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Structure Determination of Novel Orthoborate $\mathrm{NaMgBO_3}$: A Promising Birefringent Crystal

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A novel orthoborate, $\mathrm{NaMgBO_3}$, has been successfully synthesized by a standard solid-state reaction, and the crystal structure has been determined from powder X-ray diffraction data. It crystallizes in the monoclinic space group $C2/c$ with lattice parameters $a = 5.01313(6)$ Å, $b = 8.8007(1)$ Å, $c = 5.52831(7)$ Å, and $\beta = 99.6962(6)°$. Isolated $[\mathrm{BO_3}]^{3-}$ anionic groups, which are the fundamental building units, are distributed perfectly parallel to each other. It is a typical structure of big birefringent crystals. The overall structure is similar to that of $\mathrm{NaSrBO_3}$, which crystallizes in $P2_1/c$. The correlation between these two structures is discussed. The Mg atoms in $\mathrm{NaMgBO_3}$ are used instead of the position of Na in $\mathrm{NaSrBO_3}$, while the Na atoms occupy the position of Sr. Then the directions of the $\mathrm{BO_3}$ triangles are changed to balance the bond valence, which leads to a higher symmetry. They are the first pair of alkali–alkaline earth orthoborates with close space groups by exchange of the cation positions.

Introduction

Inorganic borates have long been a focus of research for their variety of structure types, transparency to a wide range of wavelengths, high laser damage tolerance, and high optical quality. Studies on alkali metal and alkaline-earth metal borates have found a large family of compounds with outstanding physical properties,[1,2] such as β-$\mathrm{BaB_2O_4}$,[3] $\mathrm{LiB_3O_5}$,[4] $\mathrm{Sr_2Be_2B_2O_7}$,[5] and $\mathrm{K_2Al_2B_2O_7}$.[6] Recently, with the development of optical communications and the semiconductor large-scale integrated circuit, the demand for birefringent crystals and nonlinear optical (NLO) crystals in the deep-UV band is soaring. A variety of BO atomic groups are considered to be a dominant factor for their physical properties, in particular the optical properties of borates. Among the various anionic groups, the planar $[\mathrm{BO_3}]^{3-}$ groups attract our attention. Because of highly localized valence electrons, low absorption (173 nm)[5] and anisotropy polarizability indicate that some borates are likely to be good candidates for future birefringent and deep-UV nonlinear optical materials. Therefore, we have investigated the system $\mathrm{M_2O{-}M'O{-}B_2O_3}$ (M $=$ Li, Na, K; M′ $=$ Mg, Ca, Sr, Ba) to search for such new useful optical materials. A total of 12 compounds, $\mathrm{LiCaBO_3}$,[7] $\mathrm{Li_4CaB_2O_6}$,[8] $\mathrm{LiSr_4(BO_3)_3}$,[9] $\mathrm{NaCaBO_3}$,[10] $\mathrm{NaCa_4(BO_3)_3}$,[11] $\mathrm{NaSrBO_3}$,[12] $\mathrm{NaSr_4(BO_3)_3}$,[9] $\mathrm{Na_3SrB_5O_{10}}$, $\mathrm{NaSrB_5O_9}$, $\mathrm{NaBa_4(BO_3)_3}$,[9] $\mathrm{KCa_4(BO_3)_3}$,[11] and $\mathrm{KSr_4(BO_3)_3}$,[11] have been synthesized successfully, and their powder X-ray diffraction (XRD) patterns had been submitted for publication in the Powder Diffraction File (International Centre for Diffraction Data) in 2003 and 2004. In this paper, we report another new orthoborate, $\mathrm{NaMgBO_3}$, in the system $\mathrm{Na_2O{-}MgO{-}B_2O_3}$. It had been mentioned 40 years ago, but the crystal structure

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[†] Nankai University.

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(1) Becker, P. *Adv. Mater.* **1998**, *10*, 979−992.

(2) Chen, C. T.; Ye, N.; Lin, J.; Jiang, J.; Zeng, W.; Wu, B. *Adv. Mater.* **1999**, *11*, 1071−1078.

(3) Chen, C. T.; Wu, B.; Jiang, A.; You, G. *Sci. China, Ser. B: Chem.* **1985**, *18*, 235−243.

