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Intermediate compounds in $\text{SrB}_2\text{O}_4 - \text{SrREE}_2\text{O}_4$

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Abstract

Strontium rare earth borates, $\text{Sr}_3\text{REE}_2(\text{BO}_3)_4$ (REE = Nd, Sm, Eu, Gd, Y and Yb), were synthesized as single phase powders starting from the respective oxides in the temperature range of 1000 °C and 1200 °C. These isostructural phases crystallise in the space group Pnma. The vibrational spectre confirms the presence of planar trigonal coordinated borates. Lattice parameters are refined by Pawley method.

Keywords: rare earth elements, Borates, PXRD, FTIR

1. Introduction

Borates were in the research focus for a long time due to their numerous crystal structures, wide transmittance spectra and wide band gaps. For example, Eu^{3+} doped $\text{Sr}_3\text{Y}_2(\text{BO}_3)_4$ was found to be a promising red vacuum ultraviolet (VUV) phosphor for plasma display panels (PDPs) (He and Wang 2007, Han et al. 2013). In the search of new optical functional materials, a systematic survey on the $\text{SrO-Dy}_2\text{O}_3\text{-B}_2\text{O}_3$ system was performed. An intermediate monophasic compound with the confirmation of borate $\text{Sr}_3\text{Dy}_2(\text{BO}_3)_4$ was synthesized successfully. Six other isostructural compounds $\text{Sr}_3\text{REE}_2(\text{BO}_3)_4$ (REE = Nd, Sm, Eu, Gd, Y and Yb) were synthesized using solid state synthesis methods.

2. Experimental

2.1 Synthesis

Powder samples were synthesized by a standard solid-state reaction. Analytical grade $\text{Sr}(\text{NO}_3)_2$, H_3BO_3 , $\text{La}(\text{OH})_3$, Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Dy_2O_3 , Y_2O_3 and Yb_2O_3 were used as starting materials. A stoichiometric mixture of the starting materials was finely ground in an agate mortar. The homogenised mixture was preheated in corundum crucibles at $600\text{ }^\circ\text{C}$ for 2 h to decompose H_3BO_3 and $\text{Sr}(\text{NO}_3)_2$, and then cooled to room temperature. Subsequently, it was reground and sintered in the temperature range from $1000\text{ }^\circ\text{C}$ to $1200\text{ }^\circ\text{C}$. The total sinter time varied from 10 h to 24 h.

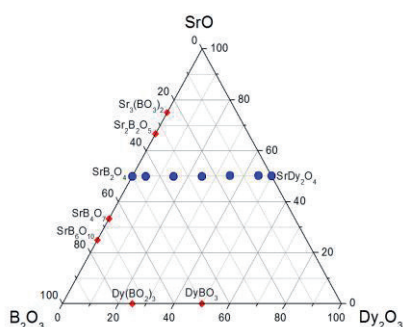


Fig. 1: ternary diagram of $\text{SrO-Dy}_2\text{O}_3\text{-B}_2\text{O}_3$

2.2 Characterization

X-ray powder diffraction (XRD) patterns were collected at room temperature between 10 and $70\text{ }^\circ 2\theta$ using a PANalytical X'pert³ Powder diffractometer equipped with an X'Celerator RTMS detector in Bragg-Brentano-geometry using $\text{Cu-K}\alpha$ -radiation at 45 kV and 40 mA . Silicon was used as internal standard at a level of 10% by mass. All phases were refined using HighScore Plus 4.7.0 software from PANalytical. Structural images were obtained using VESTA 4.3.0 and published atomic coordinates. SEM images were collected using a scanning electron microscope JSM 6300 (JOEL). Infrared spectra were recorded with a Bruker Tensor II infrared spectrophotometer in the wavenumber range from 400 to 2000 cm^{-1} .

