Optical constants and magnetic susceptibility of xLa$_2$O$_3$–30PbO–(70 − x) B$_2$O$_3$ glasses

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A B S T R A C T

Glassy system with the composition xLa$_2$O$_3$–30PbO–(70 − x)B$_2$O$_3$ with (0 ≤ x ≤ 10 mol%) has been prepared using the well known melt quenching technique. The transmittance and the reflectance spectra of the glasses have been measured and the optical constants such as: the refractive index, the optical band gap for indirect transition, the optical basicity and the average electronic polarizability have been calculated for the investigated glassy system. A correlation between the optical constants and the elastic moduli was performed. The AC magnetic susceptibility of the investigated glasses was studied above 4.3 K. The temperature dependent magnetic susceptibility deviates from the Curie law indicating that weak antiferromagnetic interactions between La ions were present in the studied system. The magnetic entropy change of the glasses was determined.

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1. Introduction

The structure and properties of lead borate glasses are strongly dependent on the nature and concentration of the constituent oxides and have been of considerably increasing interest due to their possible potential applications in enamels, photonics, and opto-electronic applications, and also are good candidates for ultrasonic materials [1]. This type of glass has some remarkable features such as low melting temperature, impressive wide glass formation region, high resistance against devitrification, high refractive index and good radiation shielding for γ-rays [2]. Moreover, PbO can enter the glass network as either a network modifier and/or as a network former, depending on its concentration. Thus, lead borate glasses are promising candidates for the occupation of rare earth ions to be suitable for these uses due to their structural units such as BO$_3$, PO$_4$, PbO$_6$ and PbO$_4$ [3].

On the other hand, rare earth ions like La$^{3+}$ and Gd$^{3+}$, are paramagnetic ions and being often used nowadays to probe the glass structure since the outer f-electron orbital function has a broad radial distribution. These ions when dissolved with glass matrices even in very small quantities make the glasses colored, have a strong influence over different physical properties and were found to be good stabilizers of borate glasses. Rare earth (RE) ions can greatly improve the nonlinear optical properties of glasses; consequently, the use of these ions can contribute to the development of the applications of optical materials. Glasses doped with Nd$^{3+}$, Er$^{3+}$, Sm$^{3+}$, and La$^{3+}$ have also been reported and are regarded as excellent laser materials [4–7]. The optical and magnetic properties of rare earth containing glasses are affected with the modification of the basic structural units of these glasses which is originated from the valence states of the rare earths as reported earlier. The content of RE ions in different valence states depends upon multitude of factors: the quantitative properties of modifiers and glass formers, the size of the ions in the glass structure, their field strength, the mobility of the modifier cation, etc. [8–12]. Also, in tellurite glasses, the modification of the basic structural units with rare earths, namely the TeO$_4$ trigonal bipyramid (bp) and the TeO$_3$ trigonal pyramid (tp), each of which has a lone pair of electrons occupying one of the equatorial positions which affect the magnetic properties of these glasses [13–15].

The most important applications of the glasses are based on their optical transparency in the visible region in the required wavelengths. Glasses can be used for making optical instruments and lenses based on the optical constants such as: the refractive index and its dispersion, which can be varied by varying the chemical composition. Other applications of the glasses in the optical technology are being used in the field of information technology through the use of glass fibers for transatlantic communication cables, telecoms and cable TV [9–12].

Thus, on the aforementioned issues, the effect of La$_2$O$_3$ on the structure of lead borate glass has been investigated by means of transmittance and reflectance measurements in the UV–Vis–NIR spectral region and then relevant optical parameters were calculated. The AC magnetic susceptibility was used to investigate the influence of lanthanum ion (La$^{3+}$) on the structural and magnetic properties of xLa$_2$O$_3$:30PbO·(70 − x)B$_2$O$_3$ (0 ≤ x ≤ 10 mol%) glass system.

