Disorder in $Ca_3RE_2(BO_3)_4$ (RE = Nd, Gd) structure

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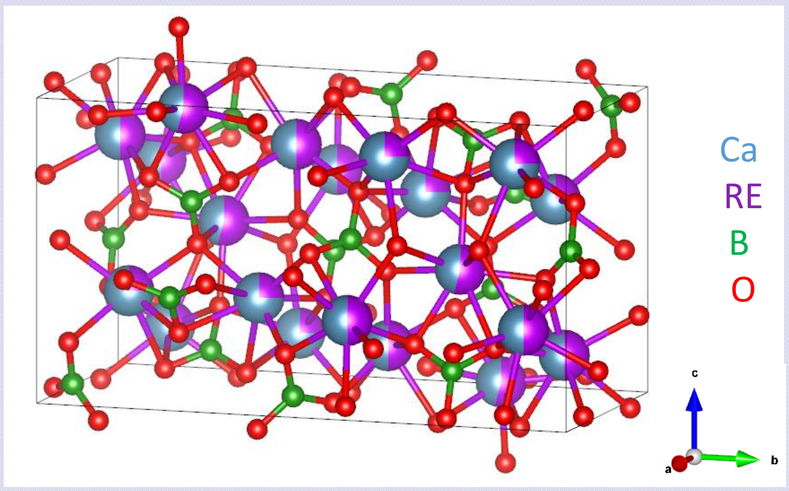
Introduction

Calcium borates of a $Ca_3RE_2(BO_3)_4$ formula are usually investigated due to their optical properties, potentially desirable for solid state lasers. The most characteristic feature of which they are known, is a disordered type of their structure, leading to a broadening of emission and absorption lines [1]. The term "disorder" is used to describe a joint occupation of some cationic sites by more than one type of element – in this case, by calcium ion and a rare earth metal. This study present a more detailed insight into the crystal structure of those materials, revealing new kinds of disorder.

Experimental

$Ca_3RE_2(BO_3)_4$ (RE = Gd, Nd) crystals were grown by Czochralski method. Full description of synthesis process can be found in [2]. Single crystal X-ray diffraction measurements were performed at 100 K (RE = Gd, Nd) and 300 K (RE = Gd), using MoKα radiation (λ = 0.71073 Å) at Xcalibur (RE = Gd) and SuperNova (Re = Nd) Oxford Diffraction 4-circle diffractometers. Data reduction was carried out using CrysAlis RED software. The structural determination procedure was performed using the SHELX package.

For comparison, a results obtained by high-resolution powder X-ray diffraction (PXRD) are presented for RE = Gd case (λ = 0.40022 Å), collected at ID22 beamline (ESRF, France).

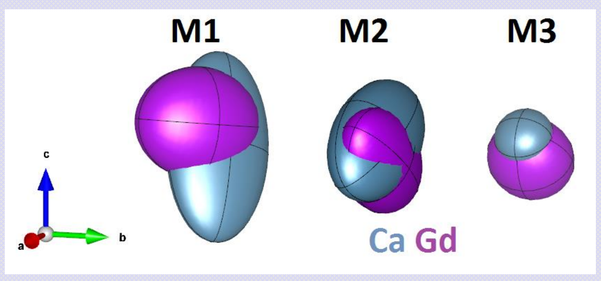


Basic model (RE = Gd, T = 100 K, based on [3])

- Space group *Pnma*, a ~7.2, b ~15.5, c ~8.6 Å.
- 3 non-equivalent cationic sites (M1-M3), shared by Ca and RE with different probability.
- M1-M3 are surrounded by 8/9 oxygen ions, irregular polyhedrons are created.
- 3 non-equivalent boron sites.
- Isolated BO_3 units, creating approximately planar triangles with a boron atom in the center.
- The model resulted with the following agreement factors: wR2 = 0.1822, GooF = 2.182, R1 = 0.0612.

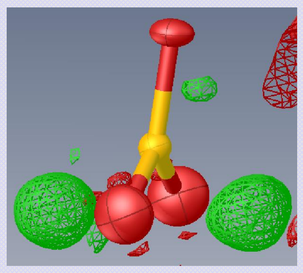
Improved model (RE = Gd, T = 100 K)

Cationic disorder



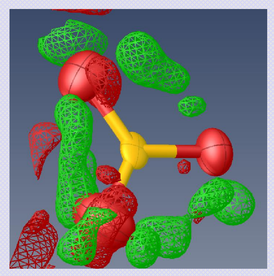
- Model: splitting of Ca/RE sites, different anisotropic thermal displacement parameters (wR2 = 0.1213, GooF = 1.449, R1 = 0.0418).
- Such attempt have been reported so far only for one M site in $Ba_3Bi_2(BO_3)_4$ of the same structure [4]. Here, splitting of each site improved quality of the refinement.