(4) Chen, C. T.; Wu, Y.; Jiang, A.; Wu, B.; You, G.; Li, R.; Lin, S. *J. Opt. Soc. Am. B* **1989**, *6*, 616−621.

(5) Chen, C. T.; Wang, Y.; Wu, B.; Wu, K.; Zeng, W.; Yu, L. *Nature* **1995**, *373*, 322−324.

(6) Hu, Z.; Higashiyama, T.; Yoshimura, M.; Mori, Y.; Sasaki, T. *Z. Kristallogr.* **1999**, *214*, 433−434.

(7) Wu, L.; Chen, X. L.; Li, H.; He, M.; Dai, L.; Li, X. Z.; Xu, Y. P. *J. Solid State Chem.* **2004**, *177*, 1111−1116.

(8) Wu, L.; Wang, C.; Chen, X. L.; Li, X. Z.; Xu, Y. P.; Cao, Y. G. *J. Solid State Chem.* **2004**, *177*, 1847−1851.

(9) Wu, L.; Chen, X. L.; Li, H.; He, M.; Xu, Y. P.; Li, X. Z. *Inorg. Chem.* **2005**, *44*, 6409−6414.

(10) Wu, L.; Chen, X. L.; Li, X. Z.; Dai, L.; Xu, Y. P.; Zhao, M. *Acta Crystallogr. C* **2005**, *61*, i32−i34.

(11) Wu, L.; Chen, X. L.; Xu, Y. P.; Sun, Y. P. *Inorg. Chem.* **2006**, *45*, 3042−3047.

(12) Wu, L.; Chen, X. L.; Zhang, Y.; Kong, Y. F.; Xu, J. J.; Xu, Y. P. *J. Solid State Chem.* **2006**, *179*, 1219−1224.

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was not given.[13] It crystallizes in the space group $C2/c$ and contains atoms with close atomic numbers, Na and Mg, which are difficult to distinguish from XRD. In this work, the method to discern them by the SDPD (Structure Determination from Powder Diffraction) method was introduced. Isolated planar $[BO_3]^{3-}$ anionic groups were found as the fundamental building units, which are distributed perfectly parallel to each other. When the cations are only alkali and alkaline-earth metals, linear optical properties of borates are determined mainly by the anionic groups.[5,14,15] In $NaMgBO_3$, which contains only light cations, the optical anisotropy will mainly come from $[BO_3]^{3-}$ groups,[15−17] which means that it is a typical structure for big birefringence. It was found that the structure of $NaMgBO_3$ had a close relationship with $NaSrBO_3$,[12] which was also discussed here.

Experimental Section

Solid-State Syntheses. Polycrystalline $NaMgBO_3$ samples were prepared by sintering at high temperature through solid-state reactions. Stoichiometric mixtures of high-purity Na_2CO_3 (analytical reagent, AR), MgO (AR), and H_3BO_3 (>99.99%) were heated at 600 °C in platinum crucibles to decompose the carbonate and eliminate the water and then elevated to sintering temperatures of 800 °C for 72 h. Between sintering steps, the samples were cooled and ground. Then pure $NaMgBO_3$ powder was obtained and characterized by powder XRD.

Data Collection and Structure Determination. The data of $NaMgBO_3$ used for structure determination and Rietveld refinement were collected by a step scan mode with a step width of $2\theta = 0.02°$ and a sampling time of 1 s in the range of 10−140° at room temperature. Additional technical details are given in Table 1. The diffraction patterns of the compound were indexed using DICVOL91.[18] This gave a monoclinic unit cell with $a = 5.01313(6)$ Å, $b = 8.8007(1)$ Å, $c = 5.52831(7)$ Å, and $\beta = 99.6962(6)°$. On the basis of the systematic absence of hkl with $h + k = 2n + 1$, $h0l$, $h00$, and $00l$ with $h = 2n + 1$ and $l = 2n + 1$, and $0k0$ with $k = 2n + 1$, the possible space groups are Cc and $C2/c$. Because the latter had a higher symmetry, it was tested first.