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2. Experimental procedures

Glass samples having the formula $xLa_2O_3·30PbO·(70−x)B_2O_3$ ($0 \leq x \leq 10$ mol%) were prepared by the well known melt-quenching technique. Required quantities of analytical reagent grade $H_2B_2O_3$, $La_2O_3$ and PbO were melted in a covered platinum crucible in an electrically heated furnace under ordinary atmospheric conditions at a temperature of about 1273 K for 0.5 h to homogenize the melt. The method of preparation of these glasses has been described elsewhere [1]. The samples were then ground and optically polished to have suitable dimensions ($2 \times 1 \times 0.15$ cm$^3$) for the present optical measurements. Non-parallelism of the two opposite side faces was less than 0.01°.

The transmittance ($T$) and the reflectance ($R$) optical spectra of the prepared glasses as shown in Fig. 1, were recorded at room temperature in the wavelength range 200–1500 nm using a computerized double beam spectrophotometer, type SHIMADZU UV-2100. The accuracy to which $\lambda$ and $T$ can be measured is ± 1 nm and ± 0.3%, respectively.

The AC susceptibility measurements were carried out in the temperature range of 5–200 K at a frequency of 625 Hz with Lake-Shore 7229 AC susceptometer using a mutual inductance with an excitation field $H_{ac} = 5$ Oe. To relate the magnetic susceptibility to atomic properties, the mass magnetic susceptibility was converted into the molar magnetic susceptibility $\chi_m$ using $\chi_m = x_\phi \cdot M_m$, where $M_m$ is the molecular weight of the sample. The temperature accuracy is ± 0.5% and the stability is ± 0.1 K. Also, the accuracy of AC/DC magnetic field (Primary Coil) is ± 1.0% and the stability is ± 0.05%.

3. Results and discussions

3.1. The optical parameters

Based on the transmission and reflection curves of the studied glasses, the values of the optical parameters such as the refractive index, the optical band gap and the oxide ion electronic polarizability can be obtained. As shown in Fig. 1, the UV–Vis–NIR transmission in the studied glasses decreases with the increase of the $La_2O_3$ content in the range 0 ≤ $x$ ≤ 5 mol% and increases beyond this limit, while the UV reflection behaves in a vice versa. The observed behavior of both glass transmittance and reflectance with the increase of $La_2O_3$ content up to 5 mol% is due to the replacement of $B_2O_3$ with molecular mass less than that of $La_2O_3$. Further increase of $La_2O_3$ ≥ 5 mol% leads to an increase in glass transmittance that can be attributed to an increase in the concentration of highly coordinated $Pb^{+2}$ in PbO$_4$ bipyramids at the expense of $B_2$ (Pb) units. The last two parameters [16,17] can be used to evaluate the optical absorption coefficient ($\alpha$) of a material by using the relation $\alpha = \frac{1}{d} \ln \frac{1}{R}$, where $d$ is the sample thickness, while the refractive index ($n$) as a function in the reflectance ($R$) and the extinction coefficient ($k$) can be determined by the quadratic equation:

$$R = \frac{(1-n)^2 + k^2}{(1+n)^2 + k^2}. \quad (1)$$

The extinction coefficient can be computed based on the wavelength ($\lambda$) and the calculated values of ($\alpha$) according to the relation: $\alpha = \frac{\pi n}{\lambda}$. It is known that the change in the refractive index is sensitive to the change in the incident wavelength and to the structural variations. The refractive index as shown in Fig. 2 decreases with increasing the wavelength of the incident photon, and increases with the increase of the $La_2O_3$ content in the range 0 ≤ $x$ ≤ 5 mol% and decreases beyond this limit. Thus, the dependence of the refractive indices on the $La_2O_3$ content of the studied glasses can be explained as follows. According to the Lorentz–Lorenz [18,19] equation, the density of the material affects the refractive index in a direct proportion. As discussed previously [1], $La_2O_3$ affects the lead borate glasses into two regions, namely, in the range 0 ≤ $x$ ≤ 5 mol% and in the range 5 ≤ $x$ ≤ 10 mol%. In the first region, $La_2O_3$ causes a decrease in both the rigidity represented with the bulk modulus and the coordination number of the structural units of the glasses. The last two parameters in the second region increase with the increase of $La_2O_3$ content. This in turn, leads to a variation in the average coordination number of the studied glasses, which affects the refractive index [20]. Also, the existence of non-bridging oxygens (NBOs) creates more ionic bonds which manifest themselves in a larger polarizability over the mostly covalent bonds of bridging oxygen providing a higher index value. Thus, the bulk modulus and the refractive index can be correlated with the relation; $n = 21.2 − 0.79 K_b + 0.008K_b^{-2}$ which is in a good agreement with the work of Reddy et al. [21,22]. The tabulated values of the computed refractive index according to this formula [Table 1] are in a good agreement with the values of the experimental data.

The average electronic polarizability of ions is an important parameter of a material which is closely related to their applicability in the field of optics and electronics. It was found that, the optical non-linearity is caused by the electronic polarization of a material upon its exposure to intense light beams, so, the non-linear response of the material is governed by the electronic polarizability [23]. For isotropic substance
such as glasses, the average molar refraction ($R_m$) was given by the Lorentz–Lorenz equation:

$$R_m = \frac{\frac{n^2 - 1}{n^2 + 2}}{M \frac{n^2 - 1}{V_m}}$$

(2)

where the quantity $\frac{n^2 - 1}{n^2 + 2}$ is called the reflection loss which is related to the structure of the glass and is proportional to the molar electronic polarizability of the material, $\alpha_m$ in cm$^3$ $\times$ 10$^{-24}$ through the Clausius–Mosotti relation: $\alpha_m = \frac{1}{N} R_m$, where N is Avogadro’s number. For various ternary oxide glasses with the general formula $y_1$La$_2$O$_3$–$y_2$B$_2$O$_3$–$y_3$CaO$_{2m}$, where ys denote the molar fraction of each oxide, the electronic polarizability of oxide ion can be calculated [8,19]. The electronic polarizability of oxygen is related to ultraviolet transparency, the wavelengths at which charge transfers bands of dissolved metal ions, the magnitude of negative charge borne by the oxide species in the glass and the optical basicity of the glass. The electronic polarizability of oxide ions can be calculated on the basis of refractive indices by using the following equation:

$$\alpha^2_{2\text{O}}(n) = \left(\frac{V_m}{N_N} \frac{n^2 - 1}{n^2 + 2} - \sum \alpha_{cat} \right),$$

(3)

where $\sum \alpha_{cat}$ is the molar cation polarizability and $N_N^-$ is the number of oxide ions in the chemical formula. The average polarizability as shown in Fig. 3 has the same behavior of the refractive index which is due to its dependence on the nature of the chemical bonding that controls the rigidity. Therefore, the bulk modulus and the oxide ion polarizability can easily be evaluated and correlated by the relation: $\alpha^2 n$ ($n$) = 823 – 52.3 $K_b$ + 1.1 $K_b^2$ – 0.0078 $K_b^3$.

On the other hand, according to Pankove [16], the indirect optical band gap energy ($E_{\text{opt}}^\text{g}$) can be obtained from Eq. (4) by extrapolating the absorption coefficient to zero absorption in the $(\alpha n h v)^{1/2} - h v$ plot as shown in Fig. 4:

$$\alpha n h v = A_0 \left(\frac{E_{\text{opt}}^g}{h v}\right)^2.$$  (4)

