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► **To cite this version:**

Nadezhda Kononova, Vyacheslav Shevchenko, Alexander Kokh, Tatiana Nabeeva, David Chapron, et al.. Synthesis of New Isostructural Orthoborates  $\text{NaBaR}(\text{BO}_3)_2$  with  $\text{R} = \text{Tb}$ . *Materials Research*, 2016, 19, pp.834-838. 10.1590/1980-5373-MR-2016-0081 . hal-01532748

**HAL Id: hal-01532748**

**<https://hal.univ-lorraine.fr/hal-01532748>**

Submitted on 3 Jun 2017

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# Synthesis of New Isostructural Orthoborates NaBaR(BO<sub>3</sub>)<sub>2</sub> with R = Tb, Dy, Ho, Er, Tm and Lu

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Received: January 31, 2016; Revised: April, 21, 2016; Accepted: June 5, 2016

Six new rare-earth orthoborates NaBaR(BO<sub>3</sub>)<sub>2</sub>, with R = Tb, Dy, Ho, Er, Tm, Lu were synthesized using a multiple-step solid-state reaction. These new orthoborates continue the previously described isostructural lines of three-cation orthoborates NaBaR(BO<sub>3</sub>)<sub>2</sub>, by R = Sc, Y, Yb. The structure of synthesized solid compounds is isotypic with the mineral eitelite, Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>, crystallizing in the trigonal system with space group R $\bar{3}$ . All prepared borates are isostructural, as evidenced by the presence of the same vibration modes in Raman spectra and of the same diffraction peaks in X-ray patterns. The photoluminescence of NaBaTb(BO<sub>3</sub>)<sub>2</sub> have been investigated in a detail.

**Keywords:** rare-earth orthoborates, NaBaR(BO<sub>3</sub>)<sub>2</sub>, solid-state synthesis, Raman spectra, luminescence

## 1. Introduction

The rare-earth borates have potential applications for laser medium, luminescent and nonlinear optical materials<sup>1-3</sup>. Many one- and two cation borates are currently used in photonics<sup>4</sup>. A current area of research is for new materials for photonic dilates using more complex borate crystal compounds. Orthoborate crystals containing three cations are among the most attractive to investigate because of their potential application as a light emitting phosphor for phosphor-converted white light emitting diodes<sup>5</sup> and as a green emitting phosphor for three-dimensional plasma panel<sup>6</sup>.

In our earlier study of solid phase formation in the system M<sub>2</sub>O<sub>3</sub>-BaO-Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub> (M = Sc, Y) we identified two new borates: NaBaSc(BO<sub>3</sub>)<sub>2</sub> and NaBaY(BO<sub>3</sub>)<sub>2</sub><sup>7-8</sup>. Further investigation in this family resulted in the discovery of new ytterbium-bearing borate NaBaYb(BO<sub>3</sub>)<sub>2</sub><sup>9</sup>. All discovered compounds of NaBaR(BO<sub>3</sub>)<sub>2</sub> (R = Sc, Y, and Yb) line are isostructural and have eitelite-like, Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>, structure with space group.

In this study, we report the synthesis of new rare-earth compounds in NaBaR(BO<sub>3</sub>)<sub>2</sub> orthoborate family (R = Tb, Dy, Ho, Er, Tm, Lu) using high-temperature solid-state reaction, and continue previously described orthoborates NaBaR(BO<sub>3</sub>)<sub>2</sub> with R = Sc, Y and Yb. The photoluminescence properties of NaBaTb(BO<sub>3</sub>)<sub>2</sub> are also reported.

## 2. Material and Methods

### 2.1 Samples preparation and Synthesis

High purity chemicals of BaCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Ce<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Pr<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Tb<sub>2</sub>O<sub>3</sub>, Dy<sub>2</sub>O<sub>3</sub>, Ho<sub>2</sub>O<sub>3</sub>,

Er<sub>2</sub>O<sub>3</sub>, Tm<sub>2</sub>O<sub>3</sub>, Lu<sub>2</sub>O<sub>3</sub> (analytical reagent) were purchased and used as starting reactants. Samples of reagents were weighed at the stoichiometric ratio, mixed thoroughly and ground into fine powder in an agate mortar. Resulting mixtures with an excess of 3 mass % H<sub>3</sub>BO<sub>3</sub> were heated to 700 °C in platinum crucible and kept at this temperature for 24 h to decompose the carbonates and boron acid.

