



Synthesis and crystal structure of a neodymium borosilicate, $\text{Nd}_3\text{BSi}_2\text{O}_{10}$

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A lanthanide borosilicate, trineodymium borosilicate or $\text{Nd}_3\text{BSi}_2\text{O}_{10}$, was synthesized using a flux method with LiCl, and its structure was determined from X-ray powder diffraction (XRD) and electron probe microanalysis (EPMA). The structure is composed of layers with $[\text{SiO}_4]^{4-}$ and $[\text{BSiO}_6]^{5-}$ anions alternating along the c axis linked by Nd^{3+} cations between them.

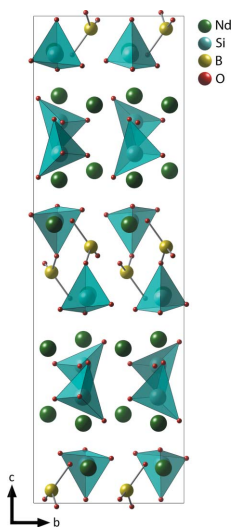
1. Chemical context

Lanthanide borosilicates (*i.e.* $\text{Ln}_3\text{BSi}_2\text{O}_{10}$) crystallize as one of the major phases within the residual glass matrix in some formulations of the glass-ceramic waste form for treatment of raffinate high-level waste (Crum *et al.*, 2012, 2014, 2016). Studies on the crystal chemistry and crystallization mechanism of lanthanide borosilicates are important in understanding the formation and durability of crystalline phases in the glass-ceramic waste forms (Crum *et al.*, 2012, 2014, 2016). In this work, we report the synthesis method and crystal structure of $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ solved by powder XRD and EPMA analysis.

Different compositions of lanthanide borosilicates including LnBSiO_5 ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$; McAndrew & Scott, 1955; Neumann *et al.*, 1966; Nekrasov & Nekrasova, 1971; Voronkov & Pyatenko, 1967; Burns *et al.*, 1993; Chi *et al.*, 1997; Shi *et al.*, 1997), $\text{Ln}_5\text{Si}_2\text{BO}_{13}$ ($\text{Ln} = \text{La}, \text{Eu}, \text{Gd}, \text{Dy}$; Mazza *et al.*, 2000; Yuan *et al.*, 2007; Naidu *et al.*, 2010), and $\text{Ln}_3\text{BSi}_2\text{O}_{10}$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}$; Chi *et al.*, 1996*a,b*; Müller-Bunz & Schleid, 1998; Chi *et al.*, 1998; Shvanskii *et al.*, 2000; Müller-Bunz *et al.*, 2001; Bräuchle & Huppertz, 2015) have been reported in the literature. LnBSiO_5 has the stillwellite structure containing single or mixed lanthanide cations with infinite helical chains composed of six-membered rings formed by two $[\text{BO}_4]^{5-}$ and one $[\text{SiO}_4]^{4-}$ tetrahedral units (Chi *et al.*, 1997; Burns *et al.*, 1993; Voronkov & Pyatenko, 1967; Shi *et al.*, 1997). $\text{Ln}_5\text{Si}_2\text{BO}_{13}$ has an apatite-like structure in which the non-tetrahedral cation sites are occupied by trivalent rare-earth cations, and B and Si occupy the same tetrahedral site (Mazza *et al.*, 2000). $\text{Ln}_3\text{BSi}_2\text{O}_{10}$ contains layers with $[\text{SiO}_4]^{4-}$ and $[\text{BSiO}_6]^{5-}$ anions alternating along the c axis linked by trivalent cations between them, and $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ in this work is isostructural to previously reported $\text{Ln}_3\text{BSi}_2\text{O}_{10}$ compounds (Chi *et al.*, 1996*a,b*, 1998, Braeuchle & Huppertz, 2015; Shvanskii *et al.*, 2000; Müller-Bunz *et al.*, 2001).

2. Structural commentary

The $[\text{BSiO}_6]^{5-}$ anion in $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ is formed by $[\text{SiO}_4]^{4-}$ and $[\text{BO}_3]^{3-}$ anions sharing an oxygen atom, with an average



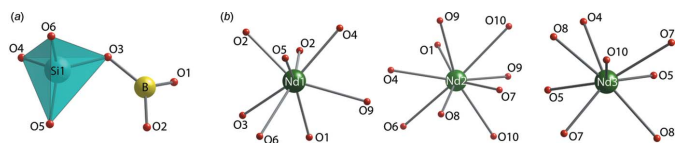


Figure 1
(a) Structure of the BSiO_6 anion and (b) coordination of oxygen atoms around Nd cations (Nd1, Nd2, and Nd3).

