Crystal Structure of $Na_2M_2(BO_3)_2O$ ($M =$ Al, Ga); Comparison with Other Layered Oxyborates and SiP_2O_7

Gwenaël Corbel[1] and Marc Leblanc

Laboratoire des Fluorures, UPRES-A 6010, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans Cedex 9, France

A new oxyborate $Na_2Ga_2(BO_3)_2O$ is evidenced. The mean crystal structure, determined by X-ray diffraction, is trigonal, space group $P\text{-}31c$ (n°163), $Z = 2$, with $a = 4.855(2)$ Å, $c = 15.441(7)$ Å, $V = 315.2(4)$ Å^3, $R_1 = 0.047$, $wR_2 = 0.123$. The three-dimensional network is built up from the stacking, along the c axis, of infinite $[NaGa_2B_2O_7]_\infty$ sheets, separated by sodium layers. $Na_2Al_2(BO_3)_2O$ is isostructural with $Na_2Ga_2(BO_3)_2O$. Ionic conductivity is expected. © 2000 Academic Press.

Key Words: oxyborate; crystal structure; structural correlations.

INTRODUCTION

The polar orientation of BO_3^{3-} ions in crystals leads to noncentrosymmetric structures (1). This feature, combined with an excellent transparency in UV region and high polarizability, implies that borates are attractive candidates in the search of new nonlinear materials (2, 3). Consequently, the chemistry of borates, oxyborates, hydroxide borates, and fluoride borates has been reinvestigated during the past 10 years. The most interesting frequency doubling compounds are $\beta\text{-}BaB_2O_4$ (BBO) (4), LiB_3O_5 (LBO) (5), and $YAl_3(BO_3)_4$: Nd^{3+} (YAB) (6). A new caesium lithium borate was recently found, $CsLiB_6O_{10}$ (CLBO) (7), and is currently displacing BBO for UV generation. In 1996, G. Aka *et al.* obtained, by the Czochralski technique, large crystals of the acentric oxyborate $Ca_4Gd(BO_3)_3O$ (GdCOB) (8), a promising self-doubling laser host.

We have undertaken the study of several mixed anionic systems. New structural families $Ln_3(BO_3)_2F_3$ (9), $Na_2Ln_2(BO_3)_2O$ (10) ($Ln =$ Sm, Eu, and Gd) and a new nonlinear hydroxide borate $Zn_2(BO_3)(OH)_{0.75}F_{0.25}$ (11) are now evidenced. We have also investigated the Na_2O–Ga_2O_3–B_2O_3 system and crystals of $Na_2Ga_2(BO_3)_2O$ have been obtained. This phase was reported by Rza-Zade *et al.* (12) in 1971, but its structure was still unknown. This paper deals with the synthesis and the crystal structure of this

oxyborate. Structural comparisons with other borates, $Sr_2Be_2(BO_3)_2O$ (SBBO) (13), $AAl_2(BO_3)_2O$ ($A =$ Ca (14), Sr (15, 16), Ba (17)), and SiP_2O_7 (18), are also presented.

One of the referees made us aware of the crystal structure description of $Na_2Al_2(BO_3)_2O$ by K.S. Chang (Ph.D. dissertation, Oregon State University, 1998). This work was not published.

EXPERIMENTAL DETAILS

Crystals of $Na_2M_2(BO_3)_2O$ ($M =$ Al, Ga) grow from the stoichiometric mixture of $1Na_2CO_3$, $1M_2O_3$, and $1B_2O_3$ in platinum tubes. This mixture is heated as follows: 7 h at 700°C (heating rate 2°C/min), 30 h at 1020 or 900°C (heating rate 0.5°C/min) respectively, and cooling at 0.1°C/min. A weight loss, corresponding to the departure of CO_2 from Na_2CO_3, is always observed. For $Na_2Ga_2(BO_3)_2O$, a small amount of impurity Ga_2O_3 can be detected on the X-ray powder diffraction pattern, recorded on a Siemens D501 diffractometer ($CuK\alpha$ radiation, room temperature).