Multi-stage high temperature solid-state synthesis was used to prepare rare-earth borates. During the first stage, the starting mixture was annealed at 700°C for approximately 1 day. The conditions of the second stage were achieved by increasing the temperature in steps of 50°C. After each heating step, intermediate reaction products were sampled and identified by gradually grinding following X-ray powder diffraction analysis to identify crystal forms. Phase equilibrium, indicated by unchanging reflections and intensities in the X-ray diffraction patterns between temperature steps, was served as a criterion for completion of the solid-state reaction. Heating to higher temperatures was observed to result in partial or complete melting.

### 2.2 Samples characterization

X-ray powder diffraction (XRD) data was obtained by a DRON-3 diffractometer with 2θ ranging from 10° to 80° (CuKα radiation; U = 30–40 kV; I = 25 mA, speed meter –1°/min, belt speed –1 cm/min) using silicon as an external standard. Unit cell parameters for new borates are calculated based on X-ray powder diffraction patterns. In addition, Raman spectra were collected using Lab RAM ARAMIS Horiba Jobin Yvon Raman spectrometer producing light at 633 and 785 nm. The photoluminescence properties of NaBaTb(BO<sub>3</sub>)<sub>2</sub> were studied with Cary Eclipse Fluorescence spectrophotometer at room temperature.

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### 3. Results and Discussion

Table 1 summarizes results of phases identified after high temperature solid-state synthesis of rare-earth borates containing sodium and barium. In some cases, we obtained simple and complex rare-earth borates. For example, a Ce<sup>3+</sup> solid state reaction resulted in formation of CeBO<sub>3</sub> simple borate, while Nd<sup>3+</sup> produced Nd<sub>2</sub>Ba<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub> and NdNa<sub>3</sub>(BO<sub>3</sub>)<sub>2</sub> complex borates. Using La<sup>3+</sup>, Pr<sup>3+</sup>, Eu<sup>3+</sup> produced La<sub>2</sub>Ba<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, Pr<sub>2</sub>Ba<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, Eu<sub>2</sub>Ba<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, respectively. These latter reactions did not result in a compound isostructural to previously obtained NaBaSc(BO<sub>3</sub>)<sub>2</sub>, probably because the ionic radii of cerium subgroup rare-earth elements are too large.

For Gd<sup>3+</sup> we observed intermediate products of reaction:

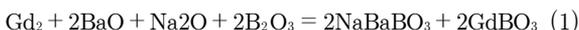


Figure 1 shows observed X-ray powder diffraction patterns of the new NaBaR(BO<sub>3</sub>)<sub>2</sub> (R = Tb, Dy, Ho, Er, Tm and Lu) together with previously prepared orthoborates of NaBaYb(BO<sub>3</sub>)<sub>2</sub> for comparison. All prepared borates are isostructural as evidenced by the presence of the same diffraction peaks in X-ray patterns. The cell parameters of the new synthesized compounds NaBaR(BO<sub>3</sub>)<sub>2</sub> were calculated on the basis of the X-ray powder diffraction data using Cellcalc software<sup>11</sup> with space group . The cell parameters for all new compounds are given in Table 2. Based on these results, it can be seen that the lattice parameters and volume of NaBaR(BO<sub>3</sub>)<sub>2</sub> decrease with the decreasing of the effective ionic radius of rare earth elements according to Shannon<sup>10</sup>.

