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Structural field of $K_2Al_2B_2O_7$-family crystals

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ABSTRACT

The known crystal structures of borate compounds with general composition $A^I_2M^{III}_2B_2O_7$ (A^I: Na, K, Cs, Rb) have been considered. The structures in space groups $P6_3/m$, $P-31c$, $P321$ and $P2_1/c$ have been found depending on cation combination. Criterion $k = (r(M^{III})+r(B)+2r(O))/r(A^I)$ has been formulated and it controls the formation of trigonal $K_2Al_2B_2O_7$ (KABO) type structure. The existence of noncentrosymmetric KABO-type borates is possible over the range of $k = 2.7 - 2.06$. This range is promising for searching new borate crystals and solid solutions with pronounced nonlinear optical properties.

Keywords: $K_2Al_2B_2O_7$, crystal structure, effective ion radii, unit volume

1. INTRODUCTION

The nonlinear optical borate crystals are the basic materials for applications in high-power frequency conversion and laser systems because of appropriate nonlinear optical coefficients, reasonable birefringence, wide transparency range including UV range and very high optical damage thresholds [1-5]. Due to the developed crystal growth technology, presently, many industrial borate crystals are available with large dimensions and a high optical quality [6-10]. Borate compounds show interesting electronic, luminescent and chemical properties and are investigated as prospective photonic and nanotechnology materials [11-19]. The $K_2Al_2B_2O_7$ (KABO), space group $P321$, $a = 8.5657(9)$, $c = 8.463(2)$, formed in ternary system $K_2O-Al_2O_3-B_2O_3$ is a well-known nonlinear crystal applicable for frequency conversion in the visible and UV spectral ranges [20,21]. KABO possesses a good chemical stability, reasonable NLO properties, optical transparency in the UV range up to $\sim$ 180 nm and as high birefringence as $\Delta n \sim -0.08$ providing a wide range lightwave phase-matching.

A search for structural analogs of KABO has been recently implemented because the isovalent element substitution may be possible in potassium or aluminum sublattices. As an example, the Al^{3+} ions in KABO structure can be substituted by Fe^{3+} ions with the formation of $K_2Fe_2B_2O_7$, space group $P321$, showing reasonable NLO properties [22]. Regrettably, within the possible parent compounds with general composition $A_2Al_2B_2O_7$ (A = Na, K, Rb), the noncentrosymmetric structure is known only for KABO. The structure with an inversion center was found for $Na_2Al_2B_2O_7$, space group $P-31c$, and, respectively, only a limited homogeneity range was obtained for solid solution $K_{2(1-x)}Na_{2x}Al_2B_2O_7$, $0 \leq x < 0.6$ [23]. The $Rb_2Al_2B_2O_7$ (RABO), space group $P2_1/c$, $a = 8.901(2)$, $b = 7.539(1)$, $c = 11.905(2)$, $\beta = 103.97(1)$ º, $V = 775.3(2)Å^3$, Z = 4 also possesses an inversion center and isovalent substitution of Rb for K in KABO structure results in the limited range solid solution $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ [24,25]. Many other elements can be tested as substitution agents in KABO structure with a purpose to create new materials with tuned optical parameters and new functional properties. Thus, the present study is aimed at the crystal chemistry analysis of all known solid solutions with general chemical composition $A^I_2M^{III}_2B_2O_7$. As a result, a field of KABO-type structure will be defined and that may yield the empirical rules of cation selection preserving the KABO structure in new solid solutions. Such rules save the experimenter's time and efforts and are very helpful in a new crystal search.