Crystals of $Na_2Ga_2(BO_3)_2O$ were selected by optical examination, and X-ray diffraction data (Table 1) were collected on a Siemens AED2 four-circle diffractometer. The conditions of intensity measurement are reported in Table 1. The unit cell and the space group were obtained from long-exposure rotation photographs. The scattering factors and anomalous dispersion corrections for all atoms were taken from the "International Tables for X-ray Crystallography" (19). Intensities were corrected for absorption with SHELX-76 (20). Structural calculations were performed with SHELXS-86 (21) and SHELXL-93 (22) programs. Structure projections were realized with the program Diamond (23).

It must be noted that the crystal quality is poor. At large diffraction 2θ angles, shoulders are observed on the peak profiles. This feature is probably significant of twinning and to the presence of several crystallites with a lower structural symmetry. The twinning plane was not determined and high-resolution synchrotron diffraction is needed in order to evidence the structural distorsion.

[1]To whom correspondence should be addressed.

TABLE 1
Crystallographic Data and Conditions of Data Collection for $Na_2Ga_2(BO_3)_2O$

Four-circle diffractometer	Siemens AED2
Radiation, temperature	$MoK\alpha$, 293 K
Crystal dimensions (mm^3)	$0.03 \times 0.21 \times 0.19$
Absorption	$\mu = 86.5$ cm^{-1}
A_{min}, A_{max}	0.303, 0.734
Symmetry	Trigonal
Space group	$P\text{-}31c$ (n°163)
Z	2
Parameters	
$\quad a$ (Å)	4.855(2)
$\quad c$ (Å)	15.441(7)
Volume (Å^3)	315.2(4)
Molecular weight	319.04
Calculated density (g/cm^3)	3.361(4)
Secondary extinction factor	3.9(8) 10^{-5}
Weighting scheme	$k = 1$
$w = k/(\sigma^2(F^2) + (0.0719P)^2$	
Number of refined parameters	25
Max Δ/σ	-0.001
Reliability factors R_1; wR_2	0.047; 0.123
Goodness-of-fit	1.19
Max, min heights in the final difference	
$\quad$ Fourier map (eÅ^{-3})	$+2.6$, -1.4
Centering reflections ($2\Theta \approx 30°$)	27
Reflections for refined cell parameters	27 (scans at $\pm\Theta$)
Scan mode $\omega - 2\Theta$ in N steps of $\Delta\omega = 0.035°$	$37 \leq N \leq 43$
Data collection range	$2\Theta \leq 70°$
Aperture	4×4 mm^2
Measured reflections	2598
Minimum h, k, l;	-7 -7 -24;
$\quad$ maximum h, k, l (2 independent sets)	7 7 24
Standard reflections	0 2 5; 2 -2 5; 2 0 -5
Maximum standard intensity variation	3.0
Independent reflections ($I > 2\sigma(I)$)	436
R_{int}	0.017

An optical second-harmonic generation test was performed by the Kurtz–Perry method (24) on a polycrystalline sample of $Na_2Ga_2(BO_3)_2O$ using the 1.06-μm line of a YAG:Nd^{3+} laser. No signal was detected.

The thermal characterizations of $Na_2Al_2(BO_3)_2O$ and $Na_2Ga_2(BO_3)_2O$ were performed by coupled TGA–DTA under argon flow (TA Instruments SDT 2960, heating rate 10°C/min, temperature range 30–1200°C). On heating, only an endothermic peak, corresponding to the melting, can be observed. A large hysteresis for recrystallisation occurs on cooling (Table 5).

The IR spectrum, realized on an ATI MATTSON Genesis series FTIR apparatus, is consistent with the presence of borate groups BO_3^{3-} (lines between 700 and 1250 cm^{-1}) (25).

