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The Crystal Structure of a New Borogermanosilicate $Nd_3BGe_{1.08}Si_{0.92}O_{10}$

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The structure of $Nd_3BGe_{1.08}Si_{0.92}O_{10}$ has been determined by a single crystal investigation. The orthorhombic cell parameters are $a = 9.845(1)$ Å, $b = 7.146(1)$ Å, and $c = 23.382(2)$ Å. The space group is *Pbca* ($Z = 8$). Out of 10,833 measured reflections, 3,099 independent reflections ($I > 3\sigma(I)$) have been used in the refinement of the structure. The R factor value is 0.026 ($wR = 0.023$). The neodymium ions occupy three different sites with eight or nine oxygen bonds in the lattice. The germanium and silicon ions are located in a distorted tetrahedral environment. The boron atom coordination is triangular with a shorter B–O distance of 1.384 Å.

INTRODUCTION

During the last decades, a great deal of effort has been devoted to obtaining laser crystals doped with trivalent rare earths (1–5). Usually in Nd^{3+} laser host structures the fluorescence lifetime of the $^4F_{3/2}$ emitting level drops sharply beyond 10^{21} cm^{-3} doping concentration (6). This "concentration quenching" can be reduced when the crystal field parameters acting at the neodymium sites are weak (7) as well as when the Nd polyhedra are isolated from each other within the structure (8). The search for new crystals fulfilling these requirements is still active.

Recently, preliminary investigations concerning the borogermanates of rare earth were reported (9, 10). In the crystal chemistry studies of the ternary system Ln_2O_3–B_2O_3–GeO_2 (Ln = rare earth), only borogermanates with the general formula $LnBGeO_5$ have been isolated (11, 12). For the larger lanthanide ions (Ln = La, Pr), the $LnBGeO_5$ cell symmetry is trigonal (space group $P3_1$), and the compounds crystallize with the $LnBSiO_5$ stillwellite structure type (13–16). However, for Ln = Nd–Er and Y, the powder X-ray spectra have been indexed assuming a monoclinic cell. For the smallest ions (Tm, Yb, Lu), the compound does not exist.

In this context, a new borogermanosilicate of neodymium with the general formula $Nd_3B(Ge, Si)_2O_{10}$ was isolated. This paper reports the elaboration and crystal structure determination of a borogermanosilicate of composition $Nd_3BGe_{1.08}Si_{0.92}O_{10}$.

EXPERIMENTAL

Crystals of $Nd_3BGe_{1.08}Si_{0.92}O_{10}$ were obtained from melting by weighing the following component powders into a platinum crucible: Nd_2O_3 (3.36 g), H_3BO_3 (1.24 g), GeO_2 (1.46 g), and SiO_2 (0.36 g). The crucible was placed in a vertical, temperature programmable furnace. Controlled cooling was carried out at 5°C/hr between 1300 and 1050°C and then at 20°C/hr between 1050 and 400°C.

A single crystal was selected for X-ray analysis by the Weissenberg technique and was then mounted on an Enraf–Nonius CAD4 automatic goniometer. The conditions of the diffraction experiment are summarized in Table 1.

STRUCTURAL DETERMINATION

The refined orthorhombic cell parameters are $a = 9.845(1)$ Å, $b = 7.146(1)$ Å, and $c = 23.382(2)$ Å. The observed reflections conditions indicate the space group *Pbca*. Out of 10,833 measured reflections, 3,099 independent reflections ($I > 3\sigma(I)$) were used for the refinement. The intensities were corrected for Lorentz and polarization effects. Scattering factors were taken from Ref. (17) and the influence of any anomalous dispersion was included (18). The structural determination was performed using the "SHELX" program (19). Series of refinement lead to the R factor value of 0.026 ($wR = 0.023$). The final positions and thermal parameters are reported in Table 2. Displacement parameters U_{ij} are given in Table 3. The selected interatomic distances with the corresponding deviations are listed in Table 4.

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TABLE 1
Crystal Data and Conditions of Data Collection and Evaluation for $Nd_3BGe_{1.08}Si_{0.92}O_{10}$

Crystal data	a = 9.845(1) Å b = 7.146(1) Å c = 23.382(2) Å V = 1644.9 Å^3 Z = 8 M = 707.8 g
Size of the crystal (mm)	0.15 × 0.07 × 0.06
Measured range (MoK_α)	$0.1 < \theta < 35°$
h (min/max)	−15/15
k	−11/11
l	0/37
Angle for ω-scan (°)	0.80 + 0.35 tg θ
measured reflections	10,833
Independent ($I > 3\sigma(I)$)	3,099
Absorption correction	Empirical
(μ = 213.7 cm^{-1})	From psi-scans
Extinction ε refined in $F_c(\text{corr.}) = F_c(1 - \varepsilon F_c^2/\sin\theta)$	0.27 × 10^{-7}
Goodness of fit S	1.685
$R = (\Sigma D/\Sigma F_O)$	0.026
$R = (\Sigma\omega D^2/\Sigma\omega F_O^2)^{1/2}$ with $D = \Sigma\|\|F_o\| - \|F_c\|\|$ and weights ω proportional to $1/\sigma^2(F_o)$	0.023

