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Growth of a new strontium borate crystal $Sr_4B_{14}O_{25}$

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Abstract

The doping of SrB_4O_7 by lanthanide ions is discussed. The phase diagram $SrO–B_2O_3$ from 50 to 75 mol% B_2O_3 concentrations was investigated. New $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystals were grown by the TSSG method. The transmissions spectra of the $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} were measured.

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Keywords: A1. Doping; A1. Phase diagrams; A2. Single crystal growth; B1. Borates

1. Introduction

The strontium borates SrB_4O_7 and SrB_6O_{10} have attracted much attention over the last years. SrB_4O_7 and SrB_6O_{10} are very suitable host lattices for luminescence of lanthanide ions. It was reported that Eu^{3+}, Sm^{3+}, Yb^{3+} and Tm^{3+} could be reduced to the corresponding divalent lanthanide ions in SrB_4O_7 by solid-state reaction at high temperature in air [1]. Phosphors SrB_4O_7:RE^{2+} show efficient luminescence at room temperature [2,3]. SrB_4O_7:Sm^{2+} is an interesting alternative to ruby for accurate optical high-pressure measurements [4]. The doped lanthanide ions SrB_4O_7 crystals are very promising as an active laser material. The weak thermal extinguishing only for SrB_4O_7 and SrB_6O_{10} from rare-earth Eu doped borates is observed at 300 K [5]. The SrB_4O_7:Sm^{2+} crystal was grown with the molar ratio Sm_2O_3/$SrO = 0.0012$ in the melt [6]. Whereas SrB_4O_7:RE could not be being grown with a higher doped concentration.

In the present paper, the possibility of growing highly lanthanide-doped SrB_4O_7 crystals is considered. The phase diagram $SrO–B_2O_3$ from 50 to 75 mol% B_2O_3 concentrations was investigated. New strontium borate $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} has been grown. The transmission spectra of new crystals are represented.

2. Experiment

2.1. Doping of SrB_4O_7 by lanthanide ions

Powder samples of SrB_4O_7 doped with lanthanide ions Pr^{3+} or Eu^{3+} were prepared by

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solid-state reactions in air as in Refs. [1,6,7]. Stoichiometric amounts of $SrCO_3$ (99.9%), H_3BO_3 (99.9%) including 2 mol% excess of H_3BO_3 to compensate for B_2O_3 evaporation, were mixed and ground. The molar ratio of RE_2O_3/SrO were varied from 0 to 0.01. The mixtures were heated in air at 700°C in platinum crucible for 5 h and then ground and heated at 900°C for another 5 h. The crystal structure of the obtained samples was checked by X-ray powder diffraction. All samples appeared to be single phase and crystallizes in the orthorhombic space group $Pnm2_1$ as the SrB_4O_7 crystals.

Powder samples of SrB_4O_7:RE were melted and then homogenized in air at 1030–1050°C for 5 h. After that the melt was cooled and the spontaneous crystallization of the melt was observed.

Polycrystalline samples of $SrB_4O_7:Pr^{3+}$ or $SrB_4O_7:Eu^{3+}$ were obtained for the molar ratio $Pr_2O_3/SrO<0.002$ or $Eu_2O_3/SrO<0.004$ of lanthanide dopants in the melt, respectively. In contrast to solid-state reactions, new strontium borate crystals in the molar ratio $Pr_2O_3/SrO>0.002$ or $Eu_2O_3/SrO>0.004$ of lanthanide dopants in the melt were obtained by spontaneous crystallization of the melt. The exact composition of the new strontium borate $Sr_4B_{14}O_{25}$:RE crystals was determined by X-ray investigation of the crystal compound and was confirmed by the precision chemical analysis.

2.2. Phase diagram of the $SrO–B_2O_3$ system

Some details of the $SrO–B_2O_3$ systems were first determined by Witzmann and Benlich [8] and Guertler [9]. They found that the crystallization temperature was 930°C [8] or 994 ± 10°C [9] for SrB_4O_7, and 1100°C [8], or 1155 ± 10°C [9] for SrB_2O_4, the eutectic temperature $SrB_4O_7–SrB_2O_4$ was 890°C [8] or 971 ± 20°C [9]. In our earlier work, crystallization temperature of SrB_4O_7 was 970°C [10]. The date difference may be explained by the high viscosity of the melt with high contents of B_2O_3.

