Synthesis, crystal structure, and thermal stability of double borate Na$_3$ErB$_2$O$_6$

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This article belongs to the regular issue.

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Abstract

Double borate Na$_3$ErB$_2$O$_6$ was synthesized by the solid-state reaction. The crystal structure of Na$_3$ErB$_2$O$_6$ was refined by the Rietveld method: $P2_1/c$, $a = 6.49775(14)$ Å, $b = 8.50424(17)$ Å, $c = 12.0067(3)$ Å, $\beta = 118.4797(9)^\circ$, $Z = 4$. The crystal structure of Na$_3$ErB$_2$O$_6$ consists of $\left[ErO_3\right]_n$ chains along the "b" axis, which are linked by BO$_3$ triangles in a three-dimensional framework. Sodium atoms occupy empty positions inside the channels. The thermal behavior of Na$_3$ErB$_2$O$_6$ was studied in detail in the range of 25–1150 °C range by DSC and TG methods. Na$_3$ErB$_2$O$_6$ congruently melts at 1116 °C. Based on the results of DSC measurements, three reversible phase transitions were found for Na$_3$ErB$_2$O$_6$.

Keywords

sodium rare-earth borate
solid-state reaction
crystal structure
Rietveld refinement
thermal analysis

1. Introduction

Borates are considered to be attractive functional materials for non-linear optic and luminescence due to their wide variety of crystal structures, low synthesis temperature, and environmental benignity [1–13]. Today commercially used nonlinear optical crystals of borates with superior optical properties are β-BaB$_2$O$_4$ [14] and LiB$_3$O$_5$ [15]. Recent studies of borates are related to birefringent materials [16] and self-frequency-doubling (SFD) laser ones [17]. SFD crystals belong to multi-functional materials and possess both laser and frequency doubling properties. The basic requirements for an efficient SFD laser crystal are excellent laser properties and excellent nonlinear optical properties with suitable birefringence. Therefore, SFD materials contained rare-earth elements and a nonlinear framework.

To search new SFD materials, the oxide systems based on alkaline, rare earth, and boron were extensively studied. Exploration of the Na$_2$O–R$_2$O–B$_2$O$_3$ systems revealed the existence of a number of double borates: Na$_2$Ru(BO$_3$)$_2$ [18–20], Na$_3$RB$_2$O$_6$ [21–23], Na$_3$ReB$_2$O$_6$ [21,24–26], Na$_3$Y$_2$B$_2$O$_6$ [27], Na$_3$Re$_2$B$_2$O$_6$ [28,29]. Our attention was attracted by double borates with the general formula Na$_3$RB$_2$O$_6$. This family of compounds includes borates with large lanthanides such as Na$_3$LaB$_2$O$_6$ [21], Na$_3$PrB$_2$O$_6$ [22], Na$_3$SmB$_2$O$_6$ [22], Na$_3$EuB$_2$O$_6$ [22], Na$_3$Yb$_2$O$_6$ [23] and Na$_3$GdB$_2$O$_6$ [23]. The subject of our study is the possibility of replacing large lanthanides with erbium. The crystal structure and thermal stability of double borate Na$_3$ErB$_2$O$_6$ was studied in the present work.

2. Experimental

The title compounds were prepared by solid state reactions using high purity starting reagents: Na$_2$CO$_3$ (99.8%, Sigma Aldrich Ltd.), Er$_2$O$_3$ (99.9%, Red Chemist, Ltd., Russia), and H$_3$BO$_3$ (99.5%, Sigma Aldrich Ltd.). Before weighing, Er$_2$O$_3$ had been preheated at 850 °C for 8 hours to remove absorbed water. The reagents were weighed on an analytical balance with an accuracy of ±0.1 mg. The mixtures of Na$_2$CO$_3$, Er$_2$O$_3$, and H$_3$BO$_3$ at molar ratio 3:1:2 were thoroughly ground in an agate mortar, slowly heated up to 300 °C, and were kept for 5 hours. Then the samples were reground and annealed at 600 °C for 5 hours and finally at 700 °C for 40 hours with intermediate grindings until equilibrium was reached. Temperature was measured with a Pt–PtRh thermocouple. The temperatures up to 1200 °C were controlled with an accuracy of ±2 °C with an OMRON instrument. The equilibrium was considered to be reached only when two successive heat treatments resulted in identical X-ray diffraction patterns.

Powder X-ray diffraction data were recorded by a D8 ADVANCE Bruker AXS diffractometer (Vantec-1 detector) at room temperature using Cu Kα radiation and scanning
from 2θ = 8° to 100° in increments of 0.02° and a counting time of 0.1 s/step. Phase purity was verified by powder X-ray diffraction (XRD) and the profile was compared to that reported for the isostructural phase Na2NdB2O6.

The TOPAS 4.2 [30] software suite was used to analyze the experimental data and to perform the Rietveld refinement of the obtained compound. All peaks in the X-ray powder diffraction pattern for Na2ErB2O6 were indexed satisfactorily in a monoclinic cell (space group P21/c).