TABLE 2
Atomic Parameters and Equivalent Isotropic Temperature Factors in $Nd_3BGe_{1.08}Si_{0.92}O_{10}$

Atoms	x	y	z	B_{eq} (Å^2)
Nd(1)	0.4886(1)	0.3634(1)	0.4279(1)	0.39
Nd(2)	0.1352(1)	0.3202(1)	0.3361(1)	0.52
Nd(3)	0.2686(2)	0.0897(3)	0.1821(1)	0.50
Ge/Si(I)	0.3779(1)	0.3589(1)	0.0771(1)	0.39
Ge/Si(II)	0.4400(1)	0.3106(1)	0.2794(2)	0.38
B	0.2427(5)	0.3426(7)	0.9696(2)	0.57
O(1)	0.3640(3)	0.3382(6)	0.0043(1)	0.93
O(2)	0.4668(4)	0.5438(5)	0.1024(2)	1.46
O(3)	0.2214(3)	0.3499(5)	0.1107(1)	0.72
O(4)	0.4543(3)	0.1699(5)	0.1069(1)	0.61
O(5)	0.3919(4)	0.4626(5)	0.3291(1)	1.26
O(6)	0.6112(3)	0.2942(5)	0.2776(1)	0.98
O(7)	0.4032(3)	0.3652(3)	0.2103(1)	0.60
O(8)	0.3418(3)	0.1220(5)	0.2895(1)	0.95
O(9)	0.6271(3)	0.4176(5)	0.5082(1)	0.78
O(10)	0.2573(4)	0.2425(6)	0.4185(1)	1.37

STRUCTURAL DESCRIPTION

Figure 1 shows the projection of the investigated structure on the (010) plane. The silicon and germanium atoms occupy statistically the M(I) and M(II) tetrahedral sites which are isolated from each other. The boron atom is in a triangular environment which is linked through the O_1 atom with the M(I) tetrahedron. Both isolated entities M(I)BO_6 and M(II) tetrahedra are connected by the neodymium atoms which are located in three independent crystallographic sites.

The structure can also be readily described as a succession, along the c axis, of alternate sheets A and B with the sequence ... $ABAB$ ..., parallel to the (001) plane.

(i) The A sheet is constituted from Nd(1), M(I)O_4, and BO_3. The chemical formula is $[NdBO_3M(I)O_4]\infty$.

(ii) The B sheet contains the atoms Nd(2), Nd(3), and

TABLE 3
Anisotropic Displacement Parameters (U_{ij} × 10^4) in $Nd_3BGe_{1.08}Si_{0.92}O_{10}$

Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Nd(1)	40(1)	71(1)	36(1)	1(1)	5(1)	−2(1)
Nd(2)	42(1)	99(1)	57(1)	22(1)	−8(1)	−8(1)
Nd(3)	70(1)	52(1)	68(1)	−6(1)	30(1)	−5(1)
Ge/Si(I)	43(2)	76(3)	28(1)	−4(2)	−1(2)	5(2)
Ge/Si(II)	30(3)	77(4)	37(3)	−5(2)	−4(2)	1(3)
O(1)	88(13)	219(17)	45(13)	−29(13)	−26(11)	21(14)
O(2)	278(20)	139(18)	139(17)	26(14)	−26(15)	−73(17)
O(3)	46(12)	165(16)	64(12)	−4(12)	−4(10)	24(13)
O(4)	91(13)	71(14)	71(13)	−34(11)	−10(11)	18(13)
O(5)	225(18)	124(17)	130(17)	−18(13)	−52(14)	36(16)
O(6)	50(13)	98(17)	223(17)	33(14)	−24(12)	14(13)
O(7)	45(12)	110(15)	72(13)	23(12)	−9(10)	−9(12)
O(8)	114(15)	129(17)	118(15)	23(13)	−21(11)	27(14)
O(9)	81(13)	175(16)	40(13)	−12(12)	−15(11)	24(13)
O(10)	94(14)	318(22)	109(15)	84(16)	−21(12)	−62(16)

Note. The vibrational coefficients are related by the expression
$T = \exp[-2\pi^2(ha^{*2}U_{12} + k^2b^{*2}U_{22} + l^2C^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