3. Results and discussions

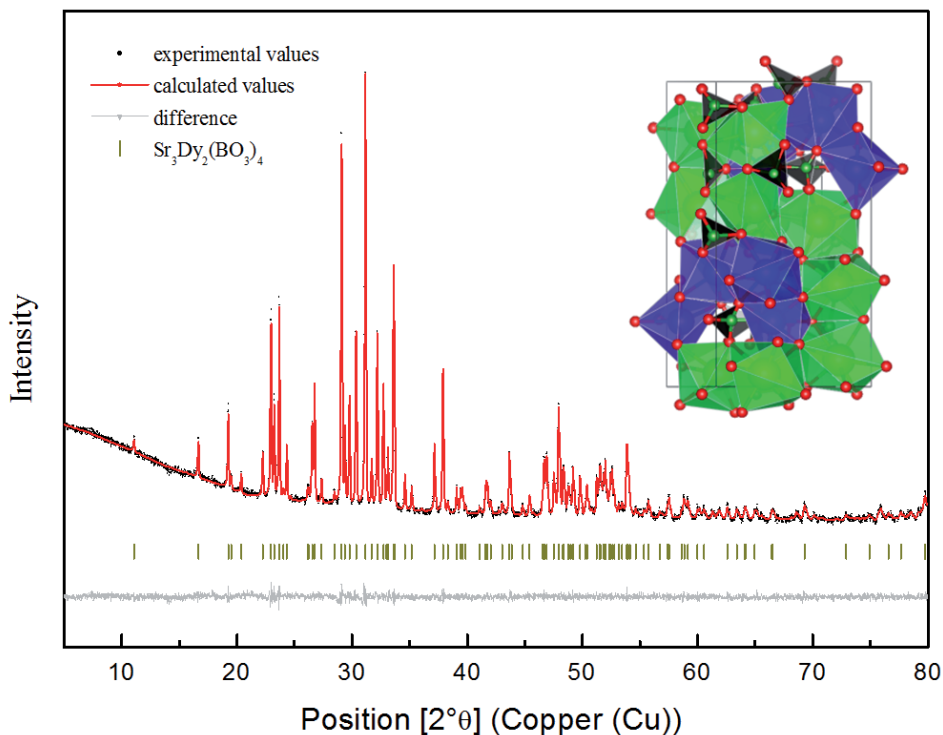
3.1 $\text{SrDy}_x\text{B}_{2-x}\text{O}_4$ ($0 \leq x \leq 2$) system

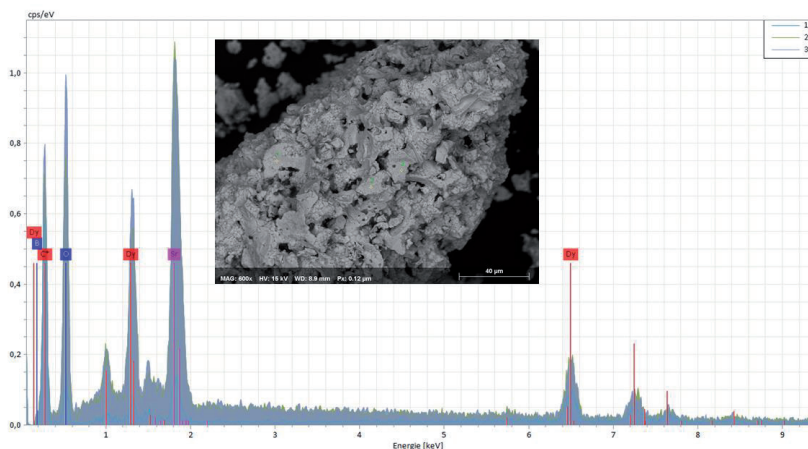
In table 1 the weighted initial calculated composition and the resulting phases are listed. These mixtures are indicated as blue dots in the ternary diagram of $\text{SrO-Dy}_2\text{O}_3\text{-B}_2\text{O}_3$ (Fig. 1).

Table 1. Calculated composition and resulting phases

	weighted initial substances [mol %]	Column B
a	0.5 SrO · 0.5 B ₂ O ₃	SrB ₂ O ₄
b	0.5 SrO · 0.05 Dy ₂ O ₃ · 0.45 B ₂ O ₃	SrB ₂ O ₄ ; Sr ₃ Dy ₂ (BO ₃) ₄
c	0.5 SrO · 0.15 Dy ₂ O ₃ · 0.35 B ₂ O ₃	Sr ₃ Dy ₂ (BO ₃) ₄ ; SrB ₂ O ₄ (6 %)
d	0.5 SrO · 0.25 Dy ₂ O ₃ · 0.25 B ₂ O ₃	Sr ₃ Dy(BO ₃) ₃ ; Dy ₂ O ₃
e	0.5 SrO · 0.35 Dy ₂ O ₃ · 0.15 B ₂ O ₃	Sr ₃ (BO ₃) ₂ ; Dy ₂ O ₃
f	0.5 SrO · 0.45 Dy ₂ O ₃ · 0.05 B ₂ O ₃	SrDy ₂ O ₄ ; Sr ₃ (BO ₃) ₂ ; Dy ₂ O ₃
g	0.5 SrO · 0.5 Dy ₂ O ₃	SrDy ₂ O ₄

