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The Crystal Chemistry of the New Rare-Earth Sodium Borates $Na_3Ln(BO_3)_2$ (Ln = La, Nd)

JOËLLE MASCETTI, MARCUS VLASSE,* AND CLAUDE FOUASSIER

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351, cours de la Libération, 33405 Talence Cédex, France

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The ternary borate systems Na_2O–Ln_2O_3–B_2O_3 (Ln = La, Nd) have been investigated in view of obtaining high-neodymium-concentration materials with weak concentration quenching. A ternary phase of composition $Na_3Ln(BO_3)_2$ (Ln = La, Nd) has been found. It crystallizes in the monoclinic space group $P2_1/c$. The structure has been determined for $Na_3Nd(BO_3)_2$. A full-matrix least-squares refinement led to $R = 0.040$. The structure is formed by isolated BO_3 triangles held together by the neodymium and sodium ions. The rare-earth atoms have a complex eightfold coordination in a covalent BO_3 matrix.

High-neodymium-concentration materials with weak concentration quenching of luminescence are attractive for laser application owing to their low pumping threshold. A requirement for weak self-quenching is a small crystal field splitting of the neodymium levels (*1, 2*). This situation is encountered in only a few oxides (*3*). Most of them are phosphates (NdP_5O_{14}, $LiNdP_4O_{12}$, etc.); only one borate, $NdAl_3B_4O_{12}$, shows such a behavior.

In the borates, boron has a tetrahedral or triangular surrounding. In phases containing only BO_3 groups, a weak crystal field may be expected at the rare-earth sites due to the high degree of covalency in the BO_3 anions. The presence of electropositive atoms in the lattice increases the covalency of the anionic groups and consequently favors the triangular (BO_3) coordination in the case of boron. In fact, all sodium-rich borates contain three-coordinated boron atoms (*4–6*). It was worthwhile therefore to study the intensity of the crystal field in sodium-rich rare-earth borates. Such phases had not been previously reported. The investigation of the Na_2O-rich portion of the ternary diagram Na_2O–Nd_2O_3–B_2O_3 was undertaken. Several sodium neodymium borates were found.

In this paper the crystal structure of $Na_3NdB_2O_6$ is described.

The Na_2O–La_2O_3–B_2O_3 system was also explored in order to get a homologous phase which could be doped with Nd^{3+} for comparison of the fluorescent properties of this ion in dilute and concentrated quantities.

Preparation

$NaBO_2$ was first prepared by heating for 15 hr in air at 700°C a mixture of equal parts of Na_2CO_3 (Carlo Erba 99.5%) and anhydrous B_2O_3 (Carlo Erba 98%). $Na_3LnB_2O_6$ was then obtained by heating a stoichiometric mixture of Na_2O, $NaBO_2$, and Ln_2O_3

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* Author to whom correspondence should be addressed.

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(RP 99.99%) in an alumina crucible for 15 hr in nitrogen at 800°C. The reactants were dried and handled in an argon-filled drybox. Phase identification was carried out by powder X-ray diffraction. Chemical analysis confirmed the formula. The densities and melting points are given in Table I.

Single crystals of $Na_3NdB_2O_6$ have been obtained by melting a mixture of equal amounts of powdered $Na_3NdB_2O_6$ and $Na_4B_2O_5$ at 970°C in a platinum crucible and then cooling at a rate of 2.5°C/hour down to 600°C and at a rate of 15°C/hour to 25°C.

Crystallographic and Physical Data of $Na_3LnB_2O_6$ (Ln = La, Nd)

Single-crystal diffraction photographs showed a monoclinic Laüe symmetry $2/m$. The systematic absences: $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ are consistent with the space group $P2_1/c$. The cell dimensions obtained and refined from powder data are given in Table I. The unit cell contains four formula units. The interplanar spacings and intensities for $Na_3NdB_2O_6$ are given in Table II.