STRUCTURE DETERMINATION

The structure determination was performed on $Na_2Ga_2(BO_3)_2O$. Reflection conditions ($hh\bar{2}hl$: $l = 2n$) lead

TABLE 2
Atomic Coordinates and Temperature Factors in $Na_2Ga_2(BO_3)_2O$

Atom	Site	x	y	z	SOF	B_{eq}[Å^2]
Ga	4f	1/3	2/3	0.63835(4)	1	1.26(2)
Na(1)	2b	0	0	0	1	1.78(6)
Na(2)	2a	0	0	1/4	1	3.7(1)
O(1)	12i	0.9523(7)	0.6113(8)	0.8946(4)	1	4.3(1)
O(2)	6h	$-0.409(2)$	0.409(2)	1/4	1/3	3.4(3)
B	4f	1/3	2/3	0.1031(6)	1	2.2(1)^a

Note. $B_{eq} = \left(\dfrac{8\pi^2}{3}\right) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ (26).

$^a B_{iso}$.

to the centric $P\bar{3}1c$ (n°163) and acentric $P31c$ (n°159) space groups. The $P\bar{3}1c$ space group was selected for the structure solution. The starting set of atomic coordinates was obtained from the analysis of the Patterson map (Patt option of the SHELXS-86 program). One gallium and two sodium were located respectively on 4f, 2a, and 2b crystallographic sites ($R_1 = 0.204$, with SHELXL-93 refinement program). The positions of boron and oxygen were given by successive refinements and difference Fourier syntheses (SHELXL-93). A statistic disorder, probably correlated with the twinning of the crystals, was observed for oxygen O(2); the site occupation factor (SOF) was refined to 1/3. Secondary extinction and anisotropic or isotropic (boron atoms) thermal parameters were refined, and the final residuals decreased to $R_1 = 0.047$ ($wR_2 = 0.123$). The results are not improved in the $P31c$ space group.

The atomic coordinates and temperature factors are reported in Table 2, the anisotropic displacement parameters are given in Table 3, and the selected interatomic distances are listed in Table 4.

STRUCTURE DESCRIPTION

In the crystal structure of $Na_2Ga_2(BO_3)_2O$, Ga^{3+} cations reside on distorted tetrahedral sites while sodium

TABLE 3
Anisotropic Displacement Parameters in $Na_2Ga_2(BO_3)_2O$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga	0.0135(3)	0.0135(3)	0.0209(4)	0	0	0.0067(2)
Na(1)	0.019(1)	0.019(1)	0.030(2)	0	0	0.009(1)
Na(2)	0.036(2)	0.036(2)	0.067(4)	0	0	0.018(1)
O(1)	0.008(1)	0.014(1)	0.139(5)	$-0.014(2)$	0.004(2)	0.004(1)
O(2)	0.060(8)	0.060(8)	0.020(4)	$-0.008(6)$	$-0.008(6)$	0.036(9)

Note. The anisotropic temperature factor expression is $T = \exp[-2\pi^2((ha^*)^2U_{11} + \cdots + 2hka^*b^*U_{12})]$ (26).

TABLE 4
Selected Interatomic Distances (Å) and Angles (°) in Na$_2$Ga$_2$(BO$_3$)$_2$O

Ga polyhedron
$3 \times$ Ga–O(1) 1.805(3)
$1 \times$ Ga–O(2) 1.836(6)
$\langle$Ga–O$\rangle$ = 1.81 Å

Na(1) polyhedron	Na(2) polyhedron
$6 \times$ Na–O(1) 2.414(4)	$2 \times$ Na–O(2) 2.547(6)
$\langle$Na(1)–O$\rangle$ = 2.414 Å	$6 \times$ Na–O(1) 2.858(5)
	$\langle$Na(2)–O$\rangle$ = 2.78 Å

Borate BO$_3^{3-}$ ion
$3 \times$ B–O(1)   1.369(3)
$3 \times$ O(1)–B–O(1) 119.93(4)

TABLE 5
Cell Parameters, Melting (T_f), and Recrystallization (T_r) Points of Na$_2M_2$(BO$_3$)$_2$O (M = Al, Ga)

	a (Å)	c (Å)	V (Å^3)	$R_{M^{3+}}$ (Å)^a	T_f (°C)	T_r (°C)
Na$_2$Al$_2$(BO$_3$)$_2$O	4.802(7)	15.29(4)	305.2(9)	0.39	1005	905
Na$_2$Ga$_2$(BO$_3$)$_2$O	4.855(2)	15.441(7)	315.2(4)	0.47	880	800