The whole pattern of $NaMgBO_3$ was fitted using the Fullprof program[19] based on the Le Bail method[20] with the possible space group $C2/c$. The final agreement factors converged to $R_p = 5.89\%$, $R_{wp} = 8.20\%$, and $R_{exp} = 2.82$. A total of 187 independent $|F_o|$ values were extracted. Lattice parameters were refined as $a = 5.01316(2)$ Å, $b = 8.80100(4)$ Å, $c = 5.52866(2)$ Å, and $\beta = 99.6971(1)°$. Direct methods were applied with the *SHELXL97* program package[21] to the extracted $|F_o|$. According to the atom distances, three peaks listed in the E map were likely to correspond to the correct positions of the atoms, in which one was assigned to the Mg atom, one was assigned to the Na atom, and the other was assigned to an O atom. The other atoms were located by using difference Fourier synthesis. In this course, once an atom was located, it would be used for the next run of difference Fourier synthesis. Because of the similar scattering factors of Na and Mg atoms, there was not much influence on the following difference Fourier synthesis even if their positions were mistaken at the first step. After the rough structure was obtained, a bond valence sum (BVS) calculation[22] was used to determine their reasonable positions, respectively. Then the structure was refined using the Rietveld method[23,24] within the Fullprof program. In the final cycle of refinement, a total of 30 parameters were refined (11 structural parameters and 19 profile parameters, including 5 background parameters and 5 peak-shape parameters). The pseudo-Voigt function was used as the peak-shape function, and the final agreement factors converged to $R_B = 2.57\%$, $R_p = 5.48\%$, $R_{wp} = 7.65\%$, and $R_{exp} = 2.81\%$. Lattice parameters were refined to be $a = 5.01313(6)$ Å, $b = 8.8007(1)$ Å, $c = 5.52831(7)$ Å, and $\beta = 99.6962(6)°$. The final result was put into the *PLATON* program package,[25] and no additional symmetry was found. The other possible space group Cc was also tried for structure determination. However, no better result was obtained. Then the final space group was determined as $C2/c$. The final refinement pattern is given in Figure 1. The crystallographic data, fractional atomic coordinates, and equivalent isotropic displacement parameters are reported in Tables 1 and 2; significant bond lengths and angles are listed in Table 3.

Table 1. Crystallographic Data, Experimental Details of the Powder XRD, and Rietveld Refinement Data for $NaMgBO_3$[a]

chemical formula	$NaMgBO_3$
fw	106.105
cryst syst	monoclinic
space group	$C2/c$
a (Å)	5.01313(6)
b (Å)	8.8007(1)
c (Å)	5.52831(7)
V (Å^3)	240.42(8)
Z	4
d_c (g cm^{-3})	2.931
diffractometer	D/Max 2500, Rigaku
radiation type	Cu Kα
wavelength (Å)	1.5418
profile range (2θ, deg)	10−140
step size (2θ, deg)	0.02
no. of observation (N)	6501
no. of contributing reflns	467 ($K\alpha_1 + K\alpha_2$)
no. of structure param (P_1)	11
no. of profile param (P_2)	19
R_{Bragg} (%)	2.57
R_p (%)	5.48
R_{wp} (%)	7.65
R_{exp} (%)	2.81

[a] $R_p = \Sigma|y_{io} - y_{ic}|/\Sigma|y_{io}|$, $R_{wp} = [\Sigma w_i(y_{io} - y_{ic})^2/\Sigma w_i y_{io}^2]^{1/2}$, and $R_{exp} = [(N - P_1 - P_2)/\Sigma w_i y_{io}^2]^{1/2}$.

Results and Discussion

Description of Crystal Structures. The $NaMgBO_3$ compound crystallizes in the space group $C2/c$. As illustrated in parts a and b of Figure 2, the fundamental building units of $NaMgBO_3$ are isolated planar $[BO_3]^{3-}$ anionic groups, which are distributed perfectly parallel. Because of the anisotropy

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(13) Wanmaker, W. L.; Bril, A.; ter Vrugt, J. W. *J. Electrochem. Soc.* **1965**, *112*, 1147−1150.

(14) Lin, Z. S.; Lin, J.; Wang, Z. Z.; Chen, C. T. *Phys. Rev. B* **2000**, *62*, 1757−1764.