A single crystal of $Na_3NdB_2O_6$ in the form of a rectangular block 0.20 × 0.20 × 0.17 mm was mounted about the b axis. The

TABLE I

Crystallographic and Physical Data for $Na_3LnB_2O_6$ Phases

Phase	$Na_3LaB_2O_6$	$Na_3NdB_2O_6$
Density (g/cm³)		
ρ_{calc}	3.49	3.68
ρ_{obs} (±0.03)	3.48	3.70
Melting point (°C)	1040	1075
Unit cell dimensions		
a (±0.005 Å)	6.691	6.618
b (±0.005 Å)	8.909	8.810
c (±0.005 Å)	12.219	12.113
β(°)	121.91	122.27
V(Å³)	618.33	597.12

TABLE II

X-Ray Diffraction Data[a] for $Na_3Nd(BO_3)_2$

I_{obs}	I_{calc}	d_{obs}	d_{calc}	$h\ k\ l$
85	72.4	6.66	6.68	0 1 1
100	100	5.59	5.59	1 0 0
20	16.6	5.51	5.52	$1\ 0\ \bar{2}$
32	32.6	5.30	5.29	$1\ 1\ \bar{1}$
16	11.2	5.12	5.12	0 0 2
64	66.0	4.68	4.68	$1\ 1\ \bar{2}$
57	53.3	4.43	4.43	0 1 2
77	77.6	4.04	4.05	0 2 1
66	50.9	3.66	3.67	$1\ 2\ \bar{1}$
	29.8		3.66	$1\ 1\ \bar{3}$
17	20.2	3.31	3.31	$2\ 0\ \bar{2}$
40	42.5	3.18	3.18	0 1 3
27	31.1	3.09	3.10	$2\ 1\ \bar{2}$
8	3.7	3.05	3.05	1 0 2
16	11.3	3.02	3.02	$1\ 0\ \bar{4}$
16	22.9	2.996	2.993	1 2 1
24	23.8	2.979	2.976	$2\ 1\ \bar{1}$
17	10.5	2.967	2.970	$1\ 2\ \bar{3}$
17	12.7	2.948	2.953	$2\ 1\ \bar{3}$
14	14.3	2.888	2.884	1 1 2
22	20.2	2.802	2.798	2 0 0
16	11.2	2.756	2.760	$2\ 0\ \bar{4}$
7	5.2	2.698	2.698	0 2 3
17	16.1	2.677	2.666	2 1 0
17	18.4	2.629	2.634	$2\ 1\ \bar{4}$
14	16.4	2.591	2.593	$1\ 3\ \bar{2}$
44	40.8	2.559	2.560	0 0 4
	1.8		2.554	$2\ 2\ \bar{3}$
58	59.7	2.548	2.547	0 3 2
11	11.2	2.368	2.372	$1\ 3\ \bar{3}$
15	12.9	2.314	2.315	1 1 3
17	15.3	2.223	2.226	0 3 3
29	26.8	2.194	2.196	$2\ 3\ \bar{2}$
28	31.8	2.139	2.139	$3\ 1\ \bar{3}$
11	15.4	2.102	2.100	$3\ 1\ \bar{2}$
44	37.7	2.088	2.091	$1\ 2\ \bar{5}$
	6.7		2.088	$3\ 1\ \bar{4}$
23	21.1	2.047	2.049	1 4 0
	10.9		2.046	$1\ 4\ \bar{2}$
12	11.6	1.988	1.987	2 1 2
31	24.7	1.856	1.857	0 2 5
10	6.4	1.853	1.855	2 3 1
10	13.9	1.829	1.832	$3\ 2\ \bar{5}$
10	7.8	1.826	1.829	$2\ 2\ \bar{6}$
12	16.5	1.729	1.731	2 4 0
15	11.3	1.719	1.719	2 1 3
9	7.1	1.675	1.675	2 3 2
9	7.6	1.654	1.653	3 1 1

[a] Cu$K\alpha_1$, λ = 1.5405 Å, using a Philips powder diffractometer.

intensities were measured on an Enraf–Nonius CAD 3 automatic diffractometer with Mo$K\alpha$ radiation (λ = 0.70929 Å) and a pyrolytic graphite monochromator (002). A scintillation counter and a $\theta/2\theta$ multiple scanning technique with a 2θ scan rate of 10°/minute was used. Three control reflections measured for every batch of 100 reflections showed a random fluctuation of about 4%. Two equivalent reflections were averaged to give a total of 5998 independent reflections ($2\theta_{max}$ = 90°) with $I > 5\sigma(I)$, which were used in the refinement. These intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu_{Mo} = 89.7\ cm^{-1}$, $\mu r_{max} = 0.9$).

Determination and Refinement of the Structure

The heavy-atom position was determined from a 3D Patterson synthesis. The sodium, boron, and oxygen atoms were located in a difference synthesis at an intermediate stage of the refinement. Full-matrix least-squares refinement (*7*) with anisotropic temperature factors reduced $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ down to 0.040, based on a data to parameter ratio of 55 to 1. A final $(F_o - F_c)$ synthesis confirmed the proposed solution.

