Synthesis of New Isostructural Orthoborates NaBaR(BO$_3$)$_2$ with R = Tb, Dy, Ho, Er, Tm and Lu

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Six new rare-earth orthoborates NaBaR(BO$_3$)$_2$, 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$_3$)$_2$, by R = Sc, Y, Yb. The structure of synthesized solid compounds is isotypic with the mineral eitelite, Na2Mg(CO$_3$)$_2$, crystallizing in the trigonal system with space group R3. 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$_3$)$_2$ have been investigated in a detail.

Keywords: rare-earth orthoborates, NaBaR(BO$_3$)$_2$, solid-state synthesis, Raman spectra, luminescence

1. Introduction

The rare-earth borates have potential applications for laser medium, luminescent and nonlinear optical materials$^{3,4}$. Many one- and two cation borates are currently used in photonics$^5$. A current area of research is for new materials for photonic diodes containing 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 photoluminescent white light emitting diodes$^6$ and as a green emitting phosphor for three-dimensional plasma panel$^6$. In our earlier study of solid phase formation in the system \( \text{MgCO}_3 - \text{B}_2\text{O}_3 \) we identified two new borates: NaBaSc(BO$_3$)$_2$ and NaBaY(BO$_3$)$_2$$^7$. Further investigation in this family resulted in the discovery of new ytterbium-bearing borate NaBaYb(BO$_3$)$_2$$. All discovered compounds of NaBaR(BO$_3$)$_2$ (R = Sc, Y, and Yb) line are isostructural and have eitelite-like, Na$_2$Mg(CO$_3$)$_2$, structure with space group R3.

In this study, we report the synthesis of new rare-earth orthoborates NaBaR(BO$_3$)$_2$ (analytical reagent) were purchased and used as starting reactants. Samples of regents 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$_2$BO$_3$ 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.

2. Material and Methods

2.1 Samples preparation and Synthesis

High purity chemicals of BaCO$_3$, Na$_2$CO$_3$, H$_2$BO$_3$, La$_2$O$_3$, Ce$_2$O$_3$, Nd$_2$O$_3$, Pr$_2$O$_3$, Eu$_2$O$_3$, Gd$_2$O$_3$, Tb$_2$O$_3$, Dy$_2$O$_3$, Ho$_2$O$_3$, Er$_2$O$_3$, Tm$_2$O$_3$, Lu$_2$O$_3$ were 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 20 ranging from 10° to 80° (CuKα radiation; \( \mu = 30–40 \text{ kV}; I = 25 \text{ mA}, \text{ speed meter} \) -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$_3$)$_2$ 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$^{3+}$ solid state reaction resulted in formation of CeBO$_3$, simple barate, while Nd$^{3+}$ produced Nd$_3$Ba$_2$(BO$_3$)$_3$ and NdNa$_2$(BO$_3$)$_3$ complex borates. Using La$^{3+}$, Pr$^{3+}$, Eu$^{3+}$ produced La$_3$Ba$_2$(BO$_3$)$_3$, Pr$_3$Ba$_2$(BO$_3$)$_3$, Eu$_3$Ba$_2$(BO$_3$)$_3$, respectively. These latter reactions did not result in a compound isostructural to previously obtained NaBaSc(BO$_3$)$_2$, probably because the ionic radii of cerium subgroup rare-earth elements are too large.

For Gd$^{3+}$ we observed intermediate products of reaction:

$$\text{Gd}^3+ + 2\text{BaO} + \text{Na}_2\text{O} + 2\text{B}_2\text{O}_3 = 2\text{NaBaBO}_3 + 2\text{GdBBO}_3$$ (1)

Figure 1 shows observed X-ray powder diffraction patterns of the new NaBaR(BO$_3$)$_2$ (R = Tb, Dy, Ho, Er, Tm and Lu) together with previously prepared orthoborates of NaBaYb(BO$_3$)$_2$ 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$_3$)$_2$ were calculated on the basis of the X-ray powder diffraction data using Cellcalc software 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$_3$)$_2$ decrease with the decreasing of the effective ionic radius of rare earth elements according to Shannon.

Using these cell parameters, it can be concluded that synthetic orthoborates are isostructural to NaBaSc(BO$_3$)$_2$, NaBaY(BO$_3$)$_2$, NaBaYb(BO$_3$)$_2$ crystallographic data of which have been fully described elsewhere. The main features of their crystal structure are anion–cation (Ba,Na)(BO$_3$)$_2$ layers, which are combined in the base building packages of two types: {R$^{3+}$[Ba$^{2+}$ (BO$_3$)$_3$]}$^+$ and {R$^{3+}$[Na$^{+}$ (BO$_3$)$_3$]}$^-$.