(15) Lin, Z. S.; Wang, Z. Z.; Chen, C. T.; Lee, M. H. *J. Appl. Phys.* **2001**, *90*, 5585−5590.

(16) Wang, D. S. *Bull. Mater. Sci.* **2003**, *26*, 159−163.

(17) Li, J.; Duan, C. G.; Gu, Z. Q.; Wang, D. S. *Phys. Rev. B* **1998**, *57*, 6925−6932.

(18) Boultif, A.; Louer, D. *J. Appl. Crystallogr.* **1991**, *24*, 987−993.

(19) Rodriquez-Carvajal, J.; Fernadez-Diaz, M. T.; Martinez, J. L. *J. Phys. Condens. Matter* **1991**, *3*, 3215−3234.

(20) Le Bail, A.; Duroy, H.; Fourquet, J. L. *Mater. Res. Bull.* **1988**, *23*, 447−452.

(21) Sheldrick, G. M. *SHELXS97* and *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(22) Brown, I. D.; Altermatt, D. *Acta Crystallogr. B* **1985**, *41*, 244−247.

(23) Rietveld, H. M. *Acta Crystallogr.* **1967**, *22*, 151−152.

(24) Rietveld, H. M. *J. Appl. Crystallogr.* **1979**, *12*, 483−485.

(25) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7−13.

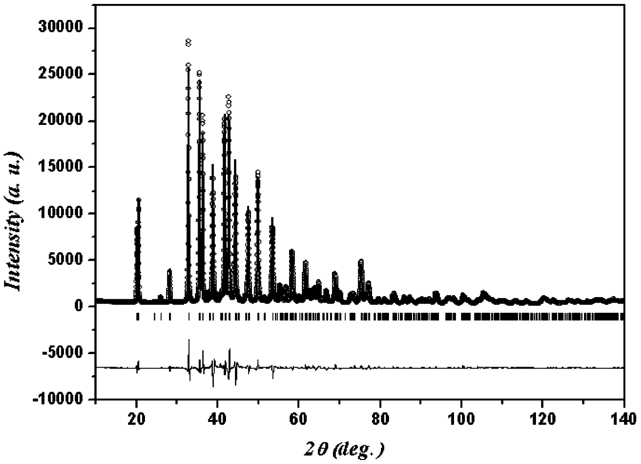

Figure 1. Final Rietveld refinement plots of NaMgBO$_3$. Small circles (○) correspond to experimental values, and the continuous lines, the calculated pattern. Vertical bars (|) indicate the positions of the Bragg peaks. The bottom trace depicts the difference between the experimental and calculated intensity values.

Table 2. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for NaMgBO$_3$

	site	*x*	*y*	*z*	U_{eq}
Mg	4a	0.000 00	0.000 00	0.000 00	0.008 05(7)
Na	4e	0.000 00	0.336 00(6)	0.250 00	0.013 54(9)
O1	8f	0.226 59(7)	0.588 74(3)	0.206 04(7)	0.009 80(9)
O2	4e	0.000 00	−0.179 40(6)	0.250 00	0.010 3(1)
B	4e	0.000 00	−0.330 2(1)	0.250 00	0.014 9(2)

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for NaMgBO$_3$^{a}

Mg−O1^{v}	2.0765(3)	Na−O1^{i}	2.5278(6)
Mg−O1^{vi}	2.0927(3)	Na−O1^{ii}	2.5278(6)
Mg−O1^{vii}	2.0765(3)	Na−O1^{iii}	2.6684(4)
Mg−O1^{viii}	2.0927(3)	Na−O1^{iv}	2.6684(4)
Mg−O2^{i}	2.0983(4)	Na−O1^{v}	2.5614(5)
Mg−O2^{iii}	2.0983(4)	Na−O1^{vi}	2.5614(5)
		Na−O2^{v}	2.5102(1)
		Na−O2^{v}	2.5102(1)
B−O1^{i}	1.3969(7)	O1^{i}−B−O1^{ii}	118.573(5)
B−O1^{ii}	1.3969(7)	O1^{i}−B−O2^{i}	120.713(7)
B−O2^{i}	1.327(1)	O1^{ii}−B−O2^{i}	120.713(7)

