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Crystallization and Structural Characteristics of New Borosilicates

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Crystals of stillwellite-like lanthanum borosilicate were obtained from high-temperature solutions. Lithium and potassium di- and trimolybdates were used as fluxes for silicate systems. In the case of borosilicate crystals, the choice of fluxes was based on the potassium trimolybdate with an excess of potassium fluoride. The composition of grown crystals was studied by electron microprobe analysis, and structural characteristics were determined for the $La_3BSi_2O_{10}$. It crystallizes in the orthorhombic system, space group *Pbca*, with cell dimensions $a = 9.977(2)$, $b = 7.269(2)$, $c = 23.410(2)$ Å, $V = 1697.8(6)$ Å^3, and final agreement factors $R = 0.059$, $R_w = 0.089$. © 2000 Academic Press

Key Words: **silicates; borosilicates; crystallization; structure refinement.**

1. INTRODUCTION

Borosilicates LnBSiO$_5$ (Ln = La and Nd) of a new ferroelectric family belong to stillwellite-type structure. These materials have nonlinear optical and piezoelectric potentialities (1). Neodymium doped stillwellite crystals can be considered as a new laser medium. First, La-stillwellite (up to 0.2–0.3 mm size) has been prepared by solid-state reactions and under hydrothermal condition (2). Then it has been obtained by flux method (up to 1–2 mm size) (3). Recently, its neodymium analog has also been synthesized (4). However, there is little known on phase formation in the Ln_2O_3–B_2O_3–SiO_2 systems. The authors of the present work have studied lanthanum and neodymium borosilicate systems with excess of $K_2Mo_3O_{10}$, KF, and LiF, PbO, closed to REBSiO$_5$ compositions.

2. EXPERIMENTAL

Starting chemicals were the following: La_2O_3 (99.93%), Nd_2O_3 (99.93%), Gd_2O_3 (99.93%), Dy_2O_3 (99.93%), SiO_2 (99.99%), LiF (99.99%), PbO (99.99%) and boric acid, H_3BO_3 (99.99%). Potassium fluoride, KF, was obtained by calcining $KF \cdot 2H_2O$ (99.99%). $K_2Mo_3O_{10}$ was first synthesized at 650°C using K_2MoO_4 (99.99%) and H_2MoO_4 (99.99%) in accordance with the reaction: $K_2MoO_4 + 2H_2MoO_4 \rightarrow K_2Mo_3O_{10} + 2H_2O\uparrow$.

The concentration of the stillwellite component in the initial mixture of the LnBSiO$_5$–KF(LiF)–$K_2Mo_3O_{10}$ systems (see Fig. 1) varied from 15 to 50 mol% (fluoride concentration in the solvent was 2–30 mol%) and from 30 to 50 mol% in the La_2O_3–B_2O_3–SiO_2–PbO system. During the spontaneous crystallization, 15-ml platinum crucibles containing the starting mixture were maintained at 1150°C for 24 h and cooled down to 200°C at the rate of 2°C/h. The conditions of spontaneous crystallization are shown in Table 1.

The X-ray powder diffraction patterns of solid phases in the 2Θ region of 15–80° (Co$K\alpha_1$ radiation, $\lambda(K\alpha_1) =$