Using these cell parameters, it can be concluded that synthetic orthoborates are isostructural to NaBaSc(BO<sub>3</sub>)<sub>2</sub>, NaBaY(BO<sub>3</sub>)<sub>2</sub>, NaBaYb(BO<sub>3</sub>)<sub>2</sub>, crystallographic data of which have been fully described elsewhere<sup>7-9</sup>. The main features of their crystal structure are anion-cation (Ba,Na)(BO<sub>3</sub>) layers, which are combined into the base building packages of two types: {R<sup>3+</sup>[Ba<sup>2+</sup>(BO<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}<sup>+</sup> and {R<sup>3+</sup>[Na<sup>+</sup>(BO<sub>3</sub>)<sub>3</sub>]<sub>2</sub>}<sup>-</sup>.

The fundamental building units of these orthoborates are RO<sub>6</sub> octahedra and BO<sub>3</sub> triangles. Furthermore, how it was determined in ref.<sup>7</sup> the new compounds are isotypic to mineral eitelite, Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub><sup>12</sup> with the same space group . XRD patterns depict a marked shift of the X-ray peaks in the transition from Sc- to Tb-compounds due to the differences between the ion radii of studied rare-earth elements, from 0.745 to 0.923, respectively.

Based on XRD results of measured intermediate solid-state reaction products, the reaction of the borates formation can be represented as follows:



Further interaction between the products of this reaction was not observed, since annealing of the sample higher than 950 °C led to complete melting of solids.

#### 3.1. Raman spectroscopy

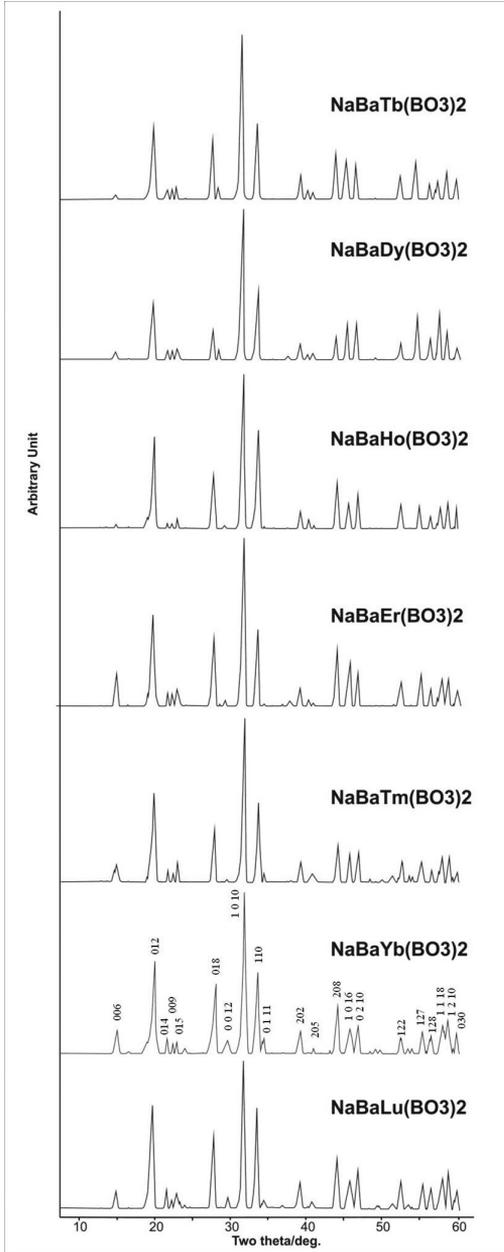
The Raman spectra of the NaBaR(BO<sub>3</sub>)<sub>2</sub> crystals were recorded with exciting laser at 633 nm and 785 nm for R = Tb, Dy, Y, Tm, Yb, Lu, Sc and Er, Ho, respectively. At 633 nm the laser was found to excite the energy levels of Er or Ho ions, interfering with the emission spectrum.

Results of Raman spectroscopy presented in Figure 2 and Figure 3 show that synthetic orthoborates are isostructural, evidenced by presence of the same modes in Raman spectra. The Raman spectra show typical vibration modes of the triangular BO<sub>3</sub> group. It is well known that isolated BO<sub>3</sub> ion with D<sub>3h</sub> symmetry characterized by four fundamental modes of which three Raman-active ν<sup>+</sup>(A<sub>1</sub>') (~950cm<sup>-1</sup>), ν<sub>3</sub><sup>+</sup>(E') (~1250-1400 cm<sup>-1</sup>), ν<sub>4</sub><sup>+</sup>(E'<sub>1</sub>') (~600 cm<sup>-1</sup>) and one infrared active<sup>13</sup>.