$\langle\text{Si}-\text{O}\rangle$ distance of 1.613 Å and an average $\langle\text{B}-\text{O}\rangle$ distance of 1.466 Å (Fig. 1a), while the $[\text{Si}_2\text{O}_4]^{4-}$ ion has an average $\langle\text{Si}-\text{O}\rangle$ distance of 1.590 Å. The $[\text{BSiO}_6]^{5-}$ and $[\text{Si}_2\text{O}_4]^{4-}$ anions are arranged alternately along the c axis (Fig. 2). The Nd cations occupy the interlayer sites between the anion units. Nd1 and Nd3 are coordinated by eight oxygen atoms with average $\langle\text{Nd1}-\text{O}\rangle$ and $\langle\text{Nd3}-\text{O}\rangle$ distances of 2.477 and 2.520 Å, respectively, and Nd2 is coordinated by nine oxygen atoms with an average $\langle\text{Nd2}-\text{O}\rangle$ distance of 2.575 Å (Fig. 1b). In our previous paper (Kroll *et al.*, 2019), we summarized the crystallographic data from the literature on other $\text{Ln}_3\text{BSi}_2\text{O}_{10}$ chemistries (Braeuchle & Huppertz, 2015; Chi *et al.*, 1996a,b, 1998; Müller–Bunz *et al.*, 2001; Shvanskii *et al.*, 2000) as a function of the ionic crystal radii (r_c) for the VIII-coordinated Ln^{3+} constituent according to Shannon (1976) to create predictive models for the unit-cell parameters (*i.e.*, a , b , and c), cell volume, and cell density. The measured values of a (9.7889 Å), b (7.1077 Å), c (23.0893 Å), cell volume (1606.5 Å³), and density (5.4551 Mg m⁻³) all fit reasonably well with the values calculated using the r_c for Nd (1.109 Å), *i.e.*, a (9.799 Å), b (7.111 Å), c (23.095 Å), cell volume (1608.4 Å³), and cell density (5.49 Mg/m³). Detailed atomic coordinates, bond lengths, and angles are given in Tables S1 and S2 in the supporting information.

3. Synthesis and crystallization

$\text{Nd}_3\text{BSi}_2\text{O}_{10}$ was synthesized by a LiCl flux method; more details are provided elsewhere (Kroll *et al.*, 2019). Powdered B_2O_3 was placed into a Pt–10%Rh crucible, melted at 1273 K in air to dehydrate fully and quenched on an Inconel plate. Appropriate amounts of Nd_2O_3 , SiO_2 , and B_2O_3 were mixed in an agate mortar and pestle. LiCl was dried at 378 K for several hours and mixed with oxides in a 1:1 ratio by mass in a Diamonite™ mortar and pestle. Mixed powder was placed into a fused quartz tube, covered with a quartz lid, heated to

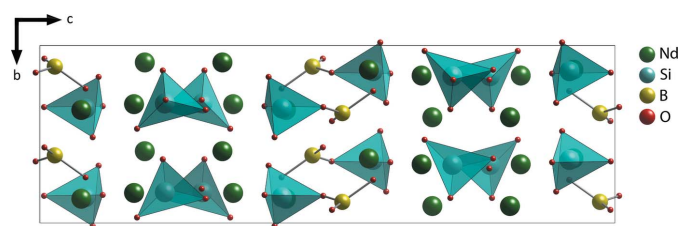


Figure 2
Crystal structure of $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ showing alternating $[\text{BSiO}_6]^{5-}$ and $[\text{Si}_2\text{O}_4]^{4-}$ anions along the c axis with Nd cations between them.