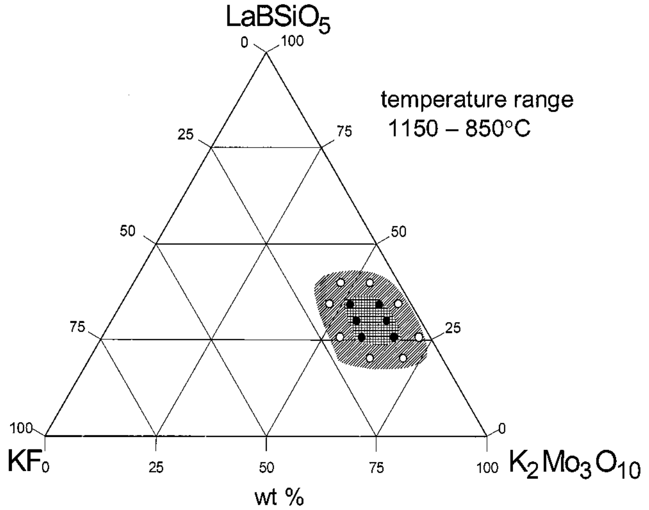

FIG. 1. Crystallization field of $LaBSiO_5$ and some molybdate phases in the system $LaBSiO_5$–$K_2Mo_3O_{10}$–KF (La_2O_3, 15.8–22.1% wt; B_2O_3, 3.4–4.7% wt; SiO_2, 5.8–8.2% wt; $K_2Mo_3O_{10}$, 45–65% wt; KF, 10–20% wt,) in the range of 1150–850°C: ▨, crystallization field of $KLa(MoO_4)_2$; ▦, crystallization field of $LaBSiO_5$ and $KLa(MoO_4)_2$.

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TABLE 1
Results of Experiments on Phase Formation

Composition of flux (%wt)				Crystallization conditions			Obtained phases	
	Fluoride							
$K_2Mo_3O_{10}$	KF	LiF	PbO	Concentration of solution (%wt)	Temperature range (°C)	Cooling speed (°C/h)	Composition	Dimensions, mm
$LaBSiO_5$–KF–$K_2Mo_3O_{10}$ system								
90	10			25	1140–750	2	$LaBSiO_5$	0.5–1
80	20			25	1145–720	2	$LaBSiO_5$	Up to 5
90	10			30	1150–700	2	$LaBSiO_5$	1–1.5
80	20			30	1150–700	2	$LaBSiO_5$	1.5–2
90	10			35	1150–700	2	$LaBSiO_5$	0.5–1
80	20			35	1150–700	2	$LaBSiO_5$	1–2
Nd_2O_3–B_2O_3–SiO_2–KF–$K_2Mo_3O_{10}$ system								
90	10			30	1140–750	2	$Nd_3BSi_2O_{10}$	0.5–1
80	20			30	1145–720	2	$Nd_3BSi_2O_{10}$	0.5–1
90	10			35	1150–700	2	$Nd_3BSi_2O_{10}$	0.5–1
80	20			35	1150–700	2	$Nd_3BSi_2O_{10}$	0.5–1
90	10			40	1150–700	2	$Nd_3BSi_2O_{10}$	0.5–1
80	20			40	1150–700	2	$Nd_3BSi_2O_{10}$	0.5–1
La_2O_3–B_2O_3–SiO_2–PbO system								
			100	30–50	1150–700	2	$LaBO_3$	Up to 1
La_2O_3–B_2O_3–SiO_2–LiF–$K_2Mo_3O_{10}$ system								
80		20		30	1068–837	2	$La_3BSi_2O_{10}$	2–3
(La,Nd)$BSiO_5$–KF–$K_2Mo_3O_{10}$ system								
80	20			30	1140–750	2	(La,Nd)$BSiO_5$	0.5–1.5
$GdBSiO_5$–KF–$K_2Mo_3O_{10}$ system								
80	20			30	1145–720	2	$Gd_3BSi_2O_{10}$	0.5–1.5
$DyBSiO_5$–KF–$K_2Mo_3O_{10}$ system								
80	20			30	1145–720	2	$Dy_3BSi_2O_{10}$	0.5–1.5
$HoBSiO_5$–KF–$K_2Mo_3O_{10}$ system								
80	20			30	1145–720	2	$Ho_2Si_2O_7$	2–3

1.7889 Å, Fe filter) were obtained using a DRON-1UM diffractometer. For structural determination, the Lorentz and polarization effects corrections were made during the data reduction procedure (5), while the correction for absorption was made with the method of Walker and Stuart (6) with a program written by Gluzinski (7). The structure was solved by direct methods with SIR97 (8) and refined by SHELX93 (9) using the isotropic thermal parameters.