TABLE 4
Selected Interatomic Distances (Å) in $Nd_3BGe_{1.08}Si_{0.92}O_{10}$

	Nd(1)	Nd(2)	Nd(3)	Ge/Si(I)	Ge/Si(II)	B
O(1)	2.601(3)			1.715(3)		1.443(6)
O(2)	2.431(3)	2.715(4)	2.993(3)	1.691(4)		
O(3)	2.466(3)		2.396(3)	1.730(3)		
			2.543(3)			
O(4)	2.403(3)	2.470(4)	2.601(3)	1.695(3)		
O(5)	2.598(3)	2.574(3)			1.660(4)	
		2.730(4)				
O(6)		2.675(3)	2.328(3)		1.690(3)	
			2.597(3)			
O(7)		2.548(3)	2.422(3)		1.700(3)	
			2.463(3)			
O(8)		2.427(3)	2.622(3)		1.676(4)	
		2.707(3)				
O(9)	2.443(3)					1.361(6)
	2.352(3)					
O(10)	2.445(4)	2.339(3)				1.349(6)

M(II)O_4 tetrahedra. The chemical formula in this case is $([Nd_2M(II)O_4]_4)\infty$.

The mixed site M(I), occupied statistically by Ge and Si, is surrounded by the oxygen atoms O(1), O(2), O(3), and O(4). The M(I)–O distance values range between 1.691 and 1.730 Å with a mean value equal to 1.707 Å. A second, smaller site M(II) showing the same mixed Ge and Si composition is built with the atoms O(5), O(6), O(7), and O(8). The M(II)–O distances are between 1.660 and 1.700 Å. The mean distance is 1.688 Å (Table 4).

The boron atom possesses a distorted triangular environment involving O(1), O(9), and O(10). The B–O distances are B–O(1) = 1.443, B–O(9) = 1.361, and B–O(10) = 1.348 Å. The angular distortion in the BO_3 polyhedra is exhibited by the O(9)–B–O(10) (127.2°) and O(1)–B–O(10) (113.5°) angle values.

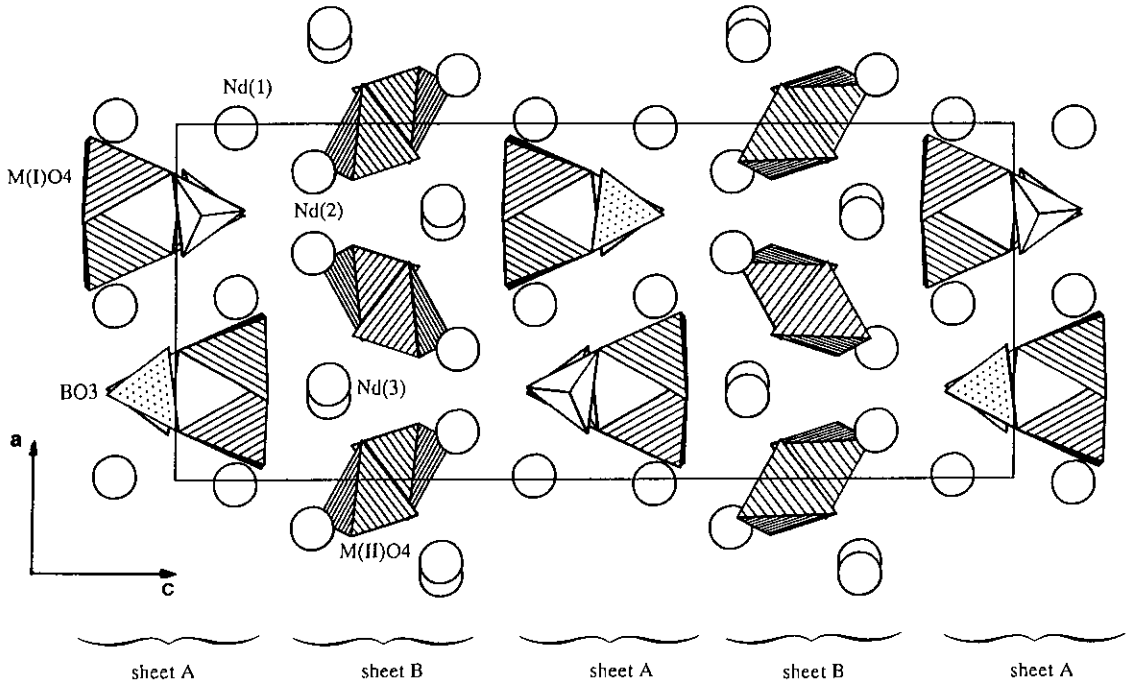

FIG. 1. Projection of the $Nd_3BGe_{1.08}Si_{0.92}O_{10}$ structure on (010) plane. Circles are neodymium atoms and triangles are BO_3 environments (see text for the meaning of the A and B sheets).