Compositions from 50 to 75 mol% B_2O_3 were investigated. The phase diagram of the $SrO–B_2O_3$ system resulting from the combined analysis of X-ray powder diffraction and differential thermal analysis techniques is shown in Fig. 1. It was determined that the melting temperature of SrB_2O_4 was 1170 ± 5°C, the temperature of the incongruent melting of $Sr_4B_{14}O_{25}$ 1012 ± 5°C and melting temperature of SrB_4O_7 1015 ± 5°C. The melting point of SrB_6O_{10} was determined at 920 ± 5°C. Endothermic peak was observed at 730–780°C for concentration of the B_2O_3 from 50 to 60 mol% and presumably corresponds to phase transition of the metastable phase of SrB_2O_4 in the orthorhombic phase [11].

It was found, that the powder samples of $Sr_4B_{14}O_{25}$ could not be prepared by solid-state reaction. Stoichiometric mixture of $4SrO:7B_2O_3$ prepared by solid-state reactions was heated at 1000°C for 5 h. Sample was checked by X-ray powder diffraction and found that the ceramics contains the mixture of SrB_2O_4 and SrB_4O_7 only. Thus the $Sr_4B_{14}O_{25}$ crystal is the high-temperature compound, but we could not determine any features of the phase diagram in this region. Only some points for concentration less than 62 mol% B_2O_3 lies below $Sr_4B_{14}O_{25}$ melting temperature. It was determined that the undoped $Sr_4B_{14}O_{25}$

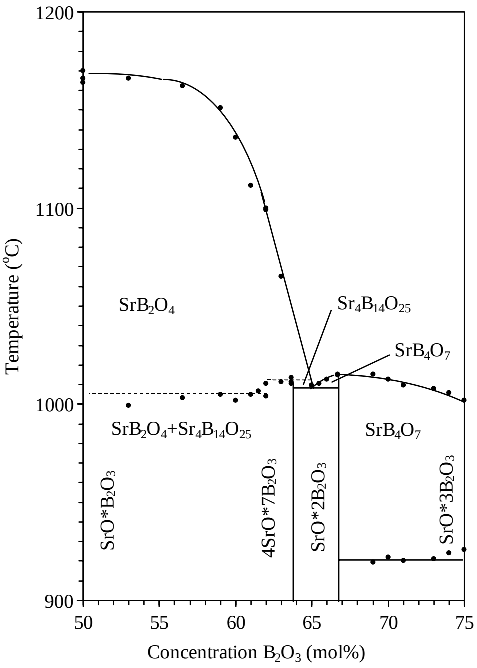

Fig. 1. Phase diagram of $SrO–B_2O_3$ system.

crystals might be obtained by crystallization from the melt with 64–65 mol% B_2O_3 concentrations. We determined that the doped strontium borate $Sr_4B_{14}O_{25}Pr^{3+}$ crystallizes from the melt SrO–$2B_2O_3$–xPr_2O_3 for $0.002<x<0.01$. Crystallization of the $Sr_4B_{14}O_{25}$:Pr^{3+} for higher concentration of Pr_2O_3 was not investigated.

2.3. X-ray powder diffraction

The powder X-ray diffractograph of $Sr_4B_{14}O_{25}$:Pr^{3+} was obtained by using HZG 4A diffractometer with Cu K_α radiation. The obtained d values, Miller index and the corresponding intensities of the peaks are represented in Table 1. It was found that the $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystals relate to the monoclinic system. The values of the crystal lattice parameters are $a = 16.384(4)$ Å, $b = 7.762(2)$ Å, $c = 16.619(4)$ Å, $\beta = 119.8(2)°$.

The density of $Sr_4B_{14}O_{25}$ is 3.20 g/cm^3, as determined by the buoyancy method. From the lattice parameter, the calculated density of $Sr_4B_{14}O_{25}$ crystal is 3.246 g/cm^3.

The habit of $Sr_4B_{14}O_{25}$ crystals obtained by spontaneous crystallization from the melt is represented in Fig. 2. Single crystals with sizes up to $7\times15\times0.5\,\text{mm}^3$ have the plate-like form extended along the Y-axis.