$\Sigma w(|F_o - F_c|)^2$ was minimized with w taken as unity for all reflections. The overall scale factor had a final value of 9.69(1) ($F_o = kF_c$). An isotropic secondary extinction correction was applied with $g = 9.73 \times 10^{-8}$. The form factors for Na, Nd, B, and O were taken from MacMaster *et al.* (*8*). The final atomic and thermal parameters are given in Table III. Table IV contains the interatomic distances.

Description and Discussion

A projection of the structure on the (010) plane is shown in Fig. 1. The structure seems to be of a new unique type never

TABLE III

ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS[a] ($\times 10^5$) FOR $Na_3Nd(BO_3)_2$ WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B (Å^2)
Nd	0.01416(3)	0.11353(2)	0.35406(1)	449(3)	546(5)	480(3)	29(5)	285(3)	47(5)	0.418(2)
Na(1)	0.4179(4)	0.8107(3)	0.3969(2)	1169(67)	1564(87)	1080(63)	−259(59)	545(55)	−317(57)	1.15(4)
Na(2)	0.1818(4)	0.2369(3)	0.1572(2)	1804(83)	1505(87)	1036(63)	458(66)	961(63)	165(57)	1.18(4)
Na(3)	0.387(1)	0.9378(4)	0.1068(3)	9910(368)	2196(148)	1200(101)	1812(191)	1705(167)	487(97)	3.6(1)
B(1)	0.1295(8)	0.4325(5)	0.3743(4)	1272(126)	690(143)	737(105)	−92(104)	537(99)	78(94)	0.75(7)
B(2)	0.4180(6)	0.5986(5)	0.1389(3)	531(88)	836(153)	655(93)	−65(84)	326(77)	−51(87)	0.57(6)
O(1)	0.1751(8)	0.3467(4)	0.4805(3)	3349(185)	1098(120)	753(79)	−571(125)	956(102)	24(81)	1.43(8)
O(2)	0.0110(6)	0.3639(3)	0.2515(3)	1569(98)	798(99)	784(65)	−43(70)	638(68)	−27(58)	0.91(5)
O(3)	0.1984(8)	0.5801(4)	0.3834(3)	3382(200)	1018(122)	828(91)	−936(124)	592(112)	22(81)	1.61(9)
O(4)	0.3775(6)	0.7105(4)	0.2048(3)	1122(92)	1575(133)	1806(112)	−431(84)	1016(89)	−930(95)	1.11(6)
O(5)	0.2503(5)	0.4815(4)	0.0838(3)	856(77)	1199(113)	1259(89)	−310(70)	636(71)	−406(76)	0.94(5)
O(6)	0.3847(6)	0.1015(5)	0.3687(4)	968(89)	2339(173)	2232(142)	539(101)	1165(101)	1003(128)	1.38(7)

[a] The anisotropic thermal parameter U_{ij} (Å^2) is defined as $T = \exp(-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23}))$.