The calculated values of $E_{\text{opt}}^g$ is tabulated in Table 1. It is clear from this table that $E_{\text{opt}}^g$ decreases in the range 0 $\leq x \leq 5$ mol% and increases beyond this limit. As discussed previously [1], as the La$_2$O$_3$ content increases there is a dilation in the structure in the range 0 $\leq x \leq 5$ mol% which is attributed to the seven coordination numbers of La$^{3+}$ which form B$_4$(La) units at the expense of B$_4$(Pb) units. The former units have low bond strength compared with the high bond strength of the latter units. Also, as the optical band gap is originated from the electronic energy levels within the glass, so it is expected that these units increasing the electron density on the B$^{3+}$ ions would result in a lower band gap, and La$^{3+}$ and Pb$^{4+}$ ions could well do this. This variation besides the formation of non-bridging oxygens decreases the optical band gap. As for La$_2$O$_3$ content exceeds 5 mol%, there is a densification in the structure which is attributed to the increase in the concentration of PbO$_4$ units which increases the rigidity and hence the optical band gap of the glasses. Thus, correlating the optical band gap to the bulk modulus can be achieved via the relation, $K_b$ = 1780 – 1668 E + 529 $E^2$ – 55.4 $E^3$. Accordingly, the computed values of the optical band gap according to this formula are in a good agreement with its experimental values and with the relation suggested by Reddy et al. [21,22].

3.2. AC magnetic susceptibility and entropy change

The magnetic susceptibility measurement technique offered useful information concerning the nature of the magnetic interactions between La$^{3+}$ ions inside the host glass matrix [24–26]. The temperature dependence of the magnetic susceptibility $\chi$ of paramagnetic materials (with local magnetic moments due to transition metals or rare earth ions) is
expected to follow the modified Curie–Weiss law corrected for the contribution of glass host matrix \(\chi_{h}\) [24–26]: Paramagnetic magnetic susceptibility \(\chi_{p}\) was calculated according to the following equation:

\[
\chi_{M} = \chi_{dia} + \frac{C_{M}}{T - \theta_{p}},
\]

where

\[
C_{M} = \frac{\mu_{eff}^{2} \cdot N_{A}}{3k_{B}} \chi_{dia},
\]

where \(\chi_{dia}\) is the molar susceptibility of the host matrix, \(C_{M}\) is molar Curie constant, \(\theta_{p}\) is the paramagnetic Curie temperature, \(T\) is the absolute temperature, \(N_{A}\) is the Avogadro's number, \(x\) is the mole part of \(La^{3+}\) ions in the prepared glass, \(k_{B}\) is the Boltzmann's constant and \(\mu_{eff}\) is the effective magnetic moment.

AC magnetic susceptibility \(\chi_{AC}\) of the investigated glasses as a function of temperature above liquid helium temperature (LHT) in the range 4.5–25 K is presented in Fig. 5. The curves of Fig. 5 were fitted according to Curie–Weiss and the values of \(C_{M}, \theta_{p}\) and \(\chi_{dia}\) were calculated using origin software. It is noticed that, \(C_{M}, \theta_{p}\) and \(\chi_{dia}\) increase with the increase of \(La^{3+}\) ion content inside the host glass matrix. It is clear that the paramagnetic susceptibility of the investigated glasses increases with the increase of the rare earth ions (\(La^{3+}\) ion content). The obtained data follows the Curie–Weiss behavior over the studied temperature range. Although the magnitude of the paramagnetic Curie temperature \(\theta_{p}\) is negative, it consistently increases with the increase of \(La^{3+}\) ion content in the studied glass as shown in Fig. 6. The absolute magnitude of \(\theta_{p}\) values increases with \(La_{2}O_{3}\) content for \((1 \leq x \leq 10 \text{ mol%})\) while for \(x = 0\) there is no any \(La^{3+}\) inside the host matrix which affected the values of \(\theta_{p}\) (diamagnetic host lattice contributions i.e. \(30PbO-(70-x)B_{2}O_{3}\)). The strength of the interactions between the magnetic ions was measured, and its higher value implies stronger interactions and/or more ions participating in the interactions can be defined as the paramagnetic Curie temperature \(\theta_{p}\). The negative values of the paramagnetic Curie temperatures indicate that the magnetic interactions are predominately antiferromagnetic in the studied glasses. This fact suggests a super exchange interaction between the gadolinium ions, which are antiferromagnetically coupled. Due to the disordered structure of glasses, the magnetic order takes place at short range making the possibility of a micro magnetic-type order [13,27,28].
molecular field constant were increased with the increase of La3+ ions. Supposed, in a first approximation, that \( z \) increases when \( N \) increases, so allowed that \( z/N \) is constant (the number of lanthanum ions that interact is proportional with the total number of lanthanum ions), results that the molecular field constant is proportional with the magnetic exchange integral. So that, according to Fig. 6, the values of the magnetic exchange integral increase when the content of lanthanum ions increases in the studied glasses [13,30].