Composition of grown crystals was studied by microprobe analysis (EMPA) with a CAMEBAX WDS analyzer with an accuracy of 2% at.

3. RESULTS AND DISCUSSION

3.1. *Phase Formation*

La-stillwellite crystallizes in a narrow concentration range of initial mixture in the $LaBSiO_5$–KF–$K_2Mo_3O_{10}$ system: from 25 to 35% wt of $LaBSiO_5$ and from 10 to 20% wt of KF (Table 2). As a rule, melting temperature of the starting mixture exceeds 1150°C, but this melting point decreases with decreasing stillwellite concentration. The stillwellite stability field corresponds to 10–20% wt of fluoride content in the solvent. Stillwellite crystals have two habits. Needle-like and isometric. The number

TABLE 2
Crystallization Range of La–Stillwellite in the $LaBSiO_5$–KF–$K_2Mo_3O_{10}$ System

Concentration of stillwellite formed oxides (%wt)	Obtained phases
< 25	$KLa(MoO_4)_2$
25–35	$LaBSiO_5$ and $KLa(MoO_4)_2$
> 35	$KLa(MoO_4)_2$

TABLE 3
EMPA Results of Solid Solution, Obtained in the (La,Nd)BSiO$_5$–KF–K$_2$Mo$_3$O$_{10}$ System (mol%)

	SiO$_2$		La$_2$O$_3$		Nd$_2$O$_3$		B$_2$O$_3$		La$_2$O$_3$/Nd$_2$O$_3$		
	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liquid	Solid	Liq/Sol
1	50.001	51.186	23.750	24.600	1.250	1.306	24.999	22.908	18.998	18.838	1.008
2	49.953	50.496	22.479	23.690	2.498	1.872	25.070	23.941	9.000	12.652	0.711
3	49.999	50.819	12.500	12.940	12.500	13.454	25.001	22.787	1.000	0.962	1.040

of isometric crystals decreases with increasing solution concentration over 35% wt. The mass of the LaBSiO$_5$ substance decreases on the edge of a crystallization field and only more stable form genesis here.

Different phases of molybdates (for example KNd(MoO$_4$)$_2$) and Nd$_3$BSi$_2$O$_{10}$ are synthesized in the Nd$_2$O$_3$–B$_2$O$_3$–SiO$_2$–KF–K$_2$Mo$_3$O$_{10}$ system in the concentration shown in Table 1. Also, new phases Gd$_3$BSi$_2$O$_{10}$ and Dy$_3$BSi$_2$O$_{10}$ were obtained in the systems *Ln*BSiO$_5$–KF–K$_2$Mo$_3$O$_{10}$ (where *Ln* = Gd and Dy, respectively). However, the chemical composition of crystals obtained in the system HoBSiO$_5$–KF–K$_2$Mo$_3$O$_{10}$ under the same conditions corresponds to Ho$_2$Si$_2$O$_7$, although the powder diffraction data of these crystals are different from the data given in Ref. 10 (Fig. 3; Table 7). The powder pattern was calculated from data of single crystal structure by Powder Cell 1.0.

In the (La,Nd)BSiO$_5$–KF–K$_2$Mo$_3$O$_{10}$ system, solid solution (La,Nd)BSiO$_5$ crystallizes up to 50% at. of neodymium (Table 3). Increasing neodymium concentration leads to formation of a new phase with chemical composition close to Nd$_3$BSi$_2$O$_{10}$. It is also not excluded that it is a new polymorph of Nd$_4$Si$_3$O$_{12}$ or a mixture of a few different phases.

Replacement of KF with LiF favors a decrease of melting temperature of the mixture and the formation of a new borosilicate La$_3$BSi$_2$O$_{10}$.