TABLE IV

INTERATOMIC DISTANCES (Å) FOR $Na_3Nd(BO_3)_2$

B_1 triangle		B_2 triangle			
B_1-O_1	1.379(6)	B_2-O_4	1.382(6)		
B_1-O_2	1.396(6)	B_2-O_5	1.396(5)		
B_1-O_3	1.363(7)	B_2-O_6'	1.357(6)		
$\langle B_1-O\rangle$	1.379(6)	$\langle B_2-O\rangle$	1.378(6)		
O_1-O_2	2.384(6)	O_4-O_5	2.368(5)		
O_1-O_3	2.415(6)	O_4-O_6'	2.385(6)		
O_2-O_3	2.367(6)	O_5-O_6'	2.408(5)		
$\langle O-O\rangle$	2.389(6)	$\langle O-O\rangle$	2.387(5)		
Na_1 oxygen environment		Na_2 oxygen environment		Na_3 oxygen environment	
Na_1-O_1'	2.667(5)	Na_2-O_1''	2.240(5)	Na_3-O_1''	2.371(6)
Na_1-O_2'	2.461(4)	Na_2-O_2	2.283(4)	Na_3-O_3'	2.960(6)
Na_1-O_3	2.451(5)	Na_2-O_3'	2.676(5)	Na_3-O_3''	2.301(6)
Na_1-O_4	2.367(4)	Na_2-O_4'	2.479(5)	Na_3-O_4	2.346(6)
Na_1-O_5'	2.568(4)	Na_2-O_5	2.464(4)	$\langle Na_3-O\rangle$	2.494(6)
Na_1-O_6	2.579(5)	Na_2-O_6	2.473(5)		
Na_1-O_6''	2.530(5)	$\langle Na_2-O\rangle$	2.436(5)		
$\langle Na_1-O\rangle$	2.518(5)				
Nd oxygen environment		metal–metal			
$Nd-O_1$	2.441(4)	Nd–Nd	4.1524(4)	(first nearest neighbor)	
$Nd-O_2$	2.527(4)	Nd–Nd	5.0291(5)	(second nearest neighbor)	
$Nd-O_2'$	2.504(4)	$Nd-Na_1'$	3.340(2)		
$Nd-O_3'$	2.454(4)	$Nd-Na_2$	3.305(2)		
$Nd-O_4'$	2.446(4)	$Nd-Na_3'$	4.096(5)		
$Nd-O_5'$	2.527(3)				
$Nd-O_5''$	2.499(3)	Na_1-Na_2'	3.718(3)		
$Nd-O_6$	2.364(4)	Na_1-Na_3	3.589(5)		
$\langle Nd-O\rangle$	2.470(4)	Na_2-Na_3	3.169(5)		

observed for any of the known borates. It is made up of isolated BO_3 triangles held together by the sodium and neodymium atoms.

The neodymium atom has an eightfold coordination with regular distances ranging from 2.364 to 2.527 Å. As can be seen in Fig. 2 it is surrounded by two B_1 triangles and three B_2 triangles, with which it shares edges or corners.

The sodium atoms Na(1) and Na(2) have sevenfold and sixfold coordinations respec-

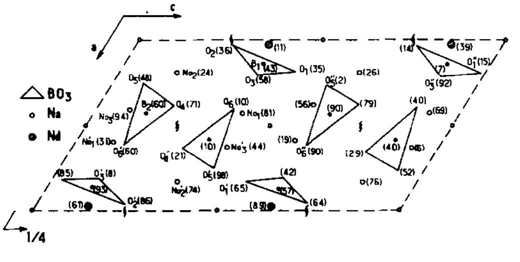

FIG. 1. Projection of the structure on the (010) plane.

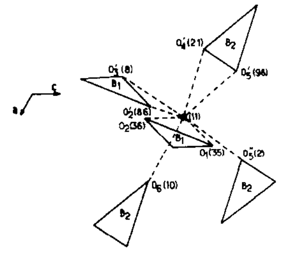

FIG. 2. Neodymium atom environment.

TABLE V

Comparison of Sodium–Oxygen Coordinations for $Na_3NdB_2O_6$ and Other Known Sodium Borates

					Temperature factors (Å²)	
Reference	Phase	Symmetry	Coordination Na [O] and distances Na–O		Isotropic, B	Anisotropic, U_{11} (10^4)
Present work	$Na_3Nd(BO_3)_2$	monoclinic	$Na_1[O] = 5 + 2$	$\langle Na_1–O\rangle = 2.518$ Å(2.367 → 2.667 Å)	1.15	117
		$P2_1/c$	$Na_2[O] = 5 + 1$	$\langle Na_2–O\rangle = 2.436$ Å(2.240 → 2.676 Å)	1.18	180
		$Z = 4$	$Na_3[O] = 3 + 1$	$\langle Na_3–O\rangle = 2.494$ Å(2.301 → 2.960 Å)	3.6	991
6	$NaBO_2$	$R\bar{3}c$	$Na\ [O] = 7$	$\langle Na–O\rangle = 2.50$ Å(2.461 → 2.607 Å)	1.77	
5	$Na_4B_2O_5$	monoclinic	$Na_1[O] = 4 + 1$	$\langle Na_1–O\rangle = 2.394$ Å (2.316 → 2.610 Å)		
		$P2_1/c$	$Na_2[O] = 5 + 1$	$\langle Na_2–O\rangle = 2.479$ Å(2.349 → 2.701 Å)		
		$Z = 4$				
4	Na_3BO_3	monoclinic	$Na_1[O] = 5 + 1$	$\langle Na_1–O\rangle = 2.528$ Å(2.406 → 3.049 Å)		
		$P2_1/c$	$Na_2[O] = 5 + 1$	$\langle Na_2–O\rangle = 2.473$ Å(2.313 → 2.944 Å)		
		$Z = 4$	$Na_3[O] = 4 + 1$	$\langle Na_3–O\rangle = 2.485$ Å(2.263 → 3.024 Å)		
9	α-$Na_2O \cdot 3B_2O_3$	monoclinic	$Na_1[O] = 5 + 1$	$\langle Na_1–O\rangle = 2.437$ Å(2.240 → 2.630 Å)		181
		$P2_1/c$	$Na_2[O] = 5 + 1$	$\langle Na_2–O\rangle = 2.450$ Å(2.280 → 2.740 Å)		181
		$Z = 6$	$Na_3[O] = 3 + 2$	$\langle Na_3–O\rangle = 2.506$ Å(2.290 → 2.703 Å)		708
10	β-$Na_2O \cdot 3B_2O_3$	monoclinic	$Na_1[O] = 4 + 3$	$\langle Na_1–O\rangle = 2.575$ Å(2.343 → 3.065 Å)		
		$P2_1/c$	$Na_2[O] = 4 + 2$	$\langle Na_2–O\rangle = 2.562$ Å(2.336 → 2.908 Å)		
		$Z = 6$	$Na_3[O] = 4 + 4$	$\langle Na_3–O\rangle = 2.629$ Å(2.237 → 3.130 Å)		
11	$Na_2O \cdot 4B_2O_3$	monoclinic	$Na_1[O] = 4 + 4$	$\langle Na_1–O\rangle = 2.563$ Å(2.259 → 2.926 Å)	1.49	
		$P2_1/a$	$Na_2[O] = 4 + 3$	$\langle Na_2–O\rangle = 2.588$ Å(2.443 → 2.887 Å)	1.40	
		$Z = 4$				
12	$Na_2[B_4O_6(OH)_2]$	orthorhombic	$Na_1[O] = 3 + 3$	$\langle Na_1–O\rangle = 2.529$ Å(2.258 → 2.749 Å)	2.08	
		$Pbca$	$Na_2[O] = 5 + 2$	$\langle Na_2–O\rangle = 2.535$ Å(2.294 → 2.981 Å)	1.76	
		$Z = 8$				

tively with distances ranging from 2.367 to 2.667 Å and 2.240 to 2.676 Å. These results are comparable to those observed in other sodium borates (see Table V). However, Na(3) shows a rather peculiar coordination with three short distances (2.301 to 2.371 Å) on one side and one very long distance (2.960 Å) on the opposite side directed along the monoclinic **a** axis. This oxygen environment around the sodium atom allows a rather large vibrational movement of this atom along the **a** axis. In fact, the anisotropic thermal vibration parameter U_{11} (motion along **a** axis) is indeed very large compared to values of the U_{11} parameters of the other sodium atoms (see Table III and V).

A similar phenomenon was observed for α-NaB_3O_5 (*9*), where a Na(3) atom surrounded by three short and two more distant oxygens shows also a comparatively large U_{11} parameter (Table V). A comparison of the various sodium–oxygen coordinations and distances in the known sodium borates leads to the conclusion that sodium shows no well-determined coordinating behavior, owing to strong ionic bonding, but will adopt an oxygen environment to suit the energy requirements of the structure. This could explain the ability of borate glasses to accommodate an important amount of sodium. However, a tendency to smaller coordination can be noticed in sodium-rich phases.

The mean boron–oxygen distances are 1.379 and 1.378 Å for the two different BO_3 triangles. This result compares well with the corresponding mean bond distances found in $LaMgB_5O_{10}$ (*13*) and $Li_5B_7O_{12.5}Cl$ (*14*).

The average Nd–O and Na–O distances are respectively 2.470 and 2.483 Å, a result close to the sum of the effective ionic radii (*15*), which indicates rather ionic bonds between Nd^{3+}, Na^+, and the BO_3^{3-} groups. This BO_3^{3-} matrix is, on the contrary, highly covalent as illustrated by the short B–O and O–O distances in the triangles.

The neodymium ions have only one nearest neighbor at a distance of 4.1524 Å. This result shows that *Ln–Ln* interactions occur predominantly in pairs. The Nd–Na distances are 3.340, 3.305, and 4.096 Å for Na(1), Na(2), and Na(3), respectively. We can then conclude that the presence of rare-earth ions in this highly covalent matrix should be favorable to interesting optical properties. The influence of the structural features on the crystal field and luminescent properties of sodium neodymium borates will be discussed in a future paper.

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