventional nomenclature [204], the $^4F_{3/2}$ and $^4I_{9/2}$ manifolds are labelled as R and Z respectively. The Stark levels within manifold are numbered consecutively starting from 1 for the lowest energy level. At low temperatures, only transitions from the lowest level R$_1$ of the $^4F_{3/2}$ manifold are observed. Transitions from the R$_2$ level are visible at higher temperatures.

A commercial Nd$^{3+}$:YAG crystal doped with 0.9 at.% Nd has been investigated in pressures up to 120 kbar. Ruby was used as a pressure sensor. Two transitions, namely R$_1 \rightarrow Z_5$ and R$_2 \rightarrow Z_5$, were not studied in [203]. As it is seen from Fig. 5.4, they show larger pressure coefficients than the rest of the transitions. In the investigated
Figure 5.3: The \(^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}\) transitions of Nd\(^{3+}\) ion. Energy diagram (left part) and corresponding luminescence spectrum at different temperatures (right part). Excitation: 514.5 nm laser line, \(T = 10\) K.

Figure 5.4: Shift of the \(^4\text{F}_{3/2} \rightarrow \ ^4\text{I}_{9/2}\) transitions with pressure.

Pressure range both transitions shift linearly to lower energies with the coefficients equal to \(-0.75 \pm 0.02\) and \(-0.99 \pm 0.02\) cm\(^{-1}\)/kbar respectively (Fig. 5.4).

The spectral positions of the luminescence lines shift slightly towards higher energies with temperature for about 3 cm\(^{-1}\) between 10 and 300 K. The FWHM of the lines increased from 7 to 9 cm\(^{-1}\) in the same temperature interval. The temperature dependence of the luminescence is not very strong, and can be neglected in proposed linear approximation of the pressure-induced luminescence shift.

In comparison with ruby, the YAG:Nd\(^{3+}\) crystal is very promising pressure sensor for DAC (see table 5.2). Both crystals are very popular, and therefore readily available, due to their laser applications. Both have intense narrow luminescence lines with similar pressure
coefficients. The $R_2 \rightarrow Z_5$ transition shows even greater pressure coefficient than the ruby lines. The YAG:Nd$^{3+}$ lines differ from the ruby ones by smaller temperature coefficients, which can be neglected while keeping high accuracy of the pressure estimation.

Table 5.2: Comparison of ruby with YAG:Nd$^{3+}$.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Al$_2$O$_3$:Cr$^{3+}$ (ruby)</th>
<th>YAG:Nd$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$, cm$^{-1}$ at 1 bar (10 K)</td>
<td>14424.8 R$_1$ 8 R$_2$</td>
<td>10572 $R_1 \rightarrow Z_5$ -</td>
</tr>
<tr>
<td>FWHM, cm$^{-1}$(10 K)</td>
<td>1.3</td>
<td>6.8</td>
</tr>
<tr>
<td>$\lambda$, cm$^{-1}$ at 1 bar (300 K)</td>
<td>14405 14435.4 R$_1$ 8.9 R$_2$</td>
<td>10574 10660</td>
</tr>
<tr>
<td>FWHM, cm$^{-1}$(300 K)</td>
<td>14.2</td>
<td>9</td>
</tr>
<tr>
<td>dE/dp, cm$^{-1}$/kbar</td>
<td>-0.776</td>
<td>-0.75</td>
</tr>
<tr>
<td>dE/dT, cm$^{-1}$/K</td>
<td>-0.14</td>
<td>0.0073</td>
</tr>
<tr>
<td>Availability</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Conclusions

It was concluded from these experiments that the luminescence lines due to the $R_1 \rightarrow Z_5$ and $R_2 \rightarrow Z_5$ transitions of Nd$^{3+}$ in the YAG crystal could be used as an accurate pressure sensor in high-pressure studies between liquid helium and room temperatures. The luminescence lines are observed at the wavelength, which is covered by the most of the commercially available detectors. YAG:Nd$^{3+}$ crystals produce no luminescence in the red visible region, which makes them a good replacement for ruby in high-pressure luminescence measurements in this spectral region.

The results are published in [205].
B. Automation of pressure evaluation

Motivation

The most popular pressure sensor for the high-pressure measurements utilizing DAC is the ruby R-line luminescence. At relatively low pressures up to 195 kbar the linear redshift of the ruby luminescence with pressure (-0.77 ± 0.03 cm⁻¹/kbar) is an appropriate scale [153]. This simple relation makes the numerical pressure estimation an easy task. A calculator is the utmost tool required for this operation.

At higher pressures, the non-linearity of the R-lines shift induces an overestimation of the pressure when using the linear scale. The more appropriate ruby pressure scale was introduced in [155]:

\[
P(k\text{bar}) = 3808 \left[ \left( \frac{\lambda_0}{\lambda} \right)^5 - 1 \right]
\]

(5.1)

where \(\lambda\) - position of ruby R₁ line under pressure, \(\lambda_0\) - position of the R₁ line at ambient pressure (in cm⁻¹).

This formula has been obtained by calibrating the ruby R₁ line shift on pressures, estimated from simultaneous specific volume measurements of four metals: Cu, Mo, Ag and Pd. The isothermal equations of state, derived from shock-wave experiments, were used for pressure evaluation. It was shown that the formula 5.1 approximates the experimental data within 6% of total random error for pressures up to 1 Mbar [155].

