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$(K_{1-x}Na_x)_2Al_2B_2O_7$ with $0 \leq x < 0.6$: A Promising Nonlinear Optical Crystal

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Up to about 60% K^+ in $K_2Al_2B_2O_7$ (KABO), a well-known nonlinear optical material, can be substituted by Na^+ with the structure type being retained. AlO_4 tetrahedra and BO_3 triangles in the Na-substituted compound tilt to adjust to the local distribution of alkali-metal atoms, which explains the large range of homogeneity. When the Na^+ substitution is higher than 50%, the decomposition and volatility of KABO are strongly inhibited and the sample melts congruently at about 940 °C, which makes it possible to grow bulk crystals from the melt directly. The second harmonic generation property of $KNaAl_2B_2O_7$ is close to that of KABO. Taking the crystal growth into account, $(K_{1-x}Na_x)_2Al_2B_2O_7$ ($0 \leq x < 0.6$) seems to be a more promising nonlinear optical material than KABO.

Introduction

Much interest has been focused on searching for new nonlinear optical materials in the borates. Besides the widely used β-BaB_2O_4 (BBO),[1] LiB_3O_5 (LBO),[2] and $CsLiB_6O_{10}$ (CLBO),[3] several other compounds, namely, $KBe_2BO_3F_2$ (KBBF),[4] $Sr_2B_2Be_2O_7$ (SBBO),[5] $BaAl_2B_2O_7$ (BABO),[6] and $K_2Al_2B_2O_7$ (KABO),[7,8] have been proposed to be promising nonlinear optical materials. However, it is very difficult to grow crystals of KBBF, SBBO, and BABO with large size and good quality for nonlinear optical applications.[8] Although it is easier to grow bulk KABO crystals of optical quality, the decomposition below its melting point makes it necessary to grow crystals using a flux method.[9] After several years of work in crystal growth,[7−15] KABO crystals with dimensions of 50 × 20 × 17 mm^3 have been obtained with a top-seeded solution growth (TSSG) method.[9] Ultraviolet pulses at 193 nm were generated with a KABO crystal.[14]

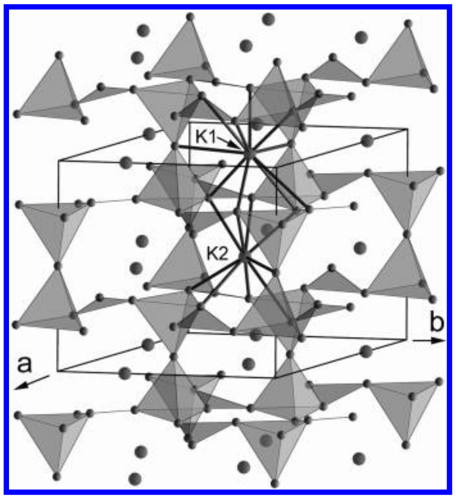

Figure 1. Perspective view of the structure of $K_2Al_2B_2O_7$. Transparent tetrahedra and triangles represent AlO_4 and BO_3 groups, respectively. Small gray balls at the vertexes of polyhedra depict oxygen atoms, and large gray balls represent potassium atoms. Sticks are used to illustrate the coordination of potassium by oxygen atoms.

KABO crystallizes in space group *P*321 (No. 150) and consists of planar $[BO_3]^{3-}$ groups and $[Al_2O_7]^{8-}$, which is built from two $[AlO_4]^{5-}$ tetrahedra sharing one vertex (see Figure 1).[16] Its Na[17,18] and Rb[19] analogues were also synthesized and structurally characterized. Although they display structural features similar to those of KABO, namely,

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Table 1. Crystallographic Data and Details of Structure Determination for $(K_{0.48(2)}Na_{0.52(2)})_2Al_2B_2O_7$

Crystal Data	
$(K_{0.48(2)}Na_{0.52(2)})_2Al_2B_2O_7$	Mo Kα radiation
$M_r = 249.01$	cell params from all reflns
trigonal, *P*321 (No. 150)	$\theta = 2.51-32.04°$
$a = 8.3887(6)$ Å	$\mu = 1.113$ mm^{-1}
$c = 8.0804(8)$ Å	$T = 293$ (2) K
$V = 492.44(7)$ Å^3	bulk, colorless
$Z = 3$	$0.180 \times 0.140 \times 0.120$ mm
$D_x = 2.519$ Mg m^{-3}	
Data Collection	
Stoe IPDS II diffractometer	$R_{int} = 0.0311$
ω scan	$R_\sigma = 0.0209$
abs correction: numerical	$\theta_{max} = 31.95°$
$T_{min} = 0.8948$, $T_{max} = 0.9355$	
5917 measured reflns	$h = -12 \rightarrow +12$
1147 independent reflns	$k = -11 \rightarrow +11$
1056 reflns with $> 2\sigma(I)$	$l = -12 \rightarrow +12$
Refinement	
refinement on F^2	
$R[F^2 > 2\sigma(F^2)] = 0.0304$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.0713$	$\Delta\rho_{max} = 0.403$ e Å^{-3}
$S = 1.088$	$\Delta\rho_{min} = -0.355$ e Å^{-3}
1147 reflns	twin laws: (100, 010, 00 −1)
73 params	fraction of twin component: 0.511(3)
$\omega = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.1138P]$, where $P = (F_o^2 + 2F_c^2)/3$	Flack param: 0.0(1) extinction correction: none

both containing $[BO_3]^{3-}$ and $[Al_2O_7]^{8-}$ groups, their structures are quite different from that of KABO. They crystallize in centrosymmetric space groups $P\bar{3}1c$ and $P2_1/c$, for $Na_2Al_2B_2O_7$ and $Rb_2Al_2B_2O_7$, respectively. Inspired by CLBO, we tried to combine different alkali-metal cations to get new structure types with the composition $M_2Al_2B_2O_7$ (M = alkali-metal cation). Here we report the results of our studies on the pseudobinary system $Na_2Al_2B_2O_7-K_2Al_2B_2O_7$.

Experimental Section

Polycrystalline $(K,Na)_2Al_2B_2O_7$ samples were prepared by solid-state reaction using a mixture of analytically pure K_2CO_3, Na_2CO_3, Al_2O_3, and H_3BO_3 in the appropriate ratio as starting materials. The mixture was ground in an agate mortar, preheated at 400 °C for about 10 h, and then sintered at 800 °C for several days. X-ray powder diffraction was used to identify the product. Single crystals were obtained by slowly cooling a melt of $(K_{0.5}Na_{0.5})_2Al_2B_2O_7$ in a Pt crucible. The heating scheme of the single-crystal growth was as follows: the temperature was first raised to 1000 °C, held for 3 h, and then decreased to 900 °C at a rate of 2 °C/h, to 760 °C in 24 h, and at last to room temperature in the furnace with the power turned off.

Powder diffraction measurements were performed using a Rigaku D/Max-2400 diffractometer equipped with a graphite monochromator and/or a Stoe Stadi powder diffraction system equipped with an incident beam curved germanium monochromator. Two different datasets for Rietveld refinement were collected in reflection mode and/or Debye−Scherrer geometry with the Rigaku and Stoe instruments, respectively. Cu radiation was used in both cases. Fullprof[20] was used to perform the Rietveld refinement.

Single-crystal diffraction data were collected with a Stoe IPDS system. Details can be found in Table 1. The single-crystal refinement was performed with the program Shelxl97.[21]

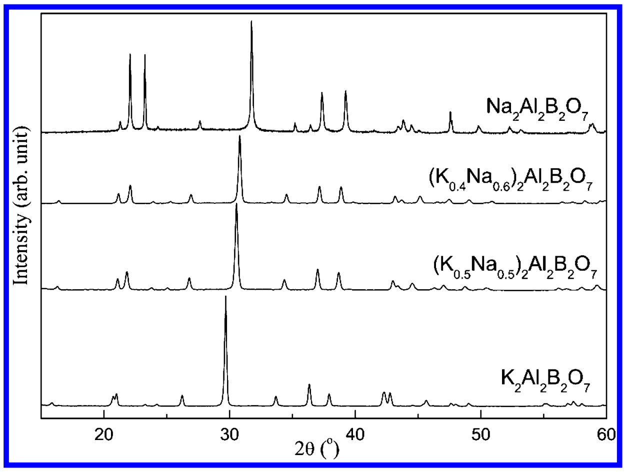

Figure 2. Powder patterns of $(K_{1-x}Na_x)_2Al_2B_2O_7$ (x = 0, 0.5, and 0.6) and $Na_2Al_2B_2O_7$.

DTA and TGA experiments were performed employing a CP-G differential thermal analyzer. The heating rate was 10 °C/min, and the interval ranged from room temperature to 1100 °C.

Results and Discussion

Neither a new structure type nor an obvious range of homogeneity at the $Na_2Al_2B_2O_7$ side was observed in the pseudobinary system $Na_2Al_2B_2O_7-K_2Al_2B_2O_7$. However, a large range of homogeneity was evidenced at the $K_2Al_2B_2O_7$ side. According to our powder diffraction measurements (see Figure 2), up to about 60% K^+ can be substituted by Na^+. The powder patterns of the Na^+-containing phases could be indexed with high figures of merit for hexagonal unit cells similar to that of KABO.

As mentioned above, $M_2Al_2B_2O_7$ (M = alkali-metal cation) compounds adopt different structure types for different cations. It is puzzling that the KABO-type structure can be retained with more than 50% K^+ being substituted by Na^+. To find the reasons for this, we tried to investigate structural changes of $(K_{1-x}Na_x)_2Al_2B_2O_7$ ($0 \leq x < 0.6$) resulting from the substitution. Attempts were first made with Rietveld techniques. Two different powder diffraction datasets were collected with great care. K^+ cations in KABO are located in two different crystallographic positions, 3e and 3f, for K1 and K2, respectively (see Figure 1). K1 and K2 are coordinated by 10 and 9 oxygen atoms, respectively, which are also the vertexes of AlO_4 tetrahedra and BO_3 triangles. We suppose Na^+ cations statistically occupy the same sites as K^+ denoted as Na1 and Na2, respectively. With the structure of KABO[16] as the starting model, Rietveld refinements converged to good residual values on both datasets. Despite the low residual values and good fit of experimental and calculated patterns, the interatomic distances were not reasonable at all. For example, the Al−O distances range from 1.03 to 2.61 Å. Then we turned to single-crystal analysis. In the refinements, we found that the structure should be inverted and the crystal was merohedrally twinned by a mirror perpendicular to the c axis. With anisotropic displacement parameters (ADPs) at all atomic

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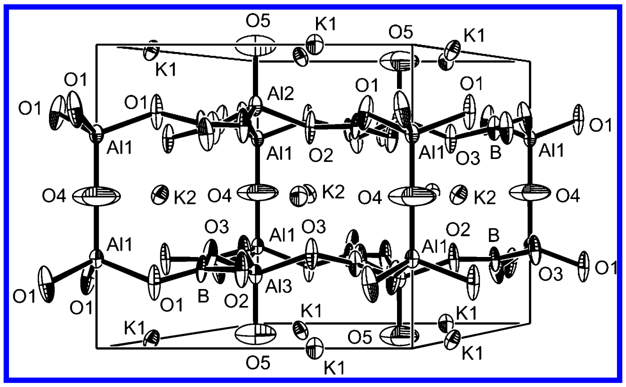

Figure 3. Perspective view of the structure model obtained by refining all atoms anisotropically. The displacement ellipsoids are drawn at 50% probability.

sites, *R* values at last decreased to 3.46% and 6.70%, for R1 and wR2, respectively. Despite the quite low *R* factors, the resulting interatomic distances and displacement parameters are still questionable. A perspective view of the structure model obtained at this stage is given in Figure 3 with atoms shown as displacement ellipsoids. It can be seen that the ellipsoids of O1−O3 are prolate whereas those of O4 and O5 are oblate. Although these features generally are in agreement with the bonding between these anions and cations, the largest root-mean-squared displacement along the principal axis is about 0.3 (for O1−O3) or 0.4 (for O4 and O5), much larger than the corresponding values for pure KABO. The bond valence sums calculated with Brown and Altermatt's parameters[22] are 1.370 and 0.562 for K1 and Na1, respectively. The corresponding values for K2 and Na2 are 1.656 and 0.670, respectively. Clearly, the bond valence sums for K^+, especially K2, are too high to be real, while those values for Na^+ are at the other extreme. Inspired by our recent findings on the structure of $Ca_{1-x}Na_{2x}Al_2B_2O_7$,[23] where all the AlO_4 tetrahedra and BO_3 triangles tilt to adjust to the bond valence sums of Na^+ and Ca^{2+} cations, we suppose that the AlO_4 tetrahedra and BO_3 triangles in this structure also tilt for similar reasons. The refinement with all cations anisotropic but anions isotropic raised R1 and wR2 to 9.33% and 28.11%, respectively. Moreover, strong residual peaks with intensities above 1.5 e Å^{-3} were observed around all O atoms in the difference Fourier map. Then atoms O1−O3 were split into two and O4, O5 into three new sites, as suggested by the difference Fourier map. The refinement with ADPs only at cation sites led to R1 = 3.56% and wR2 = 7.51%, and these *R* values further decreased to 3.44% and 7.13%, respectively, with ADPs at O4 and O5 sites. Attempts to assign ADPs at O1−O3-derived sites resulted in non-positive-definite displacement parameters even with restraints. Details about the refinement are given in Table 1. Despite the slightly higher wR2, this model is preferable to describe the real structure as discussed below.

As in the structure of $Ca_{1-x}Na_{2x}Al_2B_2O_7$,[23] the disordered O sites just represent the possible vertex positions of tilted AlO_4 tetrahedra and BO_3 triangles. The occupation of these O sites is determined by the local distribution of alkali-metal cations. When an alkali-metal site is occupied by K^+, O atoms try to stay at sites far away from it to decrease the bond valence sum of K^+. On the other hand, Na^+ will try to keep O atoms around at smaller distances to improve the bond valence sum. However, since both AlO_4 tetrahedra and BO_3 triangles are rather rigid, the occupation of the possible vertex positions should introduce as small a distortion of these groups as possible. These rigid groups can only tilt as a whole; a certain vertex approaching Na^+ or moving off K^+ might do it at the cost of another vertex moving in an opposite way. Nevertheless, the bond valence changes with bond length exponentially, so the bond length change of the shortest bond will dominate the effect of the tilting of a rigid group. With the assumption that all AlO_4 tetrahedra and BO_3 triangles tilt properly, the bond valence sums for K^+ and Na^+ are calculated and reported in Table 2. It can be seen that in the present model bond valence sums of both K^+ and Na^+ approach their expected values. This explains why the KABO-type structure can be retained at a high level of Na^+ substitution.

Table 2. K−O and Na−O Interatomic Distances in the Disordered Structure Model and Corresponding Bond Valences

atoms	distance (Å)	bond valence	sum of bond valences
K1−2 × O1B	2.693(7)	0.220	1.19
K1−2 × O5	3.03(8)	0.088	
K1−2 × O2B	2.794(8)	0.167	
K1−2 × O3A	3.232(7)	0.051	
K1−2 × O1A	3.117(6)	0.070	
Na1−2 × O1A	2.425(5)	0.186	0.78
Na1−2 × O5	2.57(1)	0.125	
Na1−2 × O2A	3.136(6)	0.027	
Na1−2 × O3A	3.232(7)	0.021	
Na1−2 × O1A	3.117(6)	0.029	
K2−2 × O3B	2.691(7)	0.221	1.19
K2−2 × O2B	2.752(8)	0.187	
K2−1 × O4	3.225(7)	0.052	
K2−1 × O1A	3.288(7)	0.044	
K2−1 × O1B	2.897(8)	0.126	
K2−2 × O3A	3.081(5)	0.077	
Na2−2 × O3A	2.447(5)	0.175	0.94
Na2−2 × O2A	2.415(6)	0.191	
Na2−1 × O4	2.64(1)	0.106	
Na2−2 × O1A	3.288(7)	0.018	
Na2−2 × O3A	3.081(5)	0.032	

In the structure of $Na_2Al_2B_2O_7$,[18] AlO_4 tetrahedra and BO_3 triangles form $[Al_2B_2O_7]_\infty^{2-}$ lamellae stacked along the *c* axis. Na^+ cations locate at two different crystallographic sites, Na1 and Na2. Na1 is between the lamellae, while Na2 is in the plane bisecting the lamellae. If K^+ occupies a Na1 site, its bond valence sum will be about 2.74, which is clearly too high to be compensated by tilting AlO_4 and BO_3 groups around it. The Na2 site is more suited to be occupied by K^+ because the bond valence sum for K^+ will be only 1.36. Nevertheless, we found that in this case the tilting of AlO_4 and BO_3 groups seems to improve the bond valence sum rather than reduce it. This might be the reason no obvious range of homogeneity was observed at the $Na_2Al_2B_2O_7$ side.

The composition of the crystal was refined to $(K_{0.48(2)}Na_{0.52(2)})_2Al_2B_2O_7$, which is in good agreement with the composition of the starting materials, $(K_{0.5}Na_{0.5})_2Al_2B_2O_7$, and the result of chemical analysis, $(K_{0.49}Na_{0.51})_2Al_2B_2O_7$.

Twinning in this crystal is not unexpected. Inserting a mirror plane at $z = 0.5$ will only change the configuration

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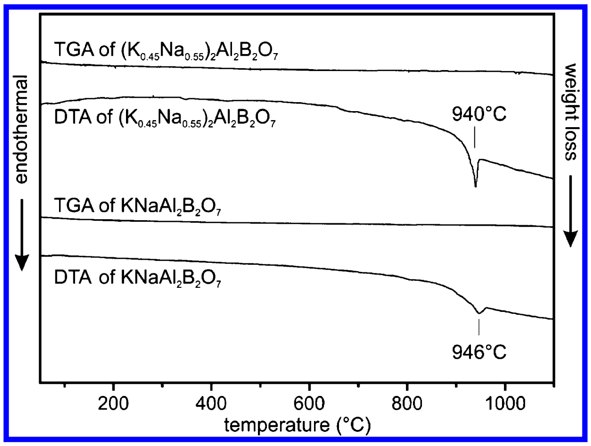

Figure 4. DTA and TGA curves for $(K_{1-x}Na_x)_2Al_2B_2O_7$ ($x = 0.5$ and 0.55).

of K2 (or Na2)−O bonds but does not change the number and lengths of them, implying that a twin boundary appears easily in the structure. The twinning can also be equally described by a mirror perpendicular to [210] or [120].

Thermogravimetric (TG) and differential thermal analyses (DTA) were performed on $(K_{1-x}Na_x)_2Al_2B_2O_7$ ($x = 0.5$ and 0.55) samples. The results are presented in Figure 4. No obvious weight loss was observed up to 1100 °C for both samples. Endothermal peaks with maxima at 946 and 940 °C, for $x = 0.50$ and $x = 0.55$ samples, respectively, appear in the DTA curves. After being heated at 1050 °C for 3 h, the quenched $KNaAl_2B_2O_7$ samples were transparent glasses, as indicated by the X-ray measurement. When the glass was ground and annealed at 800 °C for several days, the crystalline $KNaAl_2B_2O_7$ phase could be recovered. The endothermal peak in the DTA curves corresponds to the congruent melting of the sample. This was also proved by our single-crystal growth experiments.

Difficulties in crystal growth hindered SBBO, KBBF, and BABO from being practically applied as nonlinear optical materials. Because of the problems of decomposition and volatility, KABO has to be grown with flux methods,[9] and NaF was the most widely used flux to grow KABO. Virtually no Na^+ dissolved in it,[12] although up to 60% K^+ can be substituted by Na^+. As indicated by TGA and DTA results, Na^+ substitution can inhibit the problems of both decomposition and volatility, making it possible to grow $(K_{1-x}Na_x)_2Al_2B_2O_7$ crystals directly from the melt. Actually, a transparent, colorless $KNaAl_2B_2O_7$ single crystal with dimensions of 15 mm × 10 mm × 4 mm has been grown via the Czochralski technique.[24]

Second harmonic generation (SHG) was measured for a powder sample with $x = 0.5$. The intensity of the second harmonic is similar to that of KABO, as expected from their similar compositions and structures. The measurement made on the $KNaAl_2B_2O_7$ single crystal confirmed this result, revealing an SHG coefficient $d_{11} = 0.43$ pm/V and a transparent range of 180−3650 nm,[24] which are close to the corresponding values of KABO, 0.45 pm/V and 180−3600 nm.[25]

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Supporting Information Available: An X-ray crystallographic file (CIF) and a table of the indexed powder diffraction pattern of $KNaAl_2B_2O_7$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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