[a] i, *x*, *y*, *z*; ii, −*x*, *y*, −*z* + $^1/_2$; iii, −*x*, −*y*, −*z*; iv, *x*, −*y*, *z* + $^1/_2$; v, *x* + $^1/_2$, *y* + $^1/_2$, *z*; vi, −*x* + $^1/_2$, *y* + $^1/_2$, −*z* + $^1/_2$; vii, −*x* + $^1/_2$, −*y* + $^1/_2$, −*z*; viii, *x* + $^1/_2$, −*y* + $^1/_2$, *z* + $^1/_2$.

polarizability of planar BO$_3$ groups, it is likely to be a big birefringent crystal. The B−O bond lengths vary from 1.327(1) to 1.3969(7) Å with an average value of 1.374 Å, and the O−B−O angles are between 118.573(5)° and 120.713(7)°. These values are normal in a BO$_3$ plane triangle. The Mg atom is coordinated with six O atoms to form an octahedron, as illustrated in Figure 3a. Those MgO$_6$ octahedra are face-sharing each other to form infinitely long chains along the *c* axis and are corner-sharing with the adjacent BO$_3$ triangles. The coordination surroundings of the Na atoms are shown in Figure 4a,b. There are 10 O atoms around the Na atom, in which 8 are at a reasonable distance [between 2.5102(1) and 2.6684(4) Å] from the Na atom and the other two are at a longer distance [3.0887(3) Å]. The longest distance between the Na and B atoms is only 2.938(1) Å. It is illogical for a longer distance from the cations to the coordination anions than to the neighboring cations to exist.

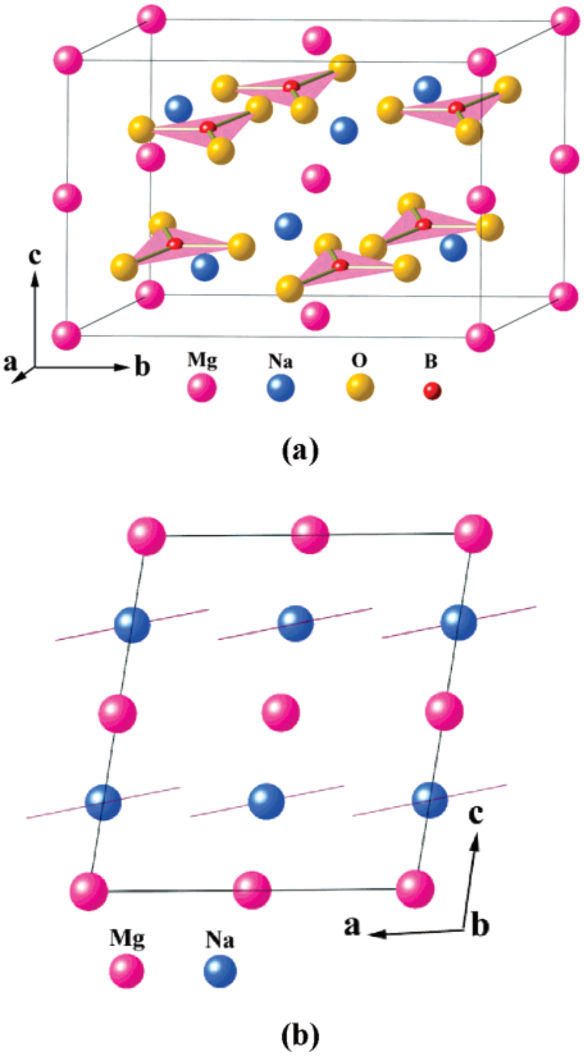

Figure 2. Structure projection of NaMgBO$_3$ viewed along [100] (a) and [010] (b). The short lines are the side faces of the planar BO$_3$ triangles (b).

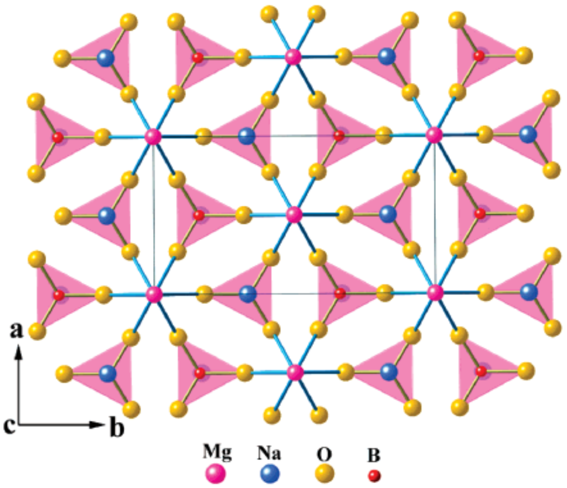

Figure 3. Coordination environments of Mg with O atoms. The triangles are BO$_3$ groups.