The fundamental building units of these orthoborates are RO$_3$ octahedra and BO$_3$ triangles. Furthermore, how it was determined in ref. the new compounds are isotopic to mineral eitelite, Na$_4$Mg(CO$_3$)$_2$ 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:

$$\text{R}_2\text{O}_3 + 2\text{BaO} + \text{Na}_2\text{O} + 2\text{B}_2\text{O}_3 = 2\text{NaBaBO}_3 + 2\text{RBO}_3$$ (2)

$$\text{NaBaBO}_3 + \text{RBO}_3 = \text{NaBaR(BO}_3)_2$$ (3)

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$_3$)$_2$ 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$_3$ group. It is well known that isolated BO$_3$ ion with D$_{3h}$ symmetry characterized by four fundamental modes of which three Raman-active v$'_1$ ($A'$) (~950 cm$^{-1}$), v$'_2$ ($E'$) (~1250-1400 cm$^{-1}$), v$'_3$ ($E''$) (~600 cm$^{-1}$) and one infrared active v$'_4$.

The peak at ~1200 cm$^{-1}$ in the Raman spectra of synthesized orthoborates are likely due to the asymmetric stretching mode v$'_4$($E''$) strong peaks at ~950 cm$^{-1}$ attributed to the

<table>
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<tr>
<th>№</th>
<th>R</th>
<th>Atomic number</th>
<th>R$^{3+}$ (coordination number - 6), Å</th>
<th>Max annealing temperature, °C</th>
<th>Determined or known compounds after X-ray research</th>
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<tr>
<td>1</td>
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<td>4</td>
<td>Ce</td>
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<td>11</td>
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Figure 1: X-ray powder diffraction patterns of the new NaBaR(BO\textsubscript{3})\textsubscript{2} orthoborates (R = Tb, Dy, Ho, Er, Tm and Lu) and NaBaYb(BO\textsubscript{3})\textsubscript{2} as a reference.

Figure 2: Raman spectra of the new NaBaR(BO\textsubscript{3})\textsubscript{2} (R = Tb, Dy, Y, Tm, Yb, Lu and Sc) at 633 nm excitation.

Figure 3: Raman spectra of the new NaBaR(BO\textsubscript{3})\textsubscript{2} (R = Ho and Er) at 785 nm excitation.

symmetric stretching modes v\textsuperscript{1}(A'\textsubscript{1}), while relatively high peak at ~600 cm\textsuperscript{-1} are from bending vibration mode of BO\textsubscript{3} group. Furthermore, the modes in the region of 420-125 cm\textsuperscript{-1} can be assigned to BO\textsubscript{3} translation and vibration\textsuperscript{14}.

### 3.2. Photoluminescence properties

Previous studies showed that rare-earth elements introduced into borate structure may present photoluminescence properties\textsuperscript{15}. Among synthesized NaBaR(BO\textsubscript{3})\textsubscript{2} borate family,
photoluminescence properties of as-prepared NaBaTb(BO$_3$)$_2$ have been investigated in this study, because Tb$^{3+}$ in host materials shows an intense characteristic green emission and relative suitable decay time, which can be used for PDP and LEDs$^{8,16}$.

Figure 4 shows the PLE and PL spectra of NaBaTb(BO$_3$)$_2$ 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$\rightarrow$ 5d transitions of Tb$^{3+}$. 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 $^3$D$_{4} \rightarrow ^7$F$_{J}$ ($J$=6, 5, 4, 3) transitions$^{15}$.

![Figure 4: The excitation and emission spectra of NaBaTb(BO$_3$)$_2$]([image]

The high level emission ($^3$D$_{4}$) is quenched by cross relaxation in favour of the $^3$D$_{4}$ emission due to high concentration of Tb$^{3+}$ in the compound$^{17}$. The estimated Tb-Tb distance (~5.36 Å) suggests that exchange interaction becomes ineffective and luminescence is predicted to become efficient$^{17}$, making the NaBaTb(BO$_3$)$_2$ compound a promising green-emitting phosphor material.

4. Conclusion

Six new rare-earth orthoborates belonging to NaBaR(BO$_3$)$_2$ 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 isomorphous to previously described orthoborates NaBaR(BO$_3$)$_2$ with $R$ = Sc, Y, Yb and fall within the trigonal system space group, and are isotypic with mineral eitelite, Na$_3$Mg(CO$_3$)$_2$. Moreover, NaBaR(BO$_3$)$_2$ 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$_3$)$_2$ showing promise as a new phosphor material.

5. Acknowledgements

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6. References


9. Svetlyakova TN, Kokh AE, Kononova NG, Fedorov PP, Rashchenko SV, Maillard A. Search for compounds of the NaBaR(BO$_3$)$_2$ family (R= La, Nd, Gd, and Yb) and the new NaBaYb(BO$_3$)$_2$ orthoborate. *Crystallization Reports*. 2013;58(1):54-60. DOI: http://dx.doi.org/10.1134/S1063774513010136


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