When a magnetic field is applied to a magnetic material, its magnetic moments tend to align themselves in the magnetic field direction and a more ordered state is achieved, so the magnetic entropy of the system decreases. According to classical thermodynamics, the infinitesimal change in temperature was observed when a magnetic field is applied adiabatically which is expressed as [31–33]:

\[
dT = -\frac{T}{C_M} \left( \frac{\partial M}{\partial T} \right)_H dH. \tag{9}
\]

Then, integrating over the magnetic field, one obtains the temperature change involved when a final magnetic field \( H_{\text{max}} \) is applied:

\[
dT = \int_0^{H_{\text{max}}} -\frac{T}{C_M} \left( \frac{\partial M}{\partial T} \right)_H dH. \tag{10}
\]

When isothermal magnetization processes are carried out, the total magnetic entropy change \( \Delta S_{\text{M}} \) under temperature for the magnetic system due to the application of a magnetic field is:

\[
\Delta S_{\text{M}}(T, H) = \left[ \frac{\partial M}{\partial T} \right]_H dH. \tag{11}
\]

where \( H_{\text{max}} \) is the final applied magnetic field. Measurements of magnetic entropy variation when a fixed magnetic field change is applied allow one to determine whether a magnetic material may be considered to be a good magnetic refrigerant. Thus, for Curie–Weiss paramagnets the entropy change \( \Delta S_{\text{M}} \) will be [31–33]:

\[
\Delta S_{\text{M}} = -\frac{C_M}{2} \left( \frac{H^2}{T-\theta_p} \right), \tag{12}
\]

where \( C_M \) in emu/mol and \( T \) and \( \theta_p \) in K and \( \Delta H \) in Oe. The entropy change as a function of temperature is shown in Fig. 7 for different percent of La ions inside the host matrix. It is clear that the entropy change decreases with the increase of the temperature and increases with the increase of the mole percent of La ions added to total matrix. This behavior was expected for the paramagnetic materials because their magnetization increases quickly when the temperature decreases at lower temperatures. Because of their paramagnetic behavior at low temperatures, the studied materials exhibit the entropy change that rapidly increases when the temperature decreases. This means that these materials can be used as active magnetic refrigerants at liquid helium temperature over a wide range of temperatures under very low external magnetic field of 5 Oe [13,14,34].

4. Conclusion

The optical transmittance and reflectance spectra of the studied glasses have been recorded in the UV–Vis–NIR. The \( E_{\text{g}}^0 \) values for the indirect transition were obtained and the refractive index and the average electronic polarizability of these oxides were calculated at different wavelengths. The exchange interactions between La3+ ions inside the investigated glasses are predominantly antiferromagnetic. Values of the molar susceptibility of the host matrix, molar Curie constant, the magnetic moment and the molecular field constant \( \theta_p \) suggest predominately the presence of weak antiferromagnetic interaction in these La borate glasses. Magnetic measurement and optical property data suggest that the La ions play both the network former and network modifier roles in the studied glasses. This borate glass modified La ions can be used as active magnetic refrigerants at liquid helium temperature (LHT).

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