On the other hand, if the O atoms with a longer distance are also taken into account as the coordination atoms, the Na−O polyhedra will have to share faces with each other, which is obviously not as stable as edge-sharing in a compound. So, the Na atom should be neighbored by eight O atoms, which

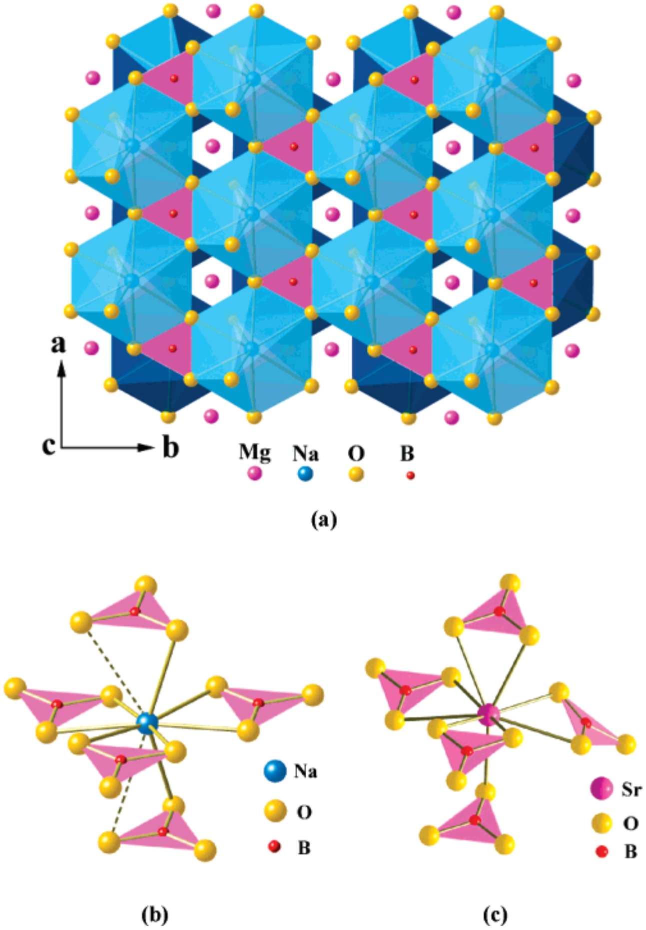

Figure 4. (a) Coordination environments of Na with O atoms. The isolated spheres stand for Mg atoms. The polyhedra are the NaO_8 dodecahedra in the upper and lower layers. The triangles are BO_3 groups. (b and c) Coordination surroundings of Na atoms in $NaMgBO_3$ (b) and Sr atoms in $NaSrBO_3$ (c). The slim dotted lines are the suspicious bonds.

form distorted dodecahedra. The NaO_8 polyhedra are connected to each other by corners along the directions parallel to the *ab* plane and by edges along the perpendicular directions and share corners or edges with the adjacent planar BO_3 triangles. The MgO_6 and NaO_8 polyhedra share bridging O atoms with each other to form an infinite three-dimensional network. The overall structure of $NaMgBO_3$ is similar to that of β-K_2CO_3,[26] which also contains chains of face-sharing octahedra, KO_6, linked by 10-coordinate K atoms and triangular CO_3 groups.

BVS Calculation. To provide a check on the consistency of the structure determination, the bond valences have been calculated according to the Brown and Altermatt parameters[22] for the structure of $NaMgBO_3$ and are listed in Table 4. It is obvious that the sums of the bond valences are reasonable for both cations and O atoms. However, if the O atoms with a longer distance from Na are also considered as the coordination atoms, the BVSs for Na and O2 will have a larger deviation from the normal values. This is another reason why they are not considered as the coordination atoms for Na.

Table 4. Mg−O, Na−O, and B−O Bond Valences in $NaMgBO_3$[a]

	O1	O2	ΣS
Mg	0.355 × 2 0.340 × 2	0.334 × 2	2.058
Na	0.141 × 2 0.096 × 2 0.129 × 2	0.148 × 2 0.031 × 2^b	1.028 1.090^b
B	0.932 × 2	1.126	2.990
ΣS	1.993	2.090 2.152^b	

[a] The sums of bond valences for O1 only account for one of those numbers without multiple 2, according to the coordination numbers. [b] These numbers are suspicious bond valences in the compound.

Comparison of the Structures of $NaMgBO_3$ and $NaSrBO_3$. Up to now, eight orthoborates were found in $M_2O-M'O-B_2O_3$ (M = Li, Na, K; M′ = Mg, Ca, Sr, Ba) systems. Because alkali and alkaline-earth metals are very active, most of them are crystallized in different structures.[7,10,12,27−29] However, it is interesting to find the close relationship between the structures of $NaMgBO_3$ and $NaSrBO_3$.[12] $NaSrBO_3$ crystallizes in monoclinic space group $P2_1/c$ (No. 14), while $NaMgBO_3$ crystallizes in $C2/c$ (No. 15). In $NaSrBO_3$, the $[BO_3]^{3-}$ anionic groups are distributed parallel along two different directions. Na atoms are coordinated by six O atoms, and Sr atoms are nine-coordinated. When Na is replaced by Mg and Sr is replaced by Na, $NaMgBO_3$ is formed. However, the different valences of the alkali metal and alkaline-earth metal cations ask for the changing direction of the BO_3 groups to improve the bond valence of the position occupied from Na^+ to Mg^{2+} and, at the same time, reduce the bond valence of another position occupied from Sr^{2+} to Na^+. Then the BO_3 triangles distribute perfectly parallel to each other and form a structure with higher symmetry. The only difference between the coordination polyhedra of the two compounds is SrO_9 and NaO_8, which can be seen from Figure 4, panels b and c. It comes from the change of the distances between the cations and the O atoms, which also leads to a change in the coordination environment of the O atoms. O1 atoms seem to have the same coordination environment in both of the two compounds, but the surrounding cations of the O2 atoms have a little bit of change. There are three Sr and two Na atoms around O2 in $NaSrBO_3$, while only two Mg and two Na atoms are a suitable distance from O2 in $NaMgBO_3$. The structural change from $NaSrBO_3$ to $NaMgBO_3$ is similar to the phase transition of K_2CO_3[26] from room temperature to a higher temperature.

Conclusions

A novel orthoborate $NaMgBO_3$, which contains atoms with close atomic numbers, was synthesized by a solid-state reaction, and the structure was solved from powder XRD data. Isolated planar $[BO_3]^{3-}$ anionic groups were found as fundamental building units, which were distributed perfectly

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(26) Becht, H. Y.; Struikmans, R. *Acta Crystallogr. B* **1976**, *32*, 3344−3346.

(27) Norrestam, R. *Z. Kristallogr.* **1989**, *187*, 103−110.

(28) Cheng, W. D.; Zhang, H.; Lin, Q. S.; Zheng, F. K.; Chen, J. T. *Chem. Mater.* **2001**, *13*, 1841−1847.

(29) Kononova, N. G.; Kokh, A. E.; Bekker, T. B.; Furmanova, N. G.; Maksimov, B. A.; Molchanov, V. N.; Fedorov, P. P. *Kristallogr.* **2003**, *48*, 1114−1116.

parallel. Because of the anisotropic polarizations of planar BO_3 groups, a considerable birefringence can be expected. It is found that the structure of $NaMgBO_3$ has a close relationship with that of $NaSrBO_3$ by exchange of the positions of the alkali metal and alkaline-earth metal atoms. The directions of the BO_3 planar triangles were changed to adjust the bond valences, which leads to a higher symmetry in $NaMgBO_3$ than in $NaSrBO_3$. BVS calculation was used to verify the validity of the structure and give an explanation of eight-coordinated Na atoms in the new compound.

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Supporting Information Available: CIF file for $NaMgBO_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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