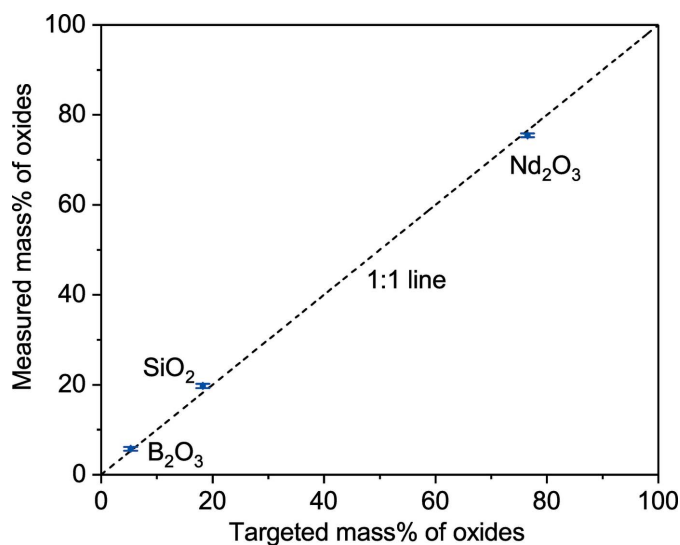


Figure 3
Comparison of oxide mass% between targeted and measured $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ from EPMA measurement.

1173 K at 5 K min⁻¹, held for 24 h at 1173 K, and then cooled down to room temperature at 1 K min⁻¹. The $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ was recovered from the LiCl through vacuum filtration with several rinsing steps using deionized water and a Büchner funnel. The recovered heat-treated powder was ground finer in the mortar and pestle and pressed into a 20 mm diameter pellet using a cold press with 110 MPa. The pellet was sintered at 1373 K. The heating condition included ramping up at 2 K min⁻¹ to 1373 K, dwelling for 4 h, and cooling to room temperature at 2 K min⁻¹. The heat-treated pellet, which was blue–violet in color, was ground for XRD and EPMA. Two EPMA measurements were performed on the sample to verify the composition of the crystal and showed that it closely matches the calculated value (Fig. 3).

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. A Rietveld plot is shown in Fig. 4. The structure of $\text{Nd}_3\text{BSi}_2\text{O}_{10}$ was determined using Rietveld refinement on the initial model with a similar chemistry and structure using *TOPAS* (version 4.2; Bruker, 2009). Based on the fitting of peak positions and profile of experimental XRD patterns to a reference pattern, $\text{Ce}_3\text{BSi}_2\text{O}_{10}$ (ICSD 94423) was used as a starting model. The Ce atoms in ICSD 94423 were replaced with Nd atoms, and all the atomic positions for Nd, B, Si, and O were refined. The profile of the model was refined from 14.5° to avoid a hump around 13.5° in the fitting of the background resulting from an instrumental artifact. The displacement parameters (B_{eq}) were not refined and fixed to 1 Å² to avoid divergence and unreasonable error values. In addition, parameters for unit cell, scale factors, microstructure effects, and preferred orientation with spherical harmonic function (Järvinen, 1993) were refined, and the background was fitted with a Chebyshev polynomial.

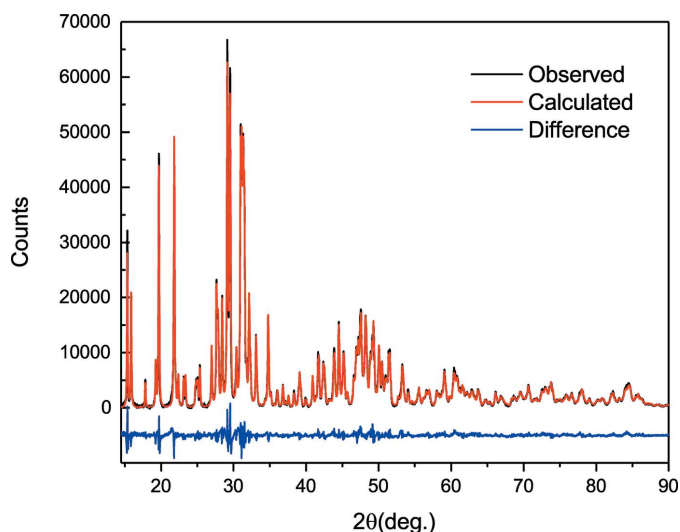


Figure 4 Observed, calculated, and difference XRD profiles of Nd₃BSi₂O₁₀.

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Table 1

Experimental details.