^{a} Values from Ref. (27).

cations Na(1)$^+$ and Na(2)$^+$ are sixfold (regular octahedron) and eightfold (bicapped octahedron (3 + 2 + 3)) coordinated respectively. The mean metal–oxygen distances found in GaO$_4$ tetrahedra ($\langle$Ga–O$\rangle$ = 1.81 Å) and Na(1)O$_6$ octahedra ($\langle$Na(1)–O$\rangle$ = 2.414 Å) are in agreement with the sum of ionic radii given by Shannon (27): Ga^{3+} (0.47 Å), Na$^+$ (1.02 Å in coordination VI), and O^{2-} (1.35 Å). In contrast, the distance $\langle$Na(2)–O$\rangle$ = 2.78 Å is clearly longer than the expected value, 2.53 Å (Na$^+$:1.18 Å in coordination VIII). The corresponding polyhedra are distorted along the

c axis. Boron atoms adopt a triangular coordination. The mean B–O distance, 1.37 Å, is close to that found generally in borates: Na$_2$Gd$_2$(BO$_3$)$_2$O (1.38 Å) (10), K$_2$Ga$_2$(BO$_3$)$_2$O (1.37 Å) (28), and Ca$_4$Gd(BO$_3$)$_3$O (1.38 Å) (8).

Two GaO$_4$ polyhedra, up and down, are connected by O(2) in order to form bitetrahedral entities [Ga$_2$O(1)$_6$ O(2)$_{2/2}$] (Fig. 1). The axis $\bar{3}$ involves a rotation of their O(1)$_3$ bases.

Borate ions define dense layers of flat-lying triangles parallel to the (a, b) plane. In a previous paper (11), we described the stacking of borate layers using (A, B, C) letters, indicative of the relative shift of the layers, and (+) or (−) symbols, associated with the orientation of B–O bonds. This notation is applied to Na$_2$Ga$_2$(BO$_3$)$_2$O and the stacking is /A(+)/A(−)/B(+)/B(−)/. Ga$_2$O$_7$ dimers and BO$_3^{3-}$ triangles share O(1) corners and create cavities occupies by Na(2)$^+$. They build up infinite sheets [NaGa$_2$B$_2$O$_7$]$_\infty$ of

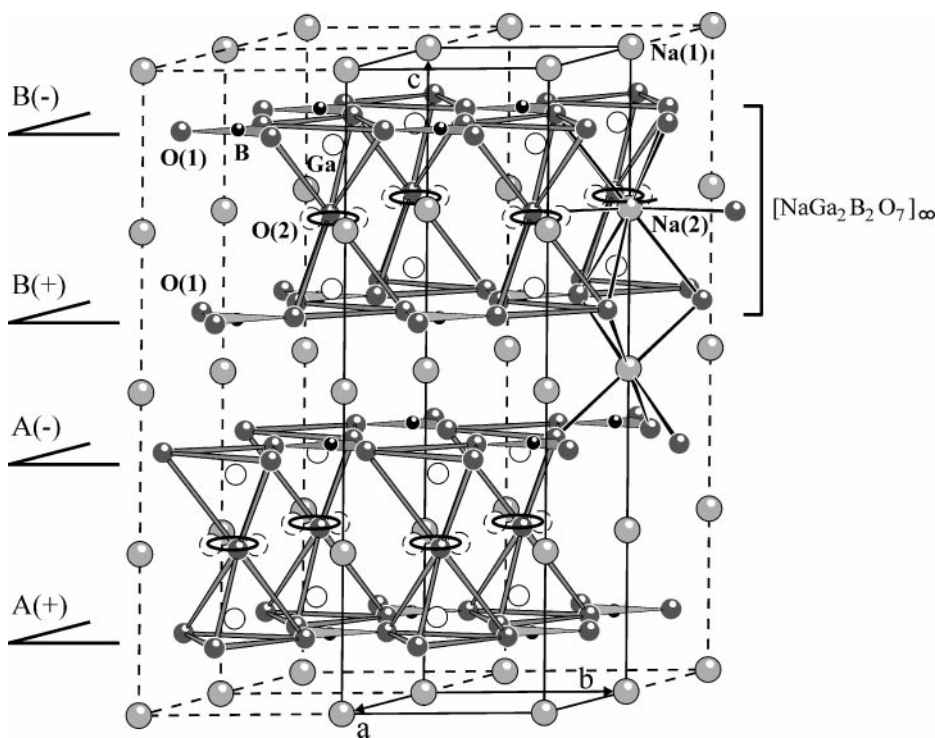**FIG. 1.**   Perspective view of Na$_2$Ga$_2$(BO$_3$)$_2$O. The statistic occupation of O(2) site is materialized by an ellipse.