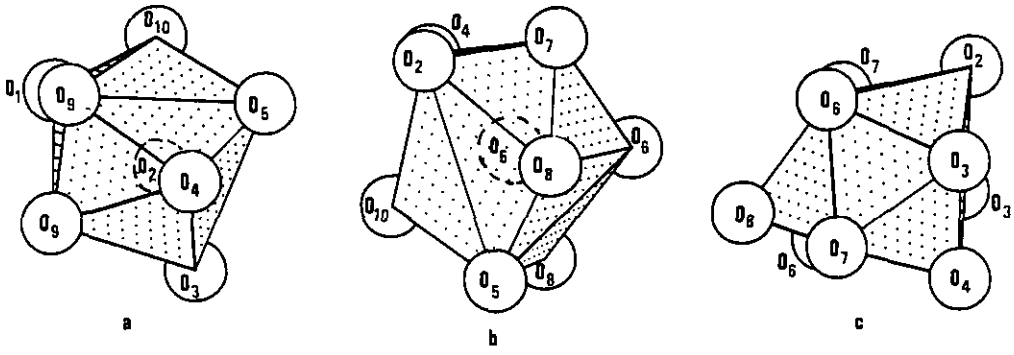

FIG. 2. Representation of NdO polyhedra seen along [010]: (a) Nd(1), (b) Nd(2), and (c) Nd(3).

The Nd(1) ion is surrounded by the following eight oxygen atoms: O(1), O(2), O(3), and O(4) (*A* sheet) and O(5), 2 × O(9), and O(10) (*B* sheet). The Nd(1)–O distances range from 2.352 to 2.601 Å. The Nd(1)–O mean value is 2.467 Å (Fig. 2).

The Nd(2) and Nd(3) atoms are located in a distorted prism with nine oxygen atoms (Fig. 2). The oxygen coordination of Nd(2) is O(2), O(4), and O(10) from the *A* sheet and 2 × O(5), O(6), O(7), 2 × O(8) from the *B* sheet. However, the atoms O(2), 2 × O(3), and O(4) from the *A* sheet and 2 × O(6), 2 × O(7), and O(8) from the *B* sheet constitute the $Nd(3)O_9$ polyhedron (Fig. 2). We noted a very high distance value (2.991 Å) between Nd(3) and the oxygen O(2) (Table 4). The Nd(2)–O and Nd(3)–O distances are, respectively between 2.339–2.730 and 2.396–2.991 Å. The mean distance value ⟨Nd(2)–O = 2.550 Å⟩ is comparable with ⟨Nd(3)–O = 2.570 Å⟩ in the same coordination.

Figure 3 gives the projection on the (010) plane of a part of the structure showing the connection of NdO polyhedra. The Nd polyhedra are sharing edges: O(5)–O(10) between Nd(1) and Nd(2); O(6)–O(8) between Nd(2) and Nd(3); and O(3)–O(4) between Nd(1) and Nd(3)'.

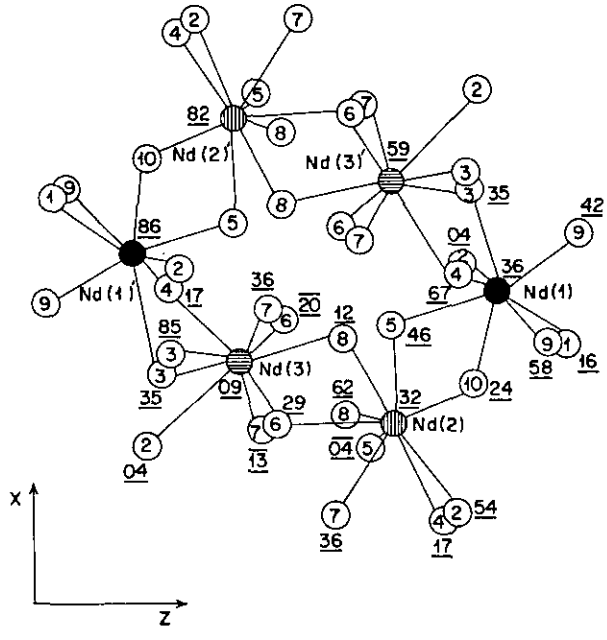

FIG. 3. Representation of the NdO polyhedra connection in $Nd_3BGe_{1.08}Si_{0.92}O_{10}$ (underlined values represent the *y* parameters).

CONCLUSION

At first sight, from these crystallographic data, the structural correlation for a weak concentration quenching of the Nd^{3+}, $^4F_{3/2}$ emission does not seem fulfilled, but the strong covalent character of the B–O bond may induce a relatively weak crystal field at the closest neodymium site, Nd(1). Therefore, a detailed spectroscopic investigation is presently underway.

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