The compound SrB₂O₄ belongs to the orthorhombic space group Pbcn, the compound SrDy₂O₄ to the orthorhombic space group Pnam. The mixture c (Table 1) contained mostly Sr₃Dy₂(BO₃)₄ and 6% of SrB₂O₄ (Rietveld analysis). By adjusting the weighted initial composition to 0,5 SrO · 0,17 Dy₂O₃ · 0,33 B₂O₃ the intermediate phase Sr₃Dy₂(BO₃)₄ is obtained at 1075 °C through standard solid state reaction. The powder diffraction file (PDF – 4 + 2011) was used for phase analysis of the sample. Its crystal structure is shown in Figure 2 along with the XRD pattern (Pnma), which consists of distorted SrO₈ polyhedra, distorted DyO₇ polyhedra and four BO₃ planar triangles. The lattice parameters were refined by Pawley method ($a_0 = 7.401 \text{ \AA}$, $b_0 = 15.97 \text{ \AA}$ and $c_0 = 8.710 \text{ \AA}$).

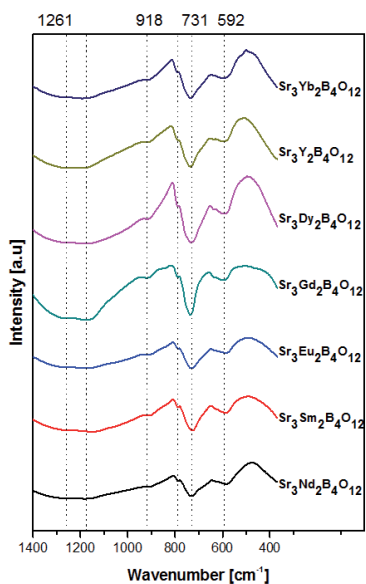
Fig. 2: XRD patterns of Sr₃Dy₂(BO₃)₄ and its crystal structure

Fig. 3: EDX analysis of $\text{Sr}_3\text{Dy}_2(\text{BO}_3)_4$

The atomic ratio of Sr, Sm and Dy, measured at three points was about 2.8:1.8:4.3 (near to 3: 2: 4), determined by EDX (Fig. 3).

3.2 $\text{Sr}_3\text{REE}_2(\text{BO}_3)_4$ ($\text{REE} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Y}, \text{Yb}$)

To study the influence of ionic radii of rare earth elements, Dy is substituted by other rare earth elements: Nd, Sm, Eu, Gd, Dy, Y and Yb. As a result the following 6 compounds were synthesized monophasically: $\text{Sr}_3\text{Nd}_2(\text{BO}_3)_4$, $\text{Sr}_3\text{Sm}_2(\text{BO}_3)_4$, $\text{Sr}_3\text{Eu}_2(\text{BO}_3)_4$, $\text{Sr}_3\text{Gd}_2(\text{BO}_3)_4$, $\text{Sr}_3\text{Y}_2(\text{BO}_3)_4$ and $\text{Sr}_3\text{Yb}_2(\text{BO}_3)_4$. These compounds are isotypic to $\text{Sr}_3\text{Dy}_2(\text{BO}_3)_4$ and crystallize in orthorhombic crystal structure.

Fig. 4: FTIR spectrum of $\text{Sr}_3\text{REE}_2(\text{BO}_3)_4$ ($\text{REE} = \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Dy}, \text{Y}$ and Yb)

To confirm the coordination surroundings of B - O in the synthesized compounds, FTIR investigation was performed (Fig 4). The bands at 592 cm^{-1} (ν_4), 731 cm^{-1} (ν_2), 787 cm^{-1} (ν_2) and 918 cm^{-1} (ν_1) correspond to vibration of BO_3^{3-} ions. Two broad peaks about 1261 cm^{-1} and 1185 cm^{-1} are due to the stretching vibration of the triangular BO_3 group (Weir and Schroeder 1964). Based on presence of these characteristic frequencies of BO_3^{3-} , it is shown that in the crystal structure of the synthesized borates, the boron atoms are trigonally coordinated by oxygen atoms.