TABLE 4
Crystallographic Data and Experimental Information of La$_3$BSi$_2$O$_{10}$

Formula	La$_3$BSi$_2$O$_{10}$
Formula weight	643.7
Crystal	
Color	Colorless
Shape	Prism
Dimensions (mm)	0.03 × 0.04 × 0.13
Crystal system	Orthorhombic
Space group	*Pbca*
Cell Constants	
a (Å)	9.977(2)
b (Å)	7.269(2)
c (Å)	23.410(2)
Cell determination	
No. of reflections	45
q Range (°)	6.4–21.2
Cell volume (Å^3)	1697.8(6)
Formula units	8
D_{calc} (g cm^{-3})	5.037
m_{calc} (cm^{-1})	152.20
Temperature	Room
Diffractometer	Philips PW110
Radiation, wavelength (Å)	Mo*Kα*, 0.71069
Standard reflection, step	One, every 100
Decay of standard	None
Independent reflections measured	2469
Reflections. observed [$I > xs(I)$]	1719 $x = 2$
q Range (°)	3–30
Indices range: *h*, *k*, *l*	0/14, 0/10, 0/32
No. of refined parameters	66
R (for obs. rfl.)	0.037
R (for all measured refl.)	0.059
R_w	0.089
Weights	$w = 1./[s^2Fo + (0.0405\ P)^2]$
$Dr_{min/max}$	– 4.49/3.78
Computer programs	
Solution	SIR97 [8]
Refinement	SHELX93 [9]

TABLE 5
Atomic Fractional Coordinates (×10^4) and Uiso (×10^4 Å^2)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	U$_{iso}$
La1	– 2322 (1)	5922 (1)	3176 (1)	15 (1)
La2	– 1346 (1)	3291 (1)	1626 (1)	21 (1)
La3	– 92 (1)	8592 (1)	724 (1)	14 (1)
Si1	– 604 (2)	8181 (3)	2213 (1)	9 (4)
O11	– 965 (6)	8692 (8)	2875 (2)	22 (11)
O12	– 1518 (6)	6351 (8)	2099 (3)	62 (13)
O13	1040 (6)	7981 (8)	2211 (3)	31 (12)
O14	– 1083 (7)	9684 (9)	1735 (3)	81 (13)
Si2	1256 (2)	3538 (3)	781 (1)	13 (4)
O21	0422 (7)	5328 (9)	999 (3)	86 (13)
O22	2725 (6)	3502 (8)	1095 (3)	46 (12)
O23	1392 (6)	3374 (9)	81 (3)	55 (12)
O24	0484 (6)	1753 (8)	1050 (3)	41 (12)
B1	2434 (10)	8503 (13)	– 300 (4)	22 (17)
O1	1301 (6)	9241 (9)	– 85 (3)	69 (13)
O2	– 2631 (7)	2219 (10)	815 (3)	149 (15)

TABLE 6
Selected Bond Distances (Å)

La1–O11	2.527 (5)	La2–O2	2.420 (2)	La3–O1	2.395 (2)
La1–O11	2.459 (1)	La2–O11	2.459 (1)	La3–O2	2.490 (1)
La1–O12	2.664 (2)	La2–O12	2.664 (2)	La3–O14	2.685 (2)
La1–O13	2.395 (1)	La2–O13	2.395 (1)	La3–O21	2.511 (6)
La1–O13	2.651 (1)	La2–O13	2.651 (1)	La3–O22	2.517 (1)
La1–O22	2.450 (1)	La2–O22	2.450 (1)	La3–O23	2.697 (1)
La1–O22	2.567 (1)	La2–O22	2.567 (1)	La3–O24	2.488 (1)
Si1–O11	1.635 (1)	Si2–O21	1.627 (3)	B1–O1	1.349 (2)
Si1–O12	1.635 (3)	Si2–O22	1.640 (3)	B1–O2	1.329 (1)
Si1–O13	1.646 (3)	Si2–O23	1.650 (1)	B1–O23	1.475 (1)
Si1–O14	1.635 (2)	Si2–O24	1.635 (3)		