The peak at ~1200 cm<sup>-1</sup> in the Raman spectra of synthesized orthoborates are likely due to the asymmetric stretching mode ν<sub>3</sub><sup>+</sup>(E') strong peaks at ~950 cm<sup>-1</sup> attributed to the

**Table 1:** Results of solid-state synthesis of NaBaR(BO<sub>3</sub>)<sub>2</sub> orthoborates (R = Sc, Y, cerium (La-Eu) subgroup and yttrium (Gd-Lu) subgroup of REEs).

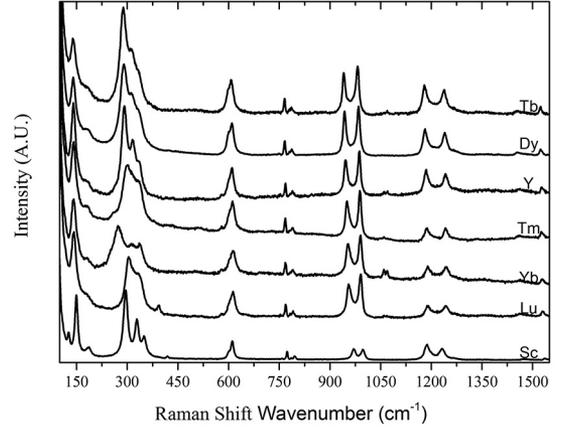
№	R	Atomic number	R3+(coordination number - 6), Å <sup>10</sup>	Max annealing temperature, °C	Determined or known compounds after X-ray research
1	Sc	21	0.745	900	NaBaSc(BO <sub>3</sub> ) <sub>2</sub> <sup>6,7</sup>
2	Y	39	0.900	900	NaBaY(BO <sub>3</sub> ) <sub>2</sub> <sup>6,7</sup>
3	La	57	1.032	1000	La <sub>2</sub> Ba <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> , Na <sub>2</sub> B <sub>2</sub> O <sub>4</sub>
4	Ce	58	1.010	900	CeBO <sub>3</sub> , CeO <sub>2</sub> , BaNaBO <sub>3</sub>
5	Pr	59	0.990	900	Pr <sub>2</sub> Ba <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> , BaNaBO <sub>3</sub>
6	Nd	60	0.983	900	Nd <sub>2</sub> Ba <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> , NdNa <sub>3</sub> (BO <sub>3</sub> ) <sub>2</sub>
7	Eu	63	0.947	900	Eu <sub>2</sub> Ba <sub>3</sub> (BO <sub>3</sub> ) <sub>4</sub> , Na <sub>2</sub> B <sub>6</sub> O <sub>10</sub>
8	Gd	64	0.938	950	GdBO <sub>3</sub> , BaNaBO <sub>3</sub>
9	Tb	65	0.923	800	NaBaTb(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>
10	Dy	66	0.912	800	NaBaDy(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>
11	Ho	67	0.901	850	NaBaHo(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>
12	Er	68	0.890	800	NaBaEr(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>
13	Tm	69	0.880	800	NaBaTm(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>
14	Yb	70	0.868	850	NaBaYb(BO <sub>3</sub> ) <sub>2</sub> <sup>8</sup>
15	Lu	71	0.861	800	NaBaLu(BO <sub>3</sub> ) <sub>2</sub> <b>NEW</b>



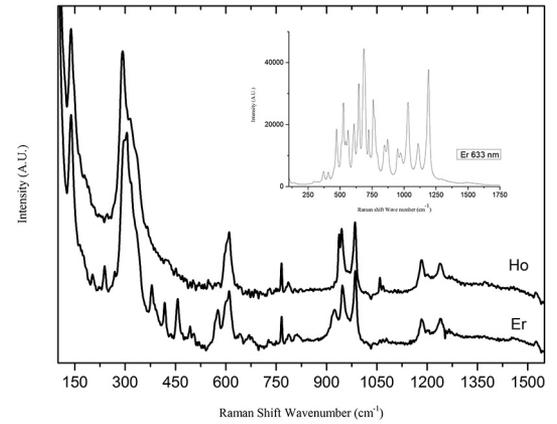
**Figure 1:** X-ray powder diffraction patterns of the new NaBaR(BO<sub>3</sub>)<sub>2</sub> orthoborates (R = Tb, Dy, Ho, Er, Tm and Lu) and NaBaYb(BO<sub>3</sub>)<sub>2</sub> as a reference.