Practically, the pressure estimation from ruby luminescence requires some preliminary work and features a few critical moments when an additional errors can be introduced:

- the temperature shift of the ruby lines and the systematical errors of the measuring equipment must be taken into account when the pressure is calculated. This is commonly done by obtaining the reference measurements of the ruby luminescence at ambient pressure on the same experimental setup for all required temperatures.

- the possible source of errors is picking the peaks positions right from the spectrum at higher temperatures, when the R-lines overlap. In this case fitting the shape of luminescence with peak-shape functions is an adequate approach in obtaining the peaks positions [196, 198].

Since the pressure evaluation is a frequent task, involving typical manipulations, its automation can improve the accuracy and reduce the time of estimation.

Solving the problem

The R₂ ruby line can be also used for pressure estimation along with the R₁ line, using the same pressure dependence (of cause at temperatures when it is well resolved). It was shown that this line is less sensitive to the non-hydrostatic conditions than the R₁ line [206]. Furthermore, the R₂ line shows smaller broadening at elevated temperatures in comparison to the R₁ line [201]. Owing to this, the R₂ line is useful as an additional
CHAPTER 5. SUMMARY

pressure gauge, which allows to improve the accuracy of pressure estimation in contrast to the situation when the only R₁ line is used.

The temperature and pressure coefficients of the ruby R-lines can be deconvoluted and considered separately, as it was shown in [207]. Therefore, it is possible to correct the R-lines temperature shift using analytical expressions, thus avoiding the reference temperature measurements. It was published in [200] that the shift of the ruby R-lines in the temperature range from liquid helium to 600 K can be approximated by:

\[ R_1(T) = R_{10} + 4.49 \cdot 10^{-2}T - 4.81 \cdot 10^{-4}T^2 + 3.71 \cdot 10^{-7}T^3 \]  \hspace{1cm} (5.2)

\[ R_2(T) = R_{20} + 3.00 \cdot 10^{-2}T - 3.88 \cdot 10^{-4}T^2 + 2.55 \cdot 10^{-7}T^3 \]  \hspace{1cm} (5.3)

where \( R_{10} \) and \( R_{20} \) are the positions of the \( R_1 \) and \( R_2 \) lines at liquid helium temperatures in \( \text{cm}^{-1} \), \( T \) is temperature in K.

Though the error estimation of the expressions 5.2 and 5.3 was not given in [200], it is thought to be much less than the accuracy of the formula 5.1.

The ruby luminescence can be approximated by peak-shape functions to improve the accuracy of reading the peaks positions, improving this way the pressure estimation. The only R-line positions at liquid helium temperature (taking into account the systematic error of measuring setup) are necessary to complete the task.

It was shown in [196] that the shape of ruby lines can be approximated very well with function:

\[ R = C_{L1}L_1 + (1 - C_{L1})G_1 + C_{L2}L_2 + (1 - C_{L2})G_2 \]  \hspace{1cm} (5.4)

where \( C_{L2} \) is a relative amplitude factors *, \( L_x \) and \( G_x \) are the Lorentzians and Gaussians respectively. It was shown in [196] that the \( C_L \) is a function of the measurement setup.

In the pressure range (1 bar – 200 kbar) and temperature range (4 – 296 K) of the high-pressure measurements, performed in this work, the only sum of two Lorentzians produce rather satisfactory fit of the ruby lines, therefore this simple function was used in data approximation. However, it was checked that application of the function 5.4 does not improve the accuracy of the pressure estimation.

The algorithm of pressure evaluation (presented in Fig. 5.5):

1. The input data is read right from a data file, containing the ruby luminescence results. The systematic error is corrected. The number of peaks and their approximate positions are found. The temperature of the ruby is either read from a file of experimental statistics or manually entered by the user.

2. The R-lines are approximated with Lorentzians, utilizing simple gradient method. The information about number of peaks and their approximate positions, found at previous step, is used as a first approximation. Correct positions and FWHM of the ruby lines are obtained.

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Figure 5.5: The algorithm of the pressure evaluation.

Figure 5.6: The main window of the program for pressure evaluation from ruby luminescence.

3. The temperature shift of the peaks is corrected using the analytical expressions 5.2 and 5.3. The pressure is calculated using the Mao-Bell formula 5.1.

4. The calculated pressure values for both R-lines and their average value are shown.

Conclusions

With use of the program:

– the pressure can be evaluated in a few seconds right after the ruby luminescence measurements;

– no preliminary ruby luminescence measurements are necessary for pressure evaluation since the proper R-line positions at ambient pressure (taking into account the systematic error) are stored in the program memory;

– the accuracy of the pressure estimation is improved by using both R-lines.
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2. Institute of Physics PAS, local presentations during Ph.D studies.

POSTER PRESENTATIONS


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2. A. Suchocki, A. Kamińska, S.W. Biernacki, S. Kobyakov, L. Arizmendi, M. Ramirez, L. Bausa, M. Grinberg, and G. Boulon, High pressure studies of Yb$^{3+}$ ions in gadolinium gallium garnet and lithium niobate, French – Polish Symposium on Spectroscopy of Modern Materials in Physics, Chemistry and Biology. July 15 – 18, 2007, Clermont-Ferrand, France (invited lecture – A. Suchocki);