TABLE 6
Structural Comparison of Oxyborates with $Na_2Ga_2(BO_3)_2O$

Compound	a (Å)	c (Å)	Space group	Sheet formulation (thickness in Å)	Stacking of borate layers	References
$Na_2Ga_2(BO_3)_2O$	4.855(2)	15.441(7)	$P\text{-}31c$ (n°163)	$[NaGa_2B_2O_7]_\infty$ (4.5)	/A(+)/A(−)/B(+)/B(−)/	This work
$Sr_2Be_2(BO_3)_2O$	4.683(3)	15.311(7)	$P\text{-}6c2$ (n°188)	$[SrBe_2B_2O_7]_\infty$ (3.9)	/A(+)/A(+)/A(−)/A(−)/	(13)
$CaAl_2(BO_3)_2O$	4.810(6)	46.633(5)	$R\text{-}3c$ (n°167)	$[[\,]Al_2B_2O_7]_\infty$ (4.7)	/A(+)/B(+)/C(−)/A(−)/B(+)/C(+)/ A(−)/B(−)/C(+)/A(+)/B(−)/C(−)/	(14)
$SrAl_2(BO_3)_2O$	4.893(1)	47.78(1)	$R\text{-}3c$ (n°167)	$[[\,]Al_2B_2O_7]_\infty$ (4.7)	/A(+)/B(+)/C(−)/A(−)/B(+)/C(+)/ A(−)/B(−)/C(+)/A(+)/B(−)/C(−)/	(16)
$BaAl_2(BO_3)_2O$	5.001(2)	24.378(3)	$R32$ (n°155)	$[[\,]Al_2B_2O_7]_\infty$ (4.8)	/A(+)/B(+)/C(+)/A(+)/B(+)/C(+)/	(17)

thickness 4.5 Å, related by the symmetry center. These sheets are separated along the c axis by infinite planes of Na(1)$^+$.

STRUCTURAL CORRELATIONS

It is interesting to compare the structure of $Na_2Ga_2(BO_3)_2O$ and those of other oxyborates: $Sr_2Be_2(BO_3)_2O$ (SBBO) (13), and $AAl_2(BO_3)_2O$ (A = Ca (14), Sr (16), Ba (17)). All these compounds exhibit $[M_2B_2O_7]_\infty$ (M = Be, Al, and Ga) sheets. Their arrangement can be either noncentrosymmetric, in SBBO, or centrosymmetric in aluminum and gallium borates. In $BaAl_2(BO_3)_2O$ (15), the noncentrosymmetric character is

due to the rotation of the tetrahedra which constitute the dimeric units $[Al_2O_7]$. As a consequence, within a $[M_2B_2O_7]_\infty$ sheet, two different layers of boron atoms (A/B, C/A, or B/C) instead of one (A/A or B/B) in $Na_2Ga_2(BO_3)_2O$ and SBBO can be distinguished (Table 6). The difference in stacking of the $[M_2B_2O_7]_\infty$ layers induces a modification of the coordination: Na(1)O$_6$ or AO$_6$ (A = Ca, Sr) octahedra in $Na_2Ga_2(BO_3)_2O$ (Fig. 1) or $CaAl_2(BO_3)_2O$ and $SrAl_2(BO_3)_2O$, or AO$_6$ (A = Sr, Ba) trigonal prisms in $Sr_2Be_2(BO_3)_2O$ (Fig. 2) or $BaAl_2(BO_3)_2O$.