**Table 2:** Lattice parameters of NaBaR(BO<sub>3</sub>)<sub>2</sub> orthoborates.

N <sup>o</sup>	R	a, Å	c, Å	V, Å <sup>3</sup>	ρ, g/cm <sup>3</sup>
1	Sc	5.23944(12)	34.5919(11)	822.38(4)	3.912
2	Y	5.3338(2)	35.8303(19)	882.78(7)	4.140
3	Tb	5.367(5)	36.30(7)	905(2)	4.806
4	Dy	5.360(3)	36.16(4)	899(1)	4.874
5	Ho	5.358(2)	35.87(4)	891(1)	4.946
6	Er	5.349(2)	35.62(4)	882(1)	5.024
7	Tm	5.343(2)	35.59(3)	880(1)	5.057
8	Yb	5.337(3)	35.58(4)	878(1)	5.116
9	Lu	5.336(3)	35.54(4)	876(1)	5.148



**Figure 2:** Raman spectra of the new NaBaR(BO<sub>3</sub>)<sub>2</sub> (R = Tb, Dy, Y, Tm, Yb, Lu and Sc) at 633 nm excitation.



**Figure 3:** Raman spectra of the new NaBaR(BO<sub>3</sub>)<sub>2</sub> (R = Ho and Er) at 785 nm excitation.

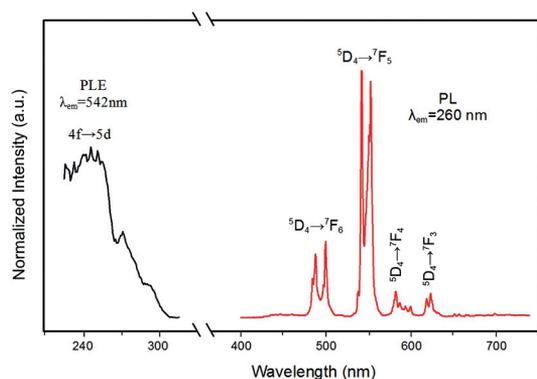
symmetric stretching modes  $\nu_1'(A_1')$ , while relatively high peak at  $\sim 600 \text{ cm}^{-1}$  are from bending vibration mode of BO<sub>3</sub> group. Furthermore, the modes in the region of 420-125  $\text{cm}^{-1}$  can be assigned to BO<sub>3</sub> translation and vibration<sup>14</sup>.

### 3.2. Photoluminescence properties

Previous studies showed that rare-earth elements introduced into borate structure may present photoluminescence properties<sup>15</sup>. Among synthesized NaBaR(BO<sub>3</sub>)<sub>2</sub> borate family,

photoluminescence properties of as-prepared NaBaTb(BO<sub>3</sub>)<sub>2</sub> have been investigated in this study, because Tb<sup>3+</sup> in host materials shows an intense characteristic green emission and relative suitable decay time, which can be used for PDP and LEDs<sup>6,16</sup>.

Figure 4 shows the PLE and PL spectra of NaBaTb(BO<sub>3</sub>)<sub>2</sub> powder sample. As shown in Figure 4, there is a broad excitation band ranging from 200 to 300 nm with a maximum at about 250 nm and shoulder peaks at ~270 and 292 nm, which can be ascribed to 4f → 5d transitions of Tb<sup>3+</sup>. The PL spectrum excited at 260 nm is composed of several narrow emission peaks at ~490, 550, 580 and 620 nm due to the well-known <sup>5</sup>D<sub>4</sub> → <sup>7</sup>F<sub>J</sub> (J=6, 5, 4, 3) transitions<sup>15</sup>.