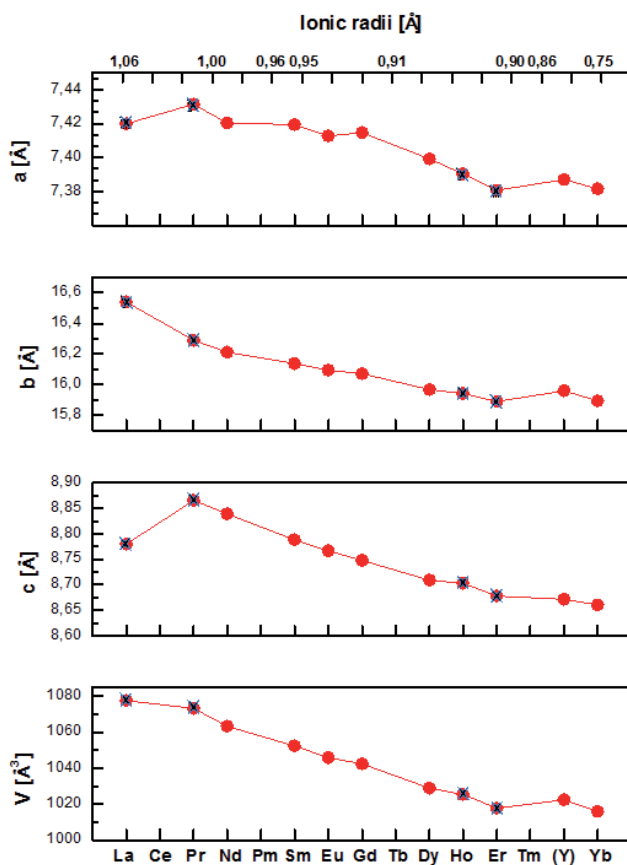


Fig. 5. Lattice parameters of $\text{Sr}_3\text{REE}_2(\text{BO}_3)_4$ versus the trivalent ionic radius of REE (REE = La – Yb), values marked with x are from lit. (Abdullaev et al., 1973; Hamaganova et al., 1990; Mill et al., 1998; Hoppe et al., 2013)

Unit cell refinements from the powder diffraction using the Pawley method are summarized in figure 5 and table 2: Unit cell dimension decreases with decreasing ionic radii of incorporated rare earth element. The cell volume decreases from 1063.259 Å^3 ($\text{Sr}_3\text{Nd}_2(\text{BO}_3)_4$) to 1015.997 Å^3 ($\text{Sr}_3\text{Yb}_2(\text{BO}_3)_4$).

Table 2. Unit cell parameters and unit cell volumes

Compound	a (Å)	b (Å)	c (Å)	Volume (Å ³)
Sr ₃ Nd ₂ (BO ₃) ₄	7,4203(5)	16,2107(9)	8,8391(5)	1063,25(9)
Sr ₃ Sm ₂ (BO ₃) ₄	7,4194(3)	16,1378(3)	8,7880(9)	1052,23(0)
Sr ₃ Eu ₂ (BO ₃) ₄	7,4128(2)	16,0938(1)	8,7662(2)	1045,81(4)
Sr ₃ Gd ₂ (BO ₃) ₄	7,4147(0)	16,0707(3)	8,7479(2)	1042,39(9)
Sr ₃ Dy ₂ (BO ₃) ₄	7,3992(6)	15,9668(1)	8,7090(2)	1028,90(8)
Sr ₃ Y ₂ (BO ₃) ₄	7,3871(0)	15,9606(5)	8,6713(5)	1022,37(8)
Sr ₃ Yb ₂ (BO ₃) ₄	7,3815(7)	15,8932(2)	8,6602(6)	1015,99(7)

4. Conclusion

Monophasic Sr₃Dy₂(BO₃)₄ powder was synthesized through the standard solid state reaction. Its crystal structure was investigated from powder X-ray diffraction data. The structure is orthorhombic, with space group Pnma and cell parameters $a_0 = 7.401 \text{ \AA}$, $b_0 = 15.97 \text{ \AA}$ and $c_0 = 8.710 \text{ \AA}$.

Six other isostructural compounds Sr₃REE₂(BO₃)₄ (REE = Nd, Sm, Eu, Gd, Y and Yb) could also be synthesized successfully. IR Investigation confirms that the boron atoms are trigonally coordinated by oxygen atoms. The unit cells were refined by Pawley method, the increase of unit cell volume is in accordance with the ionic radii of REE, incorporated in borates.

Literature on the structure of Sr₃REE₂(BO₃)₄ is still limited. Though authors agree on the orthorhombic structure, there is still disagreement on the space group. The presented compounds Sr₃REE₂(BO₃)₄ (REE = Nd, Sm, Eu, Gd, Y and Yb) have the space group Pnma. To see if there is transformation to Pna2₁ at different temperatures further studies, e.g. with in-situ XRD, are planned.

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