Oxygen disorder around $B^{(2)*}$:

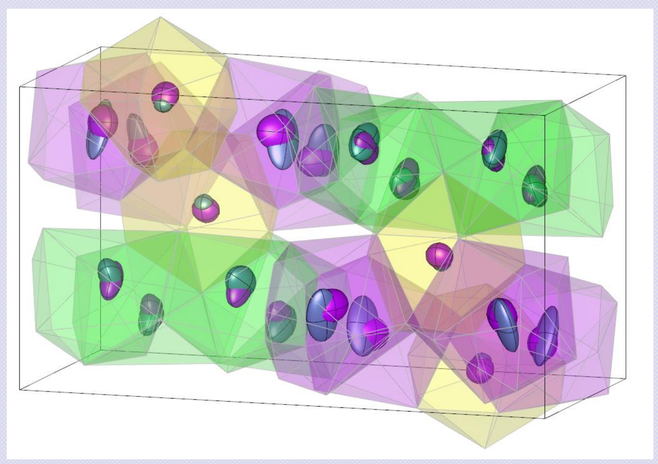


- Two well-distinguished electron density peaks, creating with another oxygen ion a BO_3 unit, approximately perpendicular to the initial one.
- Model: $B^{(2)}O_3$ unit exhibit two distinguished configurations with different probability (see Table) (wR2 = 0.0992, GooF = 1.182, R1 = 0.0350).

Oxygen disorder around $B^{(1)*}$:



- Blurred electron density between oxygen ions in the $B^{(1)}O_3$ unit.
- Model: $B^{(1)}O_3$ unit is with different probability at 2 positions (wR2 = 0.0868, GooF = 1.041, R1 = 0.0309).



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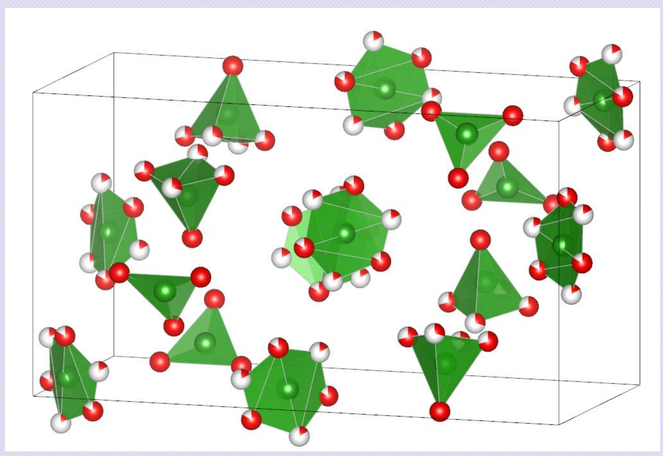

**(There's no visible oxygen disorder around $B^{(3)}$ atom)*

Model obtained for RE = Gd at T = 100 K was applied to other data (SCXRD in Table below)

RE	Gd	Gd	Gd	Nd
Method	PXRD	SCXRD	SCXRD	SCXRD
T [K]	295	300	100	100
a b [Å] c	7.1936(1) 15.5449(2) 8.6198(1)	7.1952(1) 15.5419(2) 8.6200(1)	7.1777(1) 15.5078(2) 8.6070(1)	7.2262(1) 15.6681(2) 8.6593(1)
M1 RE occup.	0.464(1)	0.488(1)	0.487(1)	0.551(1)
M2 RE occup.	0.243(1)	0.240(1)	0.241(1)	0.291(1)
M3 RE occup.	0.585(1)	0.543(2)	0.542(2)	0.317(2)
$B^{(1)}$ Ueq [Å^2]	0.052(1)	0.0267(7)	0.0244(7)	0.0243(8)
$B^{(2)}$ Ueq [Å^2]		0.0176(7)	0.0161(1)	0.0181(9)
$B^{(3)}$ Ueq [Å^2]		0.0181(7)	0.0165(7)	0.0173(9)
Probability of $B^{(2)}O_3$ triangle in initial-model position	1	0.717(7)	0.712(7)	0.760(8)

- SCXRD model allowed to lower overestimated thermal displacement parameters of boron atoms.
- Data collected for RE = Nd revealed the same features as crystal structure of $Ca_3Gd_2(BO_3)_4$ – splitting cationic sites, two discreet configurations of $B^{(2)}O_3$ unit and blurred density between oxygen ions around $B^{(1)}$ atom.
- Comparison of the data collected at 300 K and 100 K do not reveal any significant differences in the crystal structure – the disorder is rather of a static character than dynamical.

References

[1] Y. Wang et al. (2004) *J. Mater. Res*., 19(4), 1203-1207.

[2] L. V. Gudzenko et al. (2017) *Crystals*, *7*(3), 88.

[3] B.V. Mill et al. (1998) *Optika I Spektroskopiya,* 84(1), 74-81.

[4] S. N. Volkov et al. (2013) *Z. Kristallogr. Cryst. Mater.*, *228*(9), 436-443.