3. Crystal growth

Strontium borate $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystals are grown from 0.35 SrO–0.65 B_2O_3 and SrO–$2B_2O_3$–$0.0087Pr_2O_3$ melts, respectively . The started materials were obtained by solid-state synthesis, as described above. The $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystals were grown by the TSSG method with crystal being pulled in a resistance furnace in a platinum crucible of 90 cm^3 volume. The temperature gradient in the thin top layer of the melt's surface was 80–100°C/cm. A test-seeded technique was employed to measure the saturation point of the solution. The crystals were grown with a seed orientation normal to the (0 2 0) or (0 0 2) faces. The seed was set to the thermal center of the flux surface at 1020–1025°C. The melt temperature was rapidly reduced to the crystallizing temperature, and after that the cooling rate was 2–4°C/day. The pooling rate was 2–3 mm/day. The obtained crystals were 20–25 mm in diameter and about 10 mm in length (Fig. 3). When the growth was finished, the crystal was pulled out of the liquid surface, and cooled to room temperature at a cooling rate of 20°C/h.

Table 1
X-ray powder diffraction date of $Sr_4B_{14}O_{25}$

$h\,k\,l$	d_{exp} (Å)	$d_{\text{calñ}}$ (Å)	I_{exp} (%)
0 0 2	7.243	7.2549	100
1 1 0	6.8098	6.8223	7
2 0 1	5.4469	5.4478	2
0 0 3	4.8336	4.8366	2
−1 1 3	4.4647	4.4659	6
−3 1 1	4.4163	4.4178	6
3 1 0	4.0681	4.0628	5
−3 1 3	4.0461	4.0473	3
−4 0 1	3.9519	3.9482	1
0 2 0	3.8787	3.881	0.5
0 0 4	3.6261	3.6274	5
1 1 3	3.5716	3.5731	16
−3 1 4	3.527	3.5311	23
0 2 2	3.4204	3.4221	19
−2 2 3	3.1532	3.1544	17
3 1 2	3.0457	3.0461	4
−5 1 3	3.0006	3.0008	10
1 1 4	2.9323	2.9326	22
−1 1 5	2.9257	2.9268	11
−5 1 1	2.8843	2.8863	9
−5 1 4	2.8752	2.877	4
2 2 2	2.8431	2.8429	4
−2 2 4	2.8361	2.8357	3
−4 2 1	2.766	2.7677	1
−6 0 2	2.6869	2.6865	3
−5 1 5	2.6721	2.6719	1
0 2 4	2.6483	2.6501	4
−6 0 1	2.5602	2.5608	1
−6 0 5	2.5496	2.5504	3
−2 2 5	2.5178	2.5181	1
−1 1 6	2.4676	2.4671	16
−4 2 5	2.4289	2.4298	1
0 0 6	2.4175	2.4183	8
6 0 0	2.3835	2.3841	1
−6 0 6	2.372	2.3715	2
−4 0 7	2.36	2.361	1
1 3 2	2.3376	2.3397	2
−3 3 1	2.33	2.3311	3
−3 3 2	2.3289	2.3301	4
2 0 5	2.3237	2.3232	2

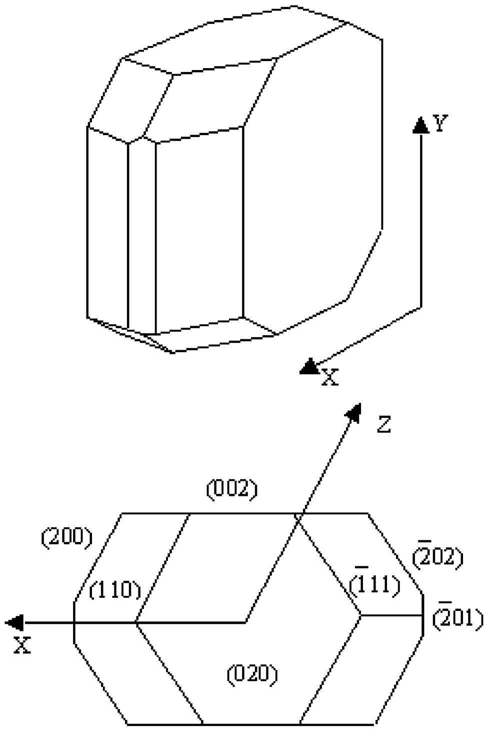

Fig. 2. Habits of the $Sr_4B_{14}O_{25}$ crystals.

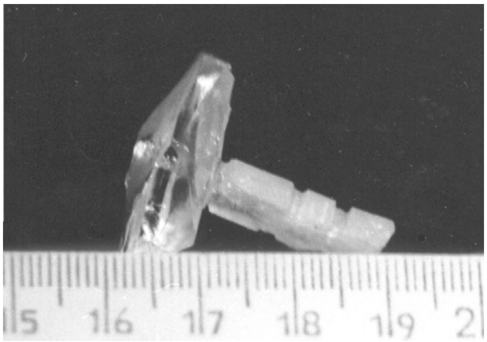

Fig. 3. The $Sr_4B_{14}O_{25}$ crystal.