3.2. *Structural Characteristics of $La_3BSi_2O_{10}$*

Crystallographic and experimental data of $La_3BSi_2O_{10}$ are summarized in Tables 4–6. The drawing of the structure is shown in Fig. 2. The lanthanum atoms show a seven-membered coordination, which results in monocapped trigonal prisms, while the silicon atoms show the usual tetrahedral coordination. The Si–O bond distances are similar, ranging from 1.627(3) to 1.650(1) Å, while, on the contrary, those of the La–O bond are significantly different, ranging from 2.395(1) to 2.685(2) Å. The La trigonal prisms and the Si tetrahedra are distributed in layers perpendicular to the *c* axis. The planar BO_3 groups are intercalated with to the preceding layers at around the 0 and $\frac{1}{2}$ *c* level. Thus, the SiO_4 tetrahedra and BO_3 triangles shared one common oxygen atom and they form island groups like $[BSiO_6]^{5-}$. Si–O–B angle is about 131.5°.

TABLE 7
The Comparison of Calculated and Experimental X-ray Powder Diffraction Patterns of $Ho_2Si_2O_7$

Calculated from (10)		Experimental	
d_{calc}	I_{calc}	d_{exp}	I_{exp}
5.4309	20	5.437	70
4.9469	20	4.982	34
4.6612	75	4.649	19
4.2834	23	4.314	12
3.8839	15	3.898	14
3.5371	12	3.545	5
3.2453	64	3.228	65
3.0971	100	3.106	64
3.0335	34	3.036	72
2.7783	12	2.781	7
2.7155	35	2.715	54
2.6917	35	2.698	100
2.5043	3	2.515	9
2.4787	26	2.481	21
2.4403	13	2.442	24
2.3463	15	2.346	12
2.3306	1	2.315	6
2.284	25	2.284	23
2.2787	16	2.277	37
2.2351	6	2.238	5
2.2034	17	2.203	20
2.1882	2	2.179	28
2.1417	0	2.140	9
2.1219	0	2.116	6
2.1054	5	2.104	6
2.066	20	2.066	8
2.0596	2	2.057	6
1.969	8	1.967	9
1.8851	18		
1.8103	14		
1.7992	11	1.796	16

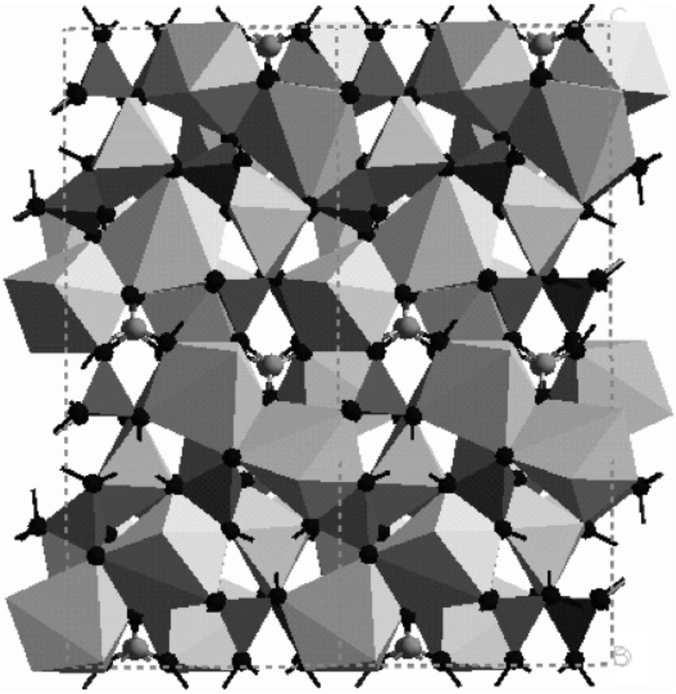

FIG. 2. Projection of the $La_3BSi_2O_{10}$ structure.