Differential scanning calorimetry (DSC) and thermogravimetric (TG) measurements were performed on an STA 449 F1 Jupiter thermoanalyzer (NETZSCH) in the temperature range of 30–1150 °C in argon flow. Pt crucibles were used as vessels. Pt–PtRh thermocouples were used for temperature measurement. The precision of temperature measurement was ±1 °C. The heating and cooling rates were 10 °C/min.

### 3. Results and discussion

The synthesized sample of Na2ErB2O6 is pink powder, which is characteristic for the Er-containing oxides. The structure of Na2NdB2O6 was used as initial model for the Rietveld refinement to define the positions of atoms. They were refined by isotropic approximation with "soft" limitations of the B–O distance and the B–O–B bond angles. The refined parameters were added sequentially with the graphical simulation of the background in continuous. The Pearson VII function was used to describe the shape of peaks. The isotropic displacement parameters (Biso) for the Er and Na atoms were refined separately, while for the O and B atoms they were taken as equivalent. The refinement process included corrections for the sample preferred orientation and anisotropic broadening of peaks within the model of spherical harmonics.

The refinement was stable and gave low R-factors (Fig. 1, Table 1). Na2ErB2O6 was crystallized in the monoclinic system with the space group P21/c. The unit cell parameters are: a = 6.49775(14) Å, b = 8.50424(17) Å, c = 12.0067(3) Å, β = 118.4797(9)°, Z = 4. Coordinates of atoms are given in Table 2. Further details of the crystal structure may be obtained from supplementary material.

In the structure of Na2ErB2O6 (Fig. 2a), Er atoms are coordinated by seven O atoms in a distorted pentagonal bipyramid. The bipyramids share corners, forming a zigzag chain along the “b” direction, and the chain is reinforced by the B2O3 group, which uses all its three B–O bonds to join the neighboring bipyramids (Fig. 2a). Along with the “a” and “c” directions, these chains are connected via the B2O3 groups, thereby constructing a three-dimensional framework. Na1 and Na3 atoms are located in the interlayer channels and Na2 atom sits in the inlayer empty positions (Fig. 2b–d). Three Na atoms are coordinated by seven, six, and four O atoms, respectively.

The main bond lengths (Å) and angles (°) of Na2ErB2O6 are shown in Table 3.

![Figure 1](image.png)

**Fig. 1** XRD data for Na2ErB2O6 refined by the Rietveld analysis: measured (red points), calculated (black profile) and difference between experimental points and calculated profile (grey curve)

| Crystallographic data for Na2ErB2O6 phase at room temperature |
|---------------------------------------------------------------|
| Chemical formula      | Na2ErB2O6 |
| Space group           | P21/c (14) |
| Formula weight, g/mol | 353.9     |
| Unit cell dimensions, Å | a = 6.49775(14) b = 8.50424(17) c = 12.0067(3) β = 118.4797(9)° |
| Cell volume, Å³       | 583.18(2) |
| Z                     | 4        |
| Calculated density (g/cm³) | 4.183 |
| Rwp, %                | 2.671    |
| Rexp, %               | 3.534    |
| Rrel, %               | 1.572    |
| Bragg R-factor, %     | 1.864    |
| Xc                    | 2.249    |

| Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters of Na2ErB2O6 structure |
|---------------------------------------------------------------------------------------------------------------|
| x   | y   | z   | Biso/Å² |
|-----|-----|-----|---------|
| Er  | 0.0970(3) | 0.1261(1) | 0.3287(1) | 0.9(2) |
| Na1 | 0.380(2)  | 0.8039(8)  | 0.3841(7)  | 1.1(3) |
| Na2 | 0.058(2)  | 0.2963(8)  | 0.0802(8)  | 0.9(3) |
| Na3 | 0.331(2)  | 0.9488(8)  | 0.1134(7)  | 3.13(3) |
| B1  | 0.139(3)  | 0.4379(7)  | 0.3955(8)  | 1.0(6) |
| B2  | 0.351(1)  | 0.5864(8)  | 0.1209(5)  | 1.0(6) |
| O1  | 0.255(2)  | 0.334(1)   | 0.4714(9)  | 0.5(2) |
| O2  | 0.049(2)  | 0.373(2)   | 0.2513(7)  | 0.5(2) |
| O3  | 0.137(2)  | 0.600(1)   | 0.3911(9)  | 0.5(2) |
| O4  | 0.226(1)  | 0.674(1)   | 0.1611(5)  | 0.5(2) |
| O5  | 0.251(2)  | 0.505(1)   | 0.0086(7)  | 0.5(2) |
| O6  | 0.413(1)  | 0.080(1)   | 0.3075(5)  | 0.5(2) |
The DSC curves recorded for Na$_3$ErB$_2$O$_6$ are shown in Fig. 3. Four endothermic signals at 717, 907, 1014, and 1116 °C were detected during the sample's first heating, as shown in Fig. 3. The endothermic peak at 1116 °C corresponds to the melting point of Na$_3$ErB$_2$O$_6$. The X-ray diffraction measurements indicate the congruent melting of the borate (Fig. 4). To determine the nature of the endothermal effects at 717, 907, 1014 °C and prove congruent melting, the same sample was recorded in the “heating-cooling” mode over the temperature range of 100–1150 °C (with melting). At first cooling, Na$_3$ErB$_2$O$_6$ shows exothermic effects at 712, 831, 1000, 1098 °C. The second cooling reveals a new exothermic effect at 706 °C that seems to correspond to Na$_3$ErB$_2$O$_6$ partial decomposition, which is confirmed by X-ray analysis. The observed temperatures hystereses are about 5, 76, 14, 18 degrees. Thus, the signature observed at 600–1150 °C reveals the existence of reversible phase transitions (type I) in Na$_3$ErB$_2$O$_6$ and, respectively, additional experiments are needed to define the structure of the high-temperature modification of β, γ - Na$_3$ErB$_2$O$_6$.