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2. K₂AL₂B₂O₇-TYPE STRUCTURES AND GENERAL RELATIONS

KABO crystal structure is shown in Figure 1 [26]. In this structure, the AlO_4 pyramids have an equilateral triangle as a base and one specific Al-O distance along the polar crystallographic axis. In KABO structure, this apex Al-O distance is shorter than other three Al-O distances in the AlO_4 pyramids. Such a compression of AlO_4 tetrahedrons is found for all the three Al positions in KABO structure. However, in $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ crystals, the continuous increase of the apex Al-O distances is observed with Rb doping, and the AlO_4 tetrahedrons become elongated in the polar crystallographic direction [24]. This mechanism provides a drastic increase of cell parameter c with the Rb-doping level increase. The contraction of the base triangles of the AlO_4 tetrahedrons with Rb doping, however, is not resulted in the cell parameter a decrease. The base triangles of AlO_4 pyramids and BO_3 triangles are linked alternatively in six-member rings.
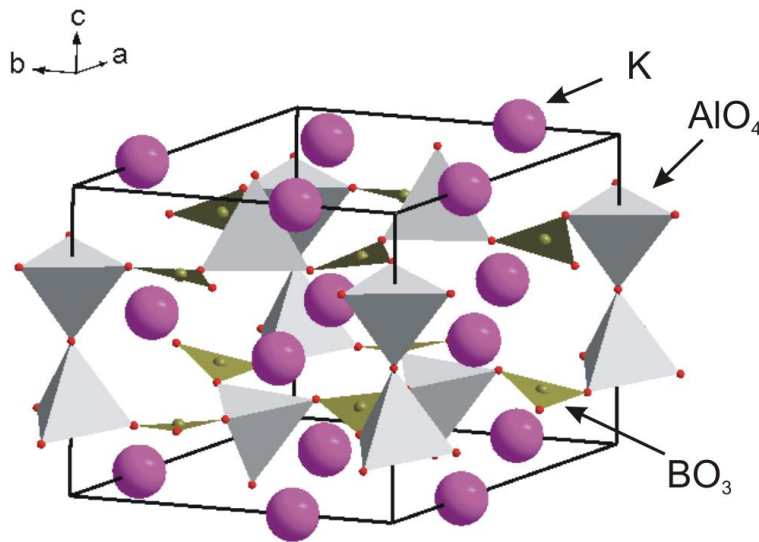
.

Figure 1. Crystal structure of $K_2Al_2B_2O_7$. The unit cell is outlined. Lone atoms are omitted for clarity.

In compounds $A^I_2M^{III}_2B_2O_7$ (A^I: Na, K, Cs, Rb) with hexagonal-trigonal crystal systems, the characteristic structural motif contains two A^I ions and three layers of six-membered rings formed by tetrahedrons $M^{III}O_4$ and triangles BO_3 as shown in Figure 2. Now, it is interesting to follow the motif variations in $A^I_2M^{III}_2B_2O_7$ crystals with different symmetry and element content. The structural parameters of the known $A^I_2M^{III}_2B_2O_7$ borates are tabulated in Table 1 and the typical structural motifs dependent on crystal symmetry are shown in Figure 3. It can be reasonably supposed that the variation of A^I cation size induces tensions and deformations in the $(M^{III}O_4-BO_3)_3$ rings as traced in Figure 3 (a-d). For large-size A^I cations, the distruption of the rings results in the disappearance of the KABO structure (Figure 3d). However, an increase of M^{III} ion size can lead to an increase of the ring size and provide ring stability for biger A^I cations. The ratio of the perimeter of the ring L to the effective radius of A^I ion, $k = L/r(A^I)$, seems to be a good structural criterion of the ring tension and parameter k can be used as an indicator of the space groups in $A^I_2M^{III}_2B_2O_7$ compounds. As it is evident from Figure 2, the perimeter of $(M^{III}O_4-BO_3)_3$ ring can be estimated by formula $L = 6r(M^{III})+6r(B)+12r(O)$ that gives relation $k = (r(M^{III})+r(B)+2r(O))/r(A^I)$.

Table 1 contains the $A^I_2M^{III}_2B_2O_7$ compounds which space group and unit cell parameters are known. The ion radii necessary to calculate k value were taken from Ref. [38]. When a mix of two cations $A1_xA2_{1-x}$ was observed in A^I positions, the averaged ion radius was calculated by formula $<r(A)>=(x\times r(A1)+(1-x)\times r(A2)$. In Table 1, the $A^I_2M^{III}_2B_2O_7$ compounds are ranged by the k value. One can see that, for specific k ranges, the compound forms devisions different in space groups. Only two compounds $Rb_{1.64}K_{0.36}Al_2B_2O_7$ and $Rb_2Ga_2B_2O_7$ are interchanged in the range of $k = 2.048$-2.075. So, the value $k = {\sim}2.06$ is critical for the KABO-type structure transformation from $P321$ to
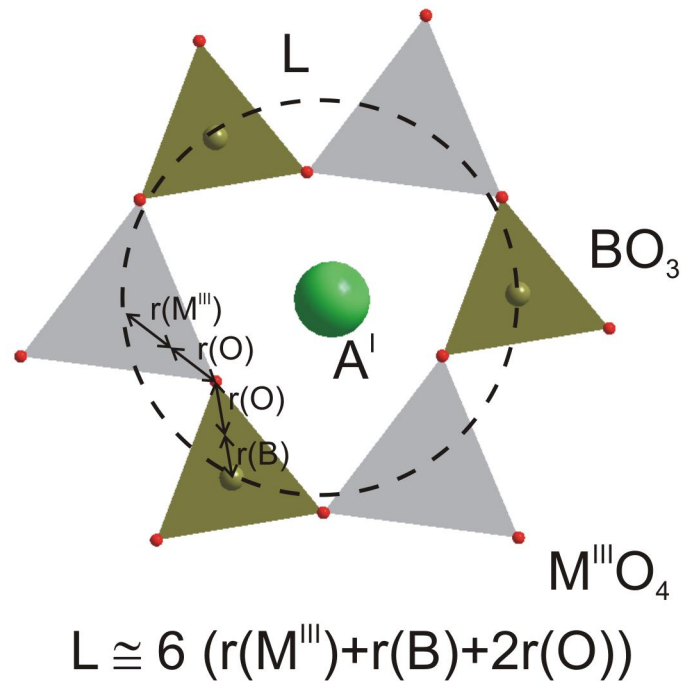
$$L \cong 6 \ (r(M^{III})+r(B)+2r(O))$$

Figure 2. Six-member $(M^{III}O_4\text{-}BO_3)_3$ ring in KABO-type structures.

$P2_1/c$. This proves the result from Ref. 24 where the upper limit of rubidium solubility in the $K_{2(1-x)}Rb_{2x}Al_2B_2O_7$ solution was estimated to be as high as $x\sim 0.83\text{-}0.9$ under ambient conditions. Another critical point is $k = \sim 2.8$, where the transformation of $P321$ to $P\text{-}31c$ takes place. Over the range of $k > \sim 2.84$ the $P6_3/m$ structure is observed. From the comparison, it can be concluded that value k is a key parameter of $A^I_2M^{III}_2B_2O_7$ compounds applicable for space group prediction in new compounds and solid solutions. As an example, in solid solution $K_{2(1-x)}Cs_{2x}Al_2B_2O_7$, the upper limit of cesium solubility can be predicted as $x \sim 0.36$ under ambient conditions. In solid solution $K_{2(1-x)}Cs_{2x}Ga_2B_2O_7$, however, the upper limit of $x \sim 0.48$ is estimated because of higher effective radii of Ga^{3+} in comparison with that of Al^{3+}. As for $K_{2(1-x)}Rb_{2x}Ga_2B_2O_7$, as high upper limit as $x \sim 1.1$ is calculated and this indicates the space group $P321$ for $Rb_2Ga_2B_2O_7$ ($x = 1$). The $Rb_2Ga_2B_2O_7$ borate, however, was recently reported in monoclinic space group $P2_1/c$ and this may be an indication of the phase transition $P2_1/c \leftrightarrow P321$ at increased temperatures [33].

In Figure 4, the dependence of formula unit volume V_{fu} in $A^I_2M^{III}_2B_2O_7$ compounds on k is shown. It is evident that the KABO structure in space group $P321$ is stable in the range of $V_{fu} = 165\text{-}190$ Å^3 ($k = 2.7 - 2.06$). When K is completely substituted by big cations of Cs^+ or Tl^+, the level of V_{fu} increases drastically and crystal lattice formation in space group $P321$ is impossible. The range of trigonal formations in space group $P\text{-}31c$ is narrow and this case is intermediate. For comparatively small A^I and M^{III} cations, hexagonal space group $P6_3/m$ is evident. The diagram shown in Figure 4 can be used for the prediction of cation combinations most promising for the creation of new noncentrosimmetric crystals with the KABO type structure.

Table 1. The formula unit volume V_{fu} and symmetry of the known $A^I_2 M^{III}_2 B_2 O_7$ (A^I = Na, K, Cs, Rb) at room temperature

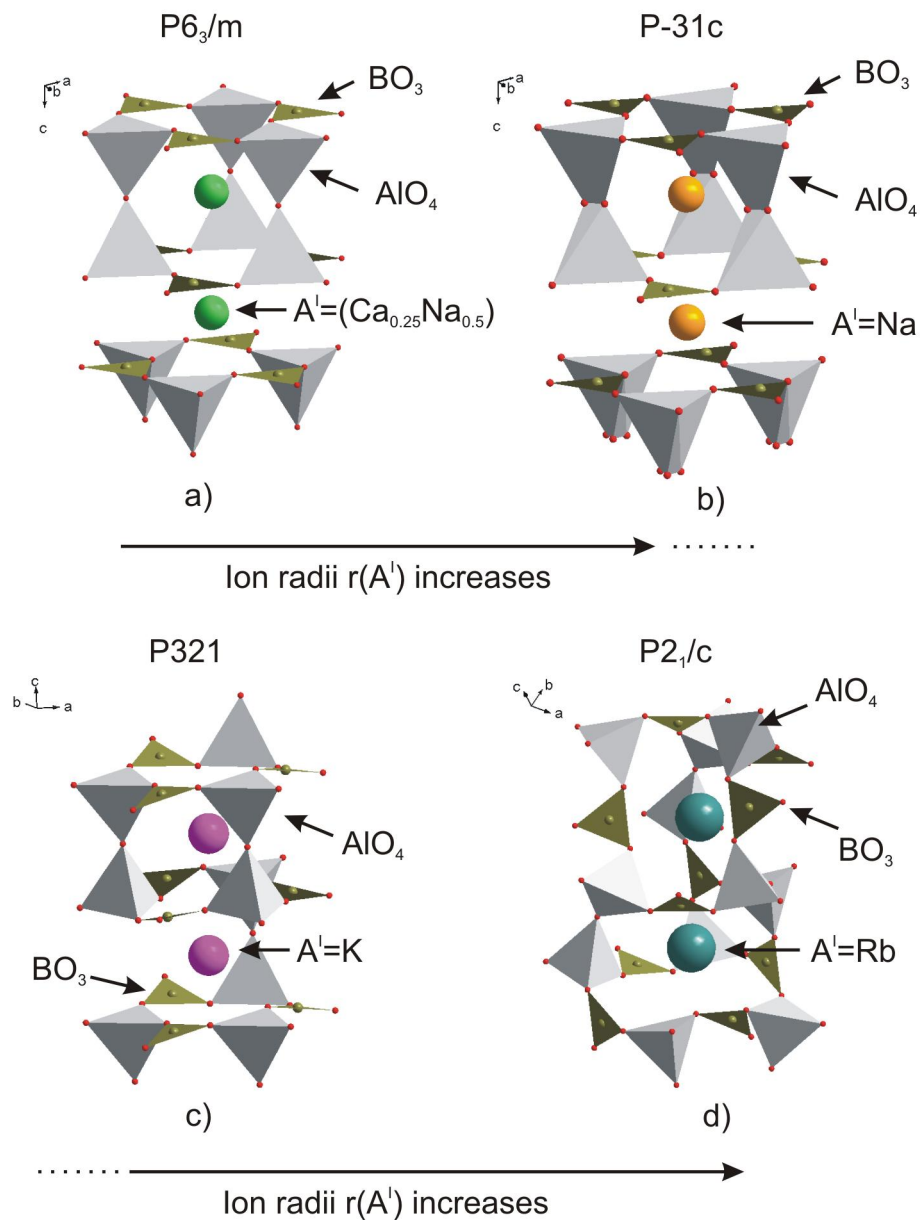| Compound	Symmetry	V_{fu}, Å^3	Reference	k
$Ca_{0.69}Na_{0.64}Al_2B_2O_7$	$P6_3/m$	155.89	[27]	4.267
$Ca_{0.5}NaAl_2B_2O_7$	$P6_3/m$	154.53	[28]	3.747
$Sr_{0.5}NaAl_2B_2O_7$	$P6_3/m$	159.97	[28]	3.602
$Ca_{0.05}Na_{1.9}AlB_2O_7$	$P6_3/m$	153.53	[27]	2.837
$Na_2Ga_2B_2O_7$	P-31c	157.23	[29]	2.831
$Na_2Al_2B_2O_7$	P-31c	153.06	[29,30]	2.763
$KLiAl_2B_2O_7$	P321	174.90	[31]	2.683
$TlLiAl_2B_2O_7$	P321	178.17	[31]	2.598
$RbLiAl_2B_2O_7$	P321	179.40	[31]	2.577
$K_{0.96}Na_{1.04}Al_2B_2O_7$	P321	164.14	[23]	2.436
$K_2Fe_2B_2O_7$	P321	188.03	[22]	2.225
$K_2Ga_2B_2O_7$	P321	183.95	[32]	2.212
$K_2Al_2B_2O_7$	P321	178.54	[26]	2.159
$Rb_{0.63}K_{1.37}Al_2B_2O_7$	P321	181.54	[24]	2.115
$Rb_{1.09}K_{0.91}Al_2B_2O_7$	P321	183.89	[24]	2.084
$Rb_2Ga_2B_2O_7$	$P2_1/c$	197.81	[33]	2.075
$Rb_{1.64}K_{0.36}Al_2B_2O_7$	P321	187.85	[24]	2.048
$Rb_2Al_2B_2O_7$	$P2_1/c$	193.81	[34]	2.025
$KCsAl_2B_2O_7$	$P2_1/c$	201.92	[35]	2.006
$TlCsAl_2B_2O_7$	$P2_1/c$	209.50	[35]	1.958
$Cs_2Ga_2B_2O_7$	$P2_1/c$	211.20	[36]	1.920
$Cs_2Al_2B_2O_7$	$P2_1/c$	208.25	[37]	1.874

Figure 3. Structural motif of compounds $A^I_2M^{III}_2B_2O_7$: a) $A^I = Ca_{0.25}Na_{0.5}$, $M^{III} = Al$; b) $A^I = Na$, $M^{III} = Al$; c) $A^I = K$, $M^{III} = Al$; d) $A^I = Rb$, $M^{III} = A$.
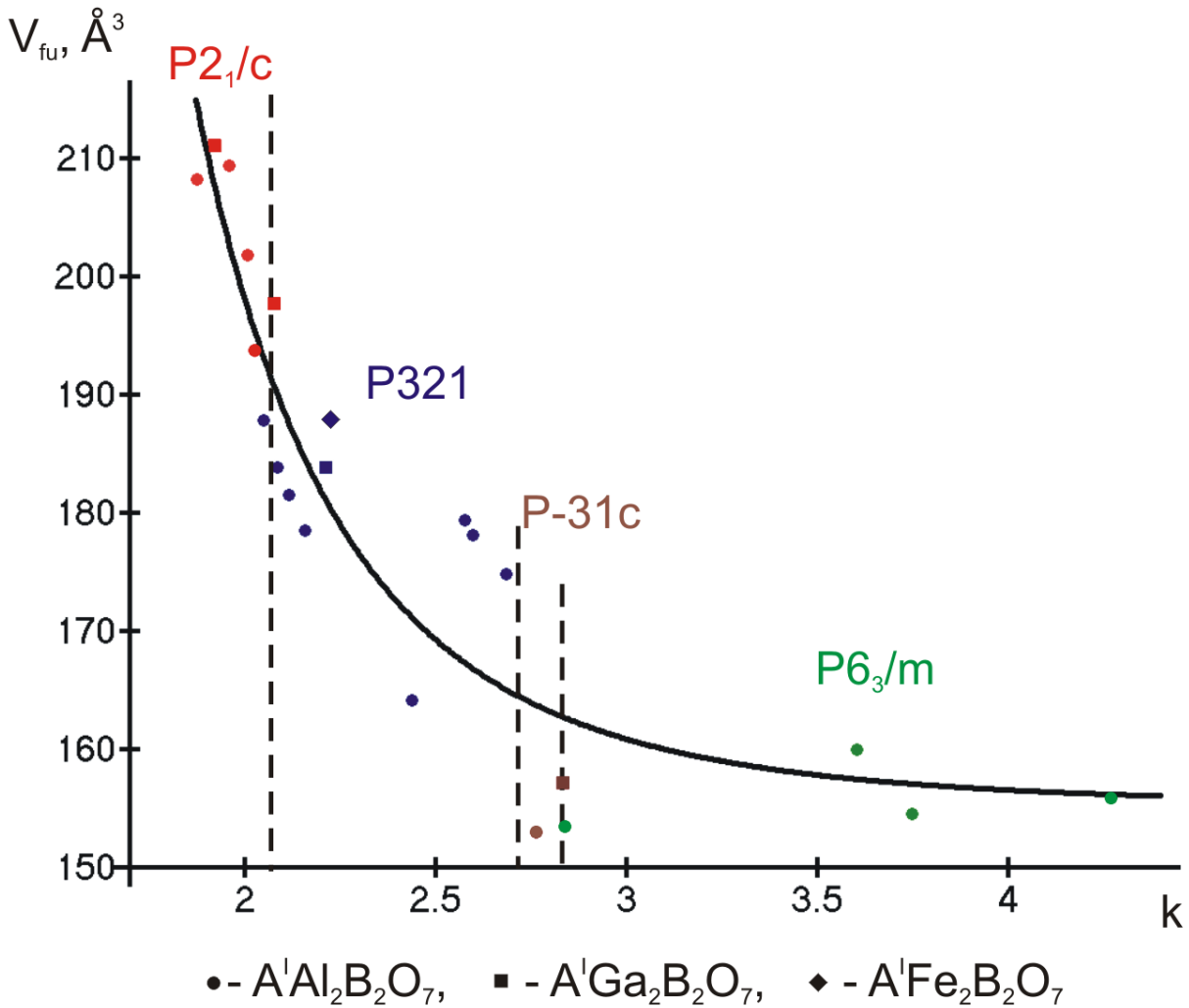
Figure 4. Dependence of formula unit volume V_{fu} in $A^I_2M^{III}_2B_2O_7$ compounds on k.

3. CONCLUSIONS

As it is shown in the present comparative study, the structural motif $(M^{III}O_4\text{-}BO_3)_3$ behavior controls the stability of the KABO-type structure in space group $P321$. The simple criterion $k = (r(M^{III})+r(B)+2r(O))/r(A^I)$ is proposed to describe the $(M^{III}O_4\text{-}BO_3)_3$ ring geometry and value k can be easily calculated using the well-known effective ion radii set. Then, the reasonable k values can be readily applied for the selection of cation combination most promising for the creation of new crystals with the KABO-type structure.

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