Crystal data	
Chemical formula	Nd ₃ BSi ₂ O ₁₀
<i>M_r</i>	659.7
Crystal system, space group	Orthorhombic, <i>Pbca</i>
Temperature (K)	295
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.78891 (17), 7.10774 (12), 23.0893 (4)
<i>V</i> (Å ³)	1606.49 (5)
<i>Z</i>	8
Radiation type	Cu <i>K</i> α, λ = 1.54188 Å
Specimen shape, size (mm)	Flat sheet, 25 × 25
Data collection	
Diffractometer	Bruker D8 Advance
Specimen mounting	Packed powder pellet
Data collection mode	Reflection
Scan method	Step
2θ values (°)	2θ _{min} = 14.5 2θ _{max} = 90 2θ _{step} = 0.014
Refinement	
<i>R</i> factors and goodness of fit	<i>R_p</i> = 0.03, <i>R_{wp}</i> = 0.04, <i>R_{exp}</i> = 0.011, <i>R_{Bragg}</i> = 0.013, χ ² = 13.250
No. of parameters	82

Computer programs: *XRD Commander* (Kienle *et al.*, 2003), *TOPAS* (Bruker, 2009), *VESTA* (Momma & Izumi, 2011) and *pubCIF* (Westrip, 2010).

Kroll, J. O., Crum, J. V., Riley, B. J., Neeway, J. J., Asmussen, R. M. & Liezers, M. (2019). *J. Nucl. Mater.* **515**, 370–381.
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supporting information

Acta Cryst. (2019). E75, 700-702 [https://doi.org/10.1107/S2056989019005024]

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Computing details

Data collection: *XRD Commander* (Kienle *et al.*, 2003); cell refinement: *TOPAS* (Bruker, 2009); program(s) used to solve structure: *TOPAS* (Bruker, 2009); program(s) used to refine structure: *TOPAS* (Bruker, 2009); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Trineodymium borosilicate

Crystal data

Nd₃BSi₂O₁₀

$M_r = 659.7$

Orthorhombic, *Pbca*

$a = 9.78891$ (17) Å

$b = 7.10774$ (12) Å

$c = 23.0893$ (4) Å

$V = 1606.49$ (5) Å³

$Z = 8$

$D_x = 5.455$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54188$ Å

$T = 295$ K

blue_violet

flat_sheet, 25 × 25 mm

Data collection

Bruker D8 Advance
diffractometer

Radiation source: sealed X-ray tube

Specimen mounting: packed powder pellet

Data collection mode: reflection

Scan method: step

$2\theta_{\min} = 14.5^\circ$, $2\theta_{\max} = 90^\circ$, $2\theta_{\text{step}} = 0.014^\circ$

Refinement

$R_p = 0.03$

$R_{wp} = 0.04$

$R_{\text{exp}} = 0.011$

$R_{\text{Bragg}} = 0.013$

5738 data points

Profile function: pseudo-Voigt

82 parameters

Weighting scheme based on measured s.u.'s

$(\Delta/\sigma)_{\max} = 0.011$

Background function: Chebychev

Preferred orientation correction: spherical
harmonic

Special details

Refinement. background fitted from 14.5 degree to avoid a hump from instrumental artifact

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}^*/B_{\text{eq}}$
Nd1	0.4909 (2)	0.3621 (3)	0.42810 (6)	1
Nd2	0.1338 (2)	0.3296 (4)	0.33652 (7)	1
Nd3	0.2655 (2)	0.0934 (3)	0.18257 (7)	1
B1	0.249 (4)	0.387 (7)	0.9703 (13)	1
Si1	0.3810 (10)	0.3516 (16)	0.0787 (3)	1

Si2	0.4381 (9)	0.3240 (17)	0.2814 (4)	1
O1	0.2558 (17)	0.254 (3)	0.9191 (7)	1
O2	0.1165 (18)	0.399 (3)	0.9903 (7)	1
O3	0.3697 (19)	0.348 (3)	0.0088 (6)	1
O4	0.4525 (17)	0.170 (3)	0.1055 (7)	1
O5	0.2286 (15)	0.346 (3)	0.1083 (7)	1
O6	0.4662 (17)	0.537 (3)	0.0938 (8)	1
O7	0.6028 (18)	0.293 (2)	0.2773 (7)	1
O8	0.4151 (15)	0.369 (2)	0.2120 (7)	1
O9	0.3903 (18)	0.466 (2)	0.3239 (7)	1
O10	0.3481 (15)	0.138 (3)	0.2880 (6)	1

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
?	?	?	?	?	?	?