Fig. 2 The crystal structure of Na$_3$RB$_2$O$_6$: a, b) ErO$_3$ chains, BO$_3$ triangles (a) and Na atoms (b) along a axis; b, c) a general view along b and c axes

Table 3 Main bond lengths (Å) and angles (°) of Na$_3$ErB$_2$O$_6$

| Bond       | Length (Å) | Angle (°) |
|------------|------------|-----------|
| Er–O1      | 2.33(1)    |           |
| Er–O2      | 2.36(1)    |           |
| Er–O3      | 2.26(2)    |           |
| Er–O4      | 2.34(2)    |           |
| Er–O5      | 2.20(1)    |           |
| Er–O6      | 2.22(1)    |           |
| Na1–O1     | 2.50(1)    |           |
| Na1–O2     | 2.53(1)    |           |
| Na1–O3     | 2.38(1)    |           |
| Na1–O4     | 2.61(1)    |           |
| Na1–O5     | 2.72(1)    |           |
| Na1–O6     | 2.56(1)    |           |
| Na2–O1     | 2.48(1)    |           |
| Na2–O2     | 2.18(1)    |           |
| Na2–O3     | 2.22(1)    |           |
| Na2–O4     | 2.60(1)    |           |

Symmetry codes: (i) –x, y+1/2, –z+1/2; (ii) x, –y+1/2, z+1/2; (iii) –x+1, y+1, –z+1; (iv) –x, y+1/2, –z+1/2; (v) –x+1, y+1/2, –z+1/2; (vi) x, –y+3/2, z+1/2; (vii) x, y+1, z; (viii) x, –y+1/2, z–1/2; (ix) –x, –y+1, z; (x) x, –y+3/2, z–1/2.
It should be pointed out that the transition was not found in Na$_3$RB$_2$O$_6$ (R = Pr, Sm, Eu) [22]. Respectively, it can be reasonably assumed that the appearance of the phase transitions is observed only for the Na$_3$RB$_2$O$_6$ borates where rare earth elements have small ionic radius.

An X-ray examination of solid-state interactions between the components of the Na$_2$O–Er$_2$O$_3$–B$_2$O$_3$ system resulted in finding double borate Na$_3$ErB$_2$O$_6$. Na$_3$ErB$_2$O$_6$ was synthesized by solid-state reaction. The crystal structure of Na$_3$ErB$_2$O$_6$ was refined by the Rietveld analysis. Na$_3$ErB$_2$O$_6$ consists of ErO$_6$ distorted pentagonal bipyramids and B$_2$O$_4$ groups. Na$_3$ErB$_2$O$_6$ congruently melts at 1116 °C. The DSC and TG experiments assume that after melting Na$_3$ErB$_2$O$_6$ decomposes with formation of Er$_2$O$_3$. The observed endothermic effects on the DSC curve are assumed to be attributed to high-temperature phase transitions of the title compound. This assumption prompts us to thoroughly investigate this family of compounds in the future.

**Conclusions**

An X-ray examination of solid-state interactions between the components of the Na$_2$O–Er$_2$O$_3$–B$_2$O$_3$ system resulted in finding the double borate, Na$_3$ErB$_2$O$_6$. Na$_3$ErB$_2$O$_6$ was synthesized by solid-state reactions. The crystal structure of Na$_3$ErB$_2$O$_6$ was refined by the Rietveld analysis. Na$_3$ErB$_2$O$_6$ consists of ErO$_6$ distorted pentagonal bipyramids and B$_2$O$_4$ groups. Na$_3$ErB$_2$O$_6$ congruently melts at 1116 °C. The DSC and TG experiments demonstrated that after melting Na$_3$ErB$_2$O$_6$ decomposes with formation of Er$_2$O$_3$. The observed endothermic effects on the DSC curve are assumed to be attributed to high-temperature phase transitions of the title compound. This assumption prompts us to thoroughly investigate this family of compounds in the future.

**Acknowledgments**

The work was supported by Basic Project of BINM SB RAS № 0273-2021-0008. X-ray powder diffraction and thermal analysis were obtained using the equipment of the Collective Use Center BINM SB RAS.

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