**Figure 4:** The excitation and emission spectra of NaBaTb(BO<sub>3</sub>)<sub>2</sub>

The high level emission (<sup>5</sup>D<sub>3</sub>) is quenched by cross relaxation in favour of the <sup>5</sup>D<sub>4</sub> emission due to high concentration of Tb<sup>3+</sup> in the compound<sup>17</sup>. The shortest estimated Tb-Tb distance (~5.36 Å) suggests that exchange interaction becomes ineffective and luminescence is predicted to become efficient<sup>17</sup>, making the NaBaTb(BO<sub>3</sub>)<sub>2</sub> compound a promising green-emitting phosphor material.

#### 4. Conclusion

Six new rare-earth orthoborates belonging to NaBaR(BO<sub>3</sub>)<sub>2</sub> crystal family were synthesized with rare earth elements Tb, Dy, Ho, Er, Tm and Lu, while several other trivalent (3+) cations: La, Ce, Pr, Nd, Eu, Gd were not. Based on calculated lattice parameters and volumes these six new borates are isostructural to previously described orthoborates NaBaR(BO<sub>3</sub>)<sub>2</sub> with R = Sc, Y, Yb and fall within the trigonal system space group, and are isotopic with mineral eitelite, Na<sub>2</sub>Mg(CO<sub>3</sub>)<sub>2</sub>. Moreover, NaBaR(BO<sub>3</sub>)<sub>2</sub> lattice parameters appear to decrease with the decreasing of the radius of rare earth elements. A strong green emission centered at 540-550 nm under UV excitation was observed for synthesized NaBaTb(BO<sub>3</sub>)<sub>2</sub> showing promise as a new phosphor material.

#### 5. Acknowledgements

The authors would like to thank Dr. Kh. Abdullin for help with the luminescence analysis.