The mean plane of bitetrahedral entities M_2O_7 which contains the apical O(2) atoms can be filled with alkaline or alkaline–earth cations ($Na_2Ga_2(BO_3)_2O$ or
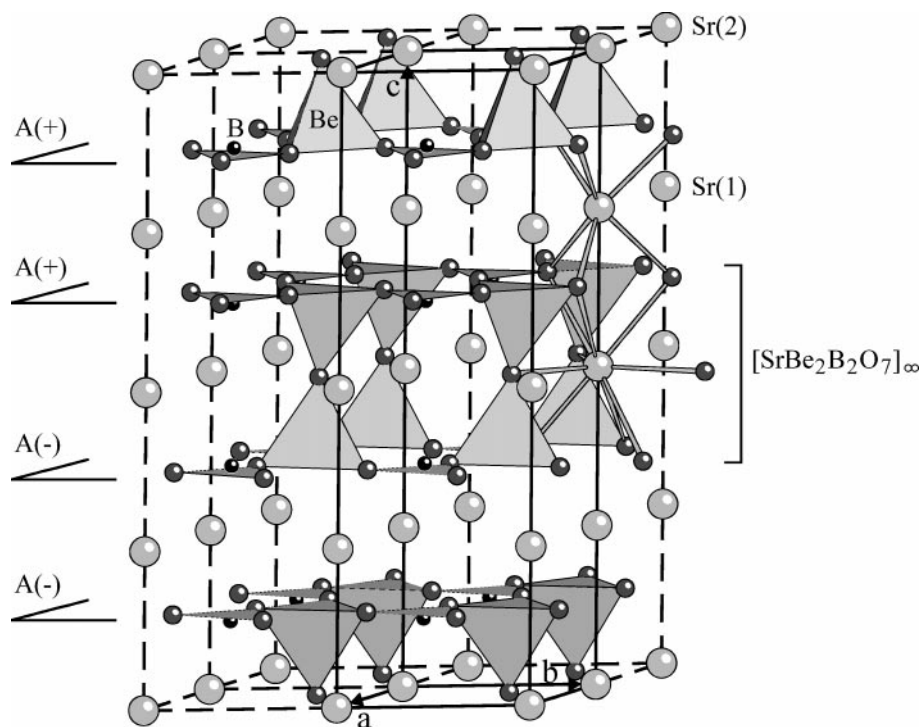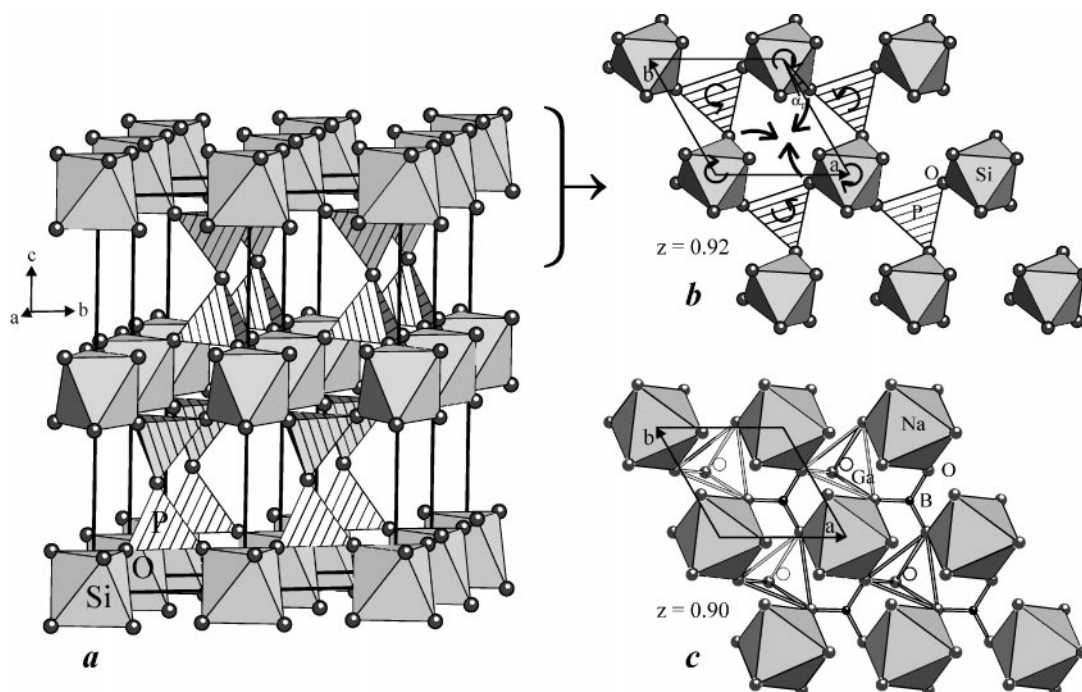