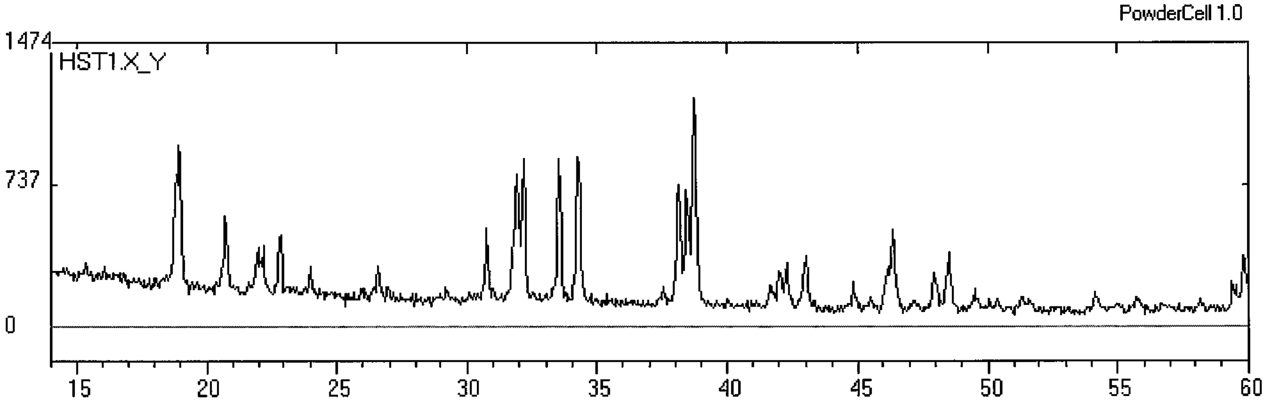

FIG. 3. X-ray diffraction pattern of $Ho_2Si_2O_7$.

4. CONCLUSION

The lanthanum stillwellite crystals of about 5 mm size were spontaneously obtained during the crystallization. Also the stillwellite-type crystals of solid solutions (La,Nd)$BSiO_5$ with Nd concentration up to 50% at. were grown as well. Distribution coefficients of Nd between initial mixture and crystals are from 0.7 to 1. For the first time, La-borosilicate $La_3BSi_2O_{10}$ was synthesized and its structure was solved. The authors also intend to study crystal structures of new phases $Ho_2Si_2O_7$ and $Nd_3BSi_2O_{10}$, which were obtained in these experiments.

REFERENCES

1. S. Yu. Stefanovich, V. N. Sigaev, A. V. Dechev, A. V. Mosunov, V. R. Samygina, N. I. Leonyuk, and P. D. Sarkisov, *Izv. Ross. Akad. Nauk Ser. Neorgan. Mater.* **31,** 819 (1995).
2. I. Ya. Nekrasov and R. A. Nekrasova, *Dokl. Akad. Nauk SSSR* **201,** 1202 (1971). [in Russian]
3. V. R. Samygina, E. A. Genkina, B. A. Maksimov, and N. I. Leonyuk, *Kristallografiya* **38,** 61 (1993). [in Russian]
4. Y. Shi, J. K. Liang, H. Zhang, J. L. Yang, W. D. Zhuang, and G. H. Rao, *J. Alloys Comp.* **259,** 163 (1997).
5. Belletti, D. FEBO, A new hardware and software system for the Philps Pw1100 single crystal diffractometer. Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. Parma, Internal report (1996) 1/96.
6. N. Walker and D. Stuart, *Acta Crystallogr. A* **39,** 158 (1983).
7. P. Gluzinski, "Set of Programs for X-ray Structural Calculations." IchO, Polish Academy of Sciences, Warszawa, Poland, 1989.
8. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, G. G. Moliterni, M. C. Burla, G. Polidori, M. Camalli, and R. Spagna, SIR97 A Package for crystal structure solution by direct methods and refinement, Private communication, 1997.
9. G. M. Sheldrick, "SHELX93 Program for the Refinement of Crystal Structures." Univ. of Gottingen, Germany, 1993.
10. A. N. Christensen, R. G. Hazell, and A. W. Hewat, *Acta Chem. Scand.* **51,** 37 (1997).