#### 6. References

- Ye N, Zhang Y, Chen W, Keszler DA, Aka G. Growth of nonlinear optical crystal Y<sub>0.57</sub>La<sub>0.72</sub>Sc<sub>2.71</sub>(BO<sub>3</sub>)<sub>4</sub>. *Journal of Crystal Growth*. 2006;292(2):464-467. DOI: <http://dx.doi.org/10.1016/j.jcrysgro.2006.04.055>
- Sasaki T, Mori Y, Yoshimura M, Yap YK, Kamimura T. Recent development of nonlinear optical borate crystals: key materials for generation of visible and UV light. *Materials Science and Engineering: R: Reports*. 2000;30(1-2):1-54. DOI: [http://dx.doi.org/10.1016/S0927-796X\(00\)00025-5](http://dx.doi.org/10.1016/S0927-796X(00)00025-5)
- Jubera V, Chaminade JP, Garcia A, Guillen F, Fouassier C. Luminescent properties of Eu<sup>3+</sup>-activated lithium rare earth borates and oxyborates. *Journal of Luminescence*. 2003;101(1-2):1-10. DOI: [http://dx.doi.org/10.1016/S0022-2313\(02\)00335-6](http://dx.doi.org/10.1016/S0022-2313(02)00335-6)
- Becker P. Borate materials in nonlinear optics. *Advanced Materials*. 1998;10(13):979-992. DOI: [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(199809\)10:13<979::AID-ADMA979>3.0.CO;2-N](http://dx.doi.org/10.1002/(SICI)1521-4095(199809)10:13<979::AID-ADMA979>3.0.CO;2-N)
- Lian Z, Sun J, Zhang L, Shen D, Shen G, Wang X, et al. Crystal structure refinement and luminescence properties of Ce<sup>3+</sup> singly doped and Ce<sup>3+</sup>/Mn<sup>2+</sup> co-doped KBaY(BO<sub>3</sub>)<sub>2</sub> for n-UV pumped white-light-emitting diodes. *RSC Advances*. 2013;3(37):16534-16541. DOI: <http://dx.doi.org/10.1039/c3ra42380h>
- Han L, Wang Y, Wang Y, Zhang J, Tao Y. Observation of efficient energy transfer from host to rare-earth ions in KBaY(BO<sub>3</sub>)<sub>2</sub>:Tb<sup>3+</sup> phosphor for plasma display panel. *Journal of Alloys and Compounds*. 2013;551:485-489. DOI: <http://dx.doi.org/10.1016/j.jallcom.2012.11.011>
- Seryotkin YV, Bakakin VV, Kokh AE, Kononova NG, Svetlyakova TN, Kokh KA, et al. Synthesis and crystal structure of new layered BaNaSc(BO<sub>3</sub>)<sub>2</sub> and BaNaY(BO<sub>3</sub>)<sub>2</sub> orthoborates. *Journal of Solid State Chemistry*. 2010;183(5):1200-1204. DOI: <http://dx.doi.org/10.1016/j.jssc.2010.03.005>
- Svetlyakova T, Kononova N, Kokh A, Urakaev F, Filatov S, Bubnova R, et al. Synthesis, growth and some physical properties of new orthoborates ScBaNa(BO<sub>3</sub>)<sub>2</sub> and YBaNa(BO<sub>3</sub>)<sub>2</sub>. *Journal of Crystal Growth*. 2011;318(1):954-957. DOI: <http://dx.doi.org/10.1016/j.jcrysgro.2010.10.017>
- Svetlyakova TN, Kokh AE, Kononova NG, Fedorov PP, Rashchenko SV, Maillard A. Search for compounds of the NaBaR(BO<sub>3</sub>)<sub>2</sub> family (R= La, Nd, Gd, and Yb) and the new NaBaYb(BO<sub>3</sub>)<sub>2</sub> orthoborate. *Crystallography Reports*. 2013;58(1):54-60. DOI: <http://dx.doi.org/10.1134/S1063774513010136>
- Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica. Section A Foundations and Advances*. 1976;A32(5):751-767. DOI: <http://dx.doi.org/10.1107/S0567739476001551>
- Miura H. CellCalc: A unit cell parameter refinement program on Windows computer. *Journal of the Crystallographic Society of Japan*. 2003;45(2):145-147. DOI: <http://dx.doi.org/10.5940/jcersj.45.145>
- Pabst A. Synthesis, properties, and structure of K<sub>2</sub>Ca(CO<sub>3</sub>)<sub>2</sub>, buetschliite. *American Mineralogist*. 1974;59:353-358.
- Kasprowicz D, Runka T, Jaroszewski K, Majchrowski A, Michalski E. Vibrational properties of nonlinear optical Bi<sub>2</sub>ZnOB<sub>2</sub>O<sub>6</sub> single crystals doped with Pr<sup>3+</sup>: μ-Raman investigations. *Journal of Alloys and Compounds*. 2014;610:600-605. DOI: <http://dx.doi.org/10.1016/j.jallcom.2014.05.071>

14. Borovikova EY, Dobretsova EA, Boldyrev KN, Kurazhkovskaya VS, Maltsev VV, Leonyuk NI. Vibrational spectra and factor group analysis of rare-earth chromium borates, RCr<sub>3</sub>(BO<sub>3</sub>)<sub>4</sub>, with R= La–Ho. *Vibrational Spectroscopy*. 2013;68:82-90. DOI: <http://dx.doi.org/10.1016/j.vibspec.2013.05.004>
15. Liu G, Jacquier B, eds. *Spectroscopic properties of rare earths in optical materials*. Berlin Heidelberg: Springer-Verlag; 2006.
16. Lian Z, Sun J, Ma Z, Zhang L, Shen D, Shen G, et al. Synthesis, crystal structure, characterization and luminescent properties of KBaTbB<sub>2</sub>O<sub>6</sub>. *Journal of Crystal Growth*. 2014;401:334-337. DOI: <http://dx.doi.org/10.1016/j.jcrysro.2013.11.007>
17. Blasse G, Grabmaier BC. Energy Transfer. In: Blasse G, Grabmaier BC. *Luminescent Materials*. Berlin Heidelberg: Springer-Verlag; 1994. p.91-107.