FIG. 2. Perspective view of $Sr_2Be_2(BO_3)_2O$.

FIG. 3. Perspective view of SiP_2O_7 (a) and projection, along the c axis, of the layers of TO_4 tetrahedra (T = P, Ga) and AO_6 octahedra (A = Si, Na) found in SiP_2O_7 (b) and $Na_2Ga_2(BO_3)_2O$ (c).

$Sr_2Be_2(BO_3)_2O)$ and with lone pairs ($Tl_4V_2O_7$ (29) or $K_2Al_2Sb_2O_7$ (30)) or can be lacunar ($CaAl_2(BO_3)_2O$, $SrAl_2(BO_3)_2O$, or $BaAl_2(BO_3)_2O$) (Table 6).

Moreover, the structural arrangement of Ga_2O_7 entities and $Na(1)O_6$ octahedra in $Na_2Ga_2(BO_3)_2O$ can be compared with that found in the hexagonal form of the diphosphate SiP_2O_7 (18). This structure is built up from infinite sheets of P_2O_7 dimers separated along the c axis by layers of SiO_6 octahedra. A perspective view of the SiP_2O_7 structure is given in Fig. 3a. In this structure type, alternating rotations ($\alpha_r \approx 17°$) of the octahedra and tetrahedra around the threefold axis (Fig. 3b) lead to triangles of oxygen atoms. In $Na_2Ga_2(BO_3)_2O$, these sites are occupied by boron atoms (Fig. 3c).

It is worthy of note that $Na_2Ga_2(BO_3)_2O$ and calcite $CaCO_3$ (31) present similar sheets of octahedra, $Na(1)O_6$ or CaO_6, and triangular entities, BO_3^{3-} or CO_3^{2-}, but the most interesting structural feature of this new oxyborate concerns the presence of $[NaM_2O_7]_\infty$ sheets similar to that found in β-alumina (32). In this last compound, ionic conductivity is ensured by the motion of Na^+ ions via a statistical occupancy of several crystallographic sites of NaO planes (33, 34).

CONCLUSION

A new oxyborate $Na_2Ga_2(BO_3)_2O$ is evidenced. The synthesis is achieved by solid state reaction. The structure is

determined by X-ray diffraction from a crystal which is probably twinned. The true cell symmetry is probably lower than trigonal, and high-resolution powder X-ray diffraction is needed in order to evidence the structural distorsion. $Na_2Al_2(BO_3)_2O$ is isostructural with the gallium phase.

The three-dimensional framework is based on double borate layers connected by Ga_2O_7 dimers. They form infinite sheets in which and between which sodium cations are located.

The presence of Na^+ planes, the observation of highly anisotropic displacement parameters for Na(2) and O(1) atoms, and the structural similarity with β-alumina suggest that ionic conductivity can be expected in $Na_2Ga_2(BO_3)_2O$. These properties are investigated by impedance measurements and NMR spectroscopy; the results will be presented in a forthcoming paper.

REFERENCES

1. Y. Xia, *Adv. Mater.* **6,** 510 (1994).
2. P. Becker, *Adv. Mater.* **10** (13), 979 (1998).
3. D. A. Keszler, *Curr. Opin. Solid State Mater. Sci.* **4,** 155 (1999).
4. C. Chen, B. Wu, A. Jiang, and G. You, *Sci. Sinica B* **28,** 235 (1985).

5. C. Chen, Y. Wu, A. Jiang, B. Wu, G. You, R. Li, and S. Lin, *J. Opt. Soc. Am. B* **6,** 616 (1989).
6. T. Y. Fan and R. L. Byer, *IEEE J. Quant. Electr.* **24,** 895 (1988).
7. T. U. Jm and D. A. Keszler, *Mater. Res. Bull.* **30,** 209 (1995).
8. G. Aka, A. Kahn-Harari, D. Vivien, J.-M. Benitez, F. Salin, and J. Godard, *Eur. J. Solid State Inorg. Chem.* **33,** 727 (1996).
9. G. Corbel, R. Retoux, and M. Leblanc, *J. Solid State Chem.* **139,** 52 (1998).
10. G. Corbel, E. Antic-Fidancev, M. Lemaître-Blaise, and M. Leblanc, *J. Solid State Chem.* **144,** 35 (1999).
11. G. Corbel, E. Suard, J. Emery, and M. Leblanc, *J. Alloys Compd.* **305,** 49 (2000).
12. P. F. Rza-Zade, S. G. Guseinova, K. L. Ganf, G. K. Abdullaev, and F. R. Samedov, *Inorg. Mater.* **7,** 1135 (1971).
13. C. Chen, Y. Wang, B. Wu, K. Wu, W. Zeng, and Y. Linhua, *Nature* **373,** 322 (1995).
14. K. S. Chang and D. A. Keszler, *Mater. Res. Bull.* **33,** 299 (1998).
15. D. A. Keszler, *Curr. Opin. Solid State Mater. Sci.* **1,** 204 (1996).
16. F. Lucas, S. Jaulmes, M. Quarton, T. Le Mercier, F. Guillen, and C. Fouassier, *J. Solid State Chem.* **150,** 404 (2000).
17. N. Ye, W. R. Zeng, B. C. Wu, X. Y. Huang, and C. T. Chen, *Z. Kristallogr. NCS* **213,** 452 (1998).
18. D. M. Poojary, R. B. Borade, F. L. Campbell III, and A. Clearfield, *J. Solid State Chem.* **112,** 106 (1994).
19. "International Tables for X-ray Crystallography," Vol. IV. Kynoch Press, Birmingham, 1968.
20. G. M. Sheldrick, SHELX-76: Program for Crystal Structure Determination. Cambridge Univ. Press, Cambridge 1976.
21. G. M. Sheldrick, *in* "Crystallographic Computing 3" (G. M. Sheldrick, C. Krüger, and R. Goddard, Eds.), p. 175. Oxford Univ. Press, Oxford, 1985.
22. G. M. Sheldrick, SHELXL-93, A Program for Crystal Structure Determination, University of Göttingen, 1993.
23. G. Bergerhoff, Diamond "Visual Crystal Structure Information System." Gerhard-Domagk-Str. 1, 53121 Bonn, Germany, 1996.
24. S. K. Kurtz and T. T. Perry, *J. Appl. Phys.* **39,** 3798 (1968).
25. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," Part A, fifth ed. Wiley–Interscience, New York, 1997.
26. B. T. M. Willis and A. W. Pryor, "Thermal Vibrations in Crystallography," Cambridge Univ. Press, Cambridge, 1975.
27. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
28. R. W. Smith, M. A. Kennard, and M. J. Dudik, *Mater. Res. Bull.* **32,** 649 (1997).
29. A. Jouanneaux, O. Joubert, M. Evain, and M. Ganne, *Powder Diffract.* **7,** 206 (1992).
30. C. Hirschle and C. Röhr, *Acta Crystallogr. Sect. C* **56,** 5 (2000).
31. H. Effenberger, K. Mereiter, and J. Zemann, *Z. Kristallogr.* **156,** 233 (1981).
32. G. Yamaguchi and K. Suzuki, *Bull. Chem. Soc. Jpn.* **41,** 93 (1968).
33. G. Aka, *Thesis* Paris, 1988.
34. A. Kahn-Harari, G. Aka, and J. Thery, *J. Solid State Chem.* **91,** 71 (1991).