Geometric parameters (Å, °)

Nd1—O1 ⁱ	2.454 (17)	Nd3—O7 ^{vi}	2.325 (16)
Nd1—O2 ⁱⁱ	2.460 (19)	B1—O2	1.38 (4)
Nd1—O2 ⁱⁱⁱ	2.265 (17)	Si1—O3	1.618 (16)
Nd1—O4 ^{iv}	2.39 (2)	Si1—O4	1.59 (2)
Nd1—O6 ^v	2.40 (2)	Si1—O5	1.641 (18)
Nd2—O1 ⁱ	2.327 (17)	Si1—O6	1.60 (2)
Nd2—O8 ^{vi}	2.432 (15)	Si2—O7	1.63 (2)
Nd2—O10 ^{vii}	2.47 (2)	Si2—O8	1.649 (19)
Nd3—Nd3 ^{viii}	3.567 (3)	Si2—O9	1.483 (19)
Nd3—Nd3 ^{vii}	3.567 (3)	Si2—O10	1.60 (2)
Nd3—O5 ^{viii}	2.457 (19)		
O1 ⁱ —Nd1—O2 ⁱⁱ	83.2 (6)	O3—Si1—O6	105.4 (11)
O1 ⁱ —Nd1—O2 ⁱⁱⁱ	128.2 (6)	O4—Si1—O5	102.6 (11)
O1 ⁱ —Nd1—O4 ^{iv}	119.9 (6)	O4—Si1—O6	110.7 (11)
O1 ⁱ —Nd1—O6 ^v	79.8 (6)	O5—Si1—O6	113.8 (11)
O2 ⁱⁱ —Nd1—O2 ⁱⁱⁱ	70.5 (6)	O7—Si2—O8	96.0 (9)
O2 ⁱⁱ —Nd1—O4 ^{iv}	69.9 (6)	O7—Si2—O9	116.3 (11)
O2 ⁱⁱ —Nd1—O6 ^v	149.5 (6)	O7—Si2—O10	116.1 (11)
O2 ⁱⁱⁱ —Nd1—O4 ^{iv}	92.2 (7)	O8—Si2—O9	117.9 (11)
O2 ⁱⁱⁱ —Nd1—O6 ^v	101.0 (7)	O8—Si2—O10	100.3 (9)
O4 ^{iv} —Nd1—O6 ^v	140.6 (6)	O9—Si2—O10	109.0 (10)
O1 ⁱ —Nd2—O8 ^{vi}	149.1 (6)	Nd1 ^{ix} —O1—Nd2 ^{ix}	117.7 (7)
O1 ⁱ —Nd2—O10 ^{vii}	124.2 (6)	Nd1 ^x —O2—Nd1 ^{xi}	109.5 (7)
O8 ^{vi} —Nd2—O10 ^{vii}	75.6 (5)	Nd1 ^x —O2—B1	104 (2)
Nd3 ^{viii} —Nd3—Nd3 ^{viii}	170.24 (8)	Nd1 ^{xi} —O2—B1	141.4 (17)
Nd3 ^{viii} —Nd3—O5 ^{viii}	44.7 (4)	Nd1 ^v —O4—Si1	135.9 (10)
Nd3 ^{viii} —Nd3—O7 ^{vi}	123.3 (4)	Nd3 ^{vii} —O5—Si1	104.6 (9)
Nd3 ^{vii} —Nd3—O5 ^{viii}	135.7 (4)	Nd1 ^{iv} —O6—Si1	147.0 (11)

Nd3 ^{vii} —Nd3—O7 ^{vi}	48.2 (4)	Nd3 ^{xii} —O7—Si2	137.5 (9)
O5 ^{viii} —Nd3—O7 ^{vi}	137.0 (5)	Nd2 ^{xii} —O8—Si2	107.8 (8)
O3—Si1—O4	113.9 (11)	Nd2 ^{viii} —O10—Si2	137.7 (9)
O3—Si1—O5	110.7 (10)		

Symmetry codes: (i) $x, -y+1/2, z-1/2$; (ii) $-x+1/2, -y+1, z-1/2$; (iii) $x+1/2, y, -z+3/2$; (iv) $-x+1, y+1/2, -z+1/2$; (v) $-x+1, y-1/2, -z+1/2$; (vi) $x-1/2, y, -z+1/2$; (vii) $-x+1/2, y+1/2, z$; (viii) $-x+1/2, y-1/2, z$; (ix) $x, -y+1/2, z+1/2$; (x) $-x+1/2, -y+1, z+1/2$; (xi) $x-1/2, y, -z+3/2$; (xii) $x+1/2, y, -z+1/2$.