The crystals have a cylindrical form with partial faces by (0 0 2) and (2 0 0) faces and are nonhygroscopic.

The color of the doped $Sr_4B_{14}O_{25}$:Pr^{3+} crystals is weak yellow-green. The praseodymium doping concentration and distribution in a crystal were measured by an X-ray microprobe Comeka-Comebax analyzer. An inhomogeneous distribution of impurity was detected. The concentration of Pr impurity was detected to be between 0.011 and 0.45 at% with an average grab factor of impurity 0.33.

4. Transmittance spectra measurement

The $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystals were cut and polished, a 5 mm thick sample without antireflection coating was obtained for optical transmittance measurements in the [1 0 0] direction. The transmittance spectrum was recorded by a Shimadzu UV 3101 PC spectrophotometer at room temperature in the range 190–3200 nm and by a Specord 40 spectrophotometer in the range 3000–4000 nm. The spectra are shown in Fig. 4. The UV absorption edge of $Sr_4B_{14}O_{25}$ was determined to be less than 190 nm as soon as the UV cut-off of $Sr_4B_{14}O_{25}$:Pr^{3+} was determined to be at 227 nm.

The IR absorption edge of $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}$:Pr^{3+} crystal lies at wavelength of 3500 nm. Wavelength shifts of the UV absorption edge of the doped crystals may be explained by 4f–5d electron transition of Pr^{3+} ions because the crystal structure of the samples does not change by small doping concentrations.

The weak absorption lines have been measured in the spectral range of $\lambda = 400-500$, 570–590, 995–1015, 1495–1515, 1900–1920, 2510–2530 nm.

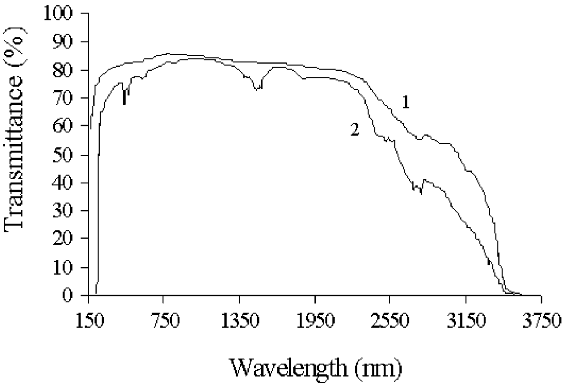

Fig. 4. The transmittance spectra of $Sr_4B_{14}O_{25}$ (1) and $Sr_4B_{14}O_{25}$:Pr^{3+}(2) crystals.

These lines relate to the electronic transitions of the Pr^{3+} ions.

5. Conclusion

New strontium borate $Sr_4B_{14}O_{25}$:RE crystals with the molar ratio $Pr_2O_3/SrO > 0.002$ or $Eu_2O_3/SrO > 0.004$ of lanthanide dopants in the SrO–$2B_2O_3$–$x$$RE_2O_3$ melts were obtained, in contrast to the formation of SrB_4O_7:RE by solid-state reactions.

New strontium borate crystals $Sr_4B_{14}O_{25}$ and $Sr_4B_{14}O_{25}:Pr^{3+}$ relate to the monoclinic system. The values of the crystal lattice parameters are $a = 16.384(4)\,\text{Å}$, $b = 7.762(2)\,\text{Å}$, $c = 16.619(4)\,\text{Å}$, $\beta = 119.8(2)^\circ$.

$Sr_4B_{14}O_{25}$ which melts at $1012 \pm 5^\circ C$ occurs in a relatively small range of compositions (from 64 to 65 mol% B_2O_3). Crystal growth was performed in air by spontaneous nucleation or by top-seeded solution growth method. Crystals with sizes of up to 20–25 mm in diameter and about 10 mm in length were obtained. The dopant $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal was grown from SrO–$2B_2O_3$–$0.0087Pr_2O_3$ melt also.

The measured range of transparency was from less than 190 to 3500 nm for $Sr_4B_{14}O_{25}$ crystals and from 227 to 3500 nm for $SrB_4O_7:Pr^{3+}$ crystal.

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