

# Preparation and structure of $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$ and $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$

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## Abstract

Two compounds  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$ , have been found to crystallize into a new structure type by Rietveld refinement from X-ray powder diffraction data. Their structure belongs to hexagonal space group  $P6_3/m$ , with lattice parameters of  $a = 4.85640(8) \text{ \AA}$ ,  $c = 15.6635(4) \text{ \AA}$  for  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $a = 4.81292(10) \text{ \AA}$ ,  $c = 15.4056(4) \text{ \AA}$  for  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$ , respectively. The structure is built up by  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer and  $\text{Na}^+/\text{Ca}^{2+}$  or  $\text{Na}^+/\text{Sr}^{2+}$  ions alternatively stacking along the  $c$ -axis. The sites in the inter-double layer are fully occupied jointly by Na and Ca or Sr, but the intra-double layer sites are only half occupied solely by Na. A mechanism of the transition of the structure from  $\text{CaAl}_2\text{B}_2\text{O}_7$  to present structure type by replacing only 1% Ca by Na (2%) as observed by Chang and Keszler (Mater. Res. Bull. 33 (1998) 299) is also proposed.

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**Keywords:** Alumino-borate; Rietveld refinement; Layered structure

## 1. Introduction

After the discovery of a new nonlinear optical (NLO) crystal  $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$  (SBBO) with potential deep UV applications [1], many efforts have been paid to the beryllio-borate and alumino-borate systems in order to obtain new NLO crystals with improved UV properties. Some compounds, including  $\text{KBe}_2\text{BO}_3\text{F}$  (KBBF) [2],  $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$  (KABO) [3,4] and  $\text{BaAl}_2\text{B}_2\text{O}_7$  (BABO) [5], showing NLO effects, have subsequently been reported. Among them, SBBO, KBBF and BABO have been found either with crystal growth difficulties or poor crystal quality, hindering their practical applications. In contrast, KABO crystal can easily be grown in KF or NaF flux [6]; however, it has been found that all the crystals obtained so far have an absorption band around 266 nm [4], which, therefore, also limits its UV applications.

Besides the above-mentioned NLO crystals, many alumino-borates with new structure types have also been reported, which includes  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  [7,8],  $A'\text{Al}_2\text{B}_2\text{O}_7$  ( $A' = \text{Ca}, \text{Sr}$ ) [9,10]. The common feature of  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ ,  $A'\text{Al}_2\text{B}_2\text{O}_7$  and BABO is that in their structures the  $\text{AlO}_4$  tetrahedra and  $\text{BO}_3$  triangles share their three in-plane oxygen atoms to form an  $[\text{AlBO}_3]$  layer, two such layers are jointed by sharing the fourth oxygen atom of the  $\text{AlO}_4$  tetrahedron to form a  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer. The structures of these compounds are built up by alternatively stacking the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layers and the corresponding cations along the  $c$ -axis. A similar double layer  $[\text{Be}_2\text{B}_2\text{O}_7]^{4-}$  can also be found in SBBO. In  $A'\text{Al}_2\text{B}_2\text{O}_7$  ( $A' = \text{Ca}, \text{Sr}, \text{Ba}$ ), the cations only occupy the inter-double layer positions, whereas in  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  and SBBO the cations occupy both the inter- and intra-double layer spaces. In an attempt to produce new NLO compounds with the merits of easy growing habit like KABO, we tried to introduce  $\text{K}^+$  or  $\text{Na}^+$  ion into the empty sites within the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer in  $A'\text{Al}_2\text{B}_2\text{O}_7$  ( $A' = \text{Ca}, \text{Sr}, \text{Ba}$ ). As a result,

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two compounds with the compositions of  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  were obtained.

In 1998, Chang and Keszler [9] mentioned a related series of solid solution with the composition  $\text{Ca}_{1-x}\text{Na}_{2x}\text{Al}_2\text{B}_2\text{O}_7$  and noticed that inclusion of only 2% Na ( $x = 0.01$ ) will produce substantial changes of the XRD pattern from that of the  $\text{CaAl}_2\text{B}_2\text{O}_7$  sample. They pointed out that the XRD pattern can be indexed based on the space group  $P6_322$  and is consistent with the results of the  $\alpha$ -phase of  $\text{CaAl}_2\text{B}_2\text{O}_7$  previously reported by Schäfer and Kuzel [11], but no detailed information about the structure was reported. From Rietveld refinements of the XRD patterns of the two title compounds, we found that their structure can be best described in space group  $P6_3/m$  and a mechanism for the structure change of  $\text{CaAl}_2\text{B}_2\text{O}_7$  induced by Na doping will be discussed.

## 2. Experimental

Samples of  $AA'_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  ( $A = \text{Na}, \text{K}; A' = \text{Ca}, \text{Sr}, \text{Ba}$ ) were prepared from analytically pure chemicals of  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{BaCO}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$ . The mixtures of the starting materials with

appropriate compositions were fired at  $400^\circ\text{C}$  for 5 h initially, then heated at  $600^\circ\text{C}$  for another 5 h and finally sintered at  $900\text{--}1000^\circ\text{C}$  for 1 day with several intermediate grindings. X-ray diffraction (XRD) patterns were collected with a Siemens D-5000 diffractometer (monochromated  $\text{CuK}\alpha_1$  radiation source, transmission mode, position sensitive detector, step size  $0.02^\circ(2\theta)$ ). The samples were spread over 3 M Scotch Magic™ tape and the counting times were set as 2 or 3 s per step for the Ca or Sr samples, respectively. Rietveld structure refinements were carried out using the XRD data and the GSAS package [12].

## 3. Results and discussion

From the XRD patterns, only the samples of  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  appeared as single phases. As noticed by Chang and Keszler [9], the patterns bear no resemblance to that of  $\text{CaAl}_2\text{B}_2\text{O}_7$  but are very close to that of  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  with only one noticeable difference of the appearance of the (111) and (113) peaks. The  $(11\ell, \ell = \text{odd})$  peaks are not allowed in the space group  $P\text{-}31c$ , to which  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  belongs, therefore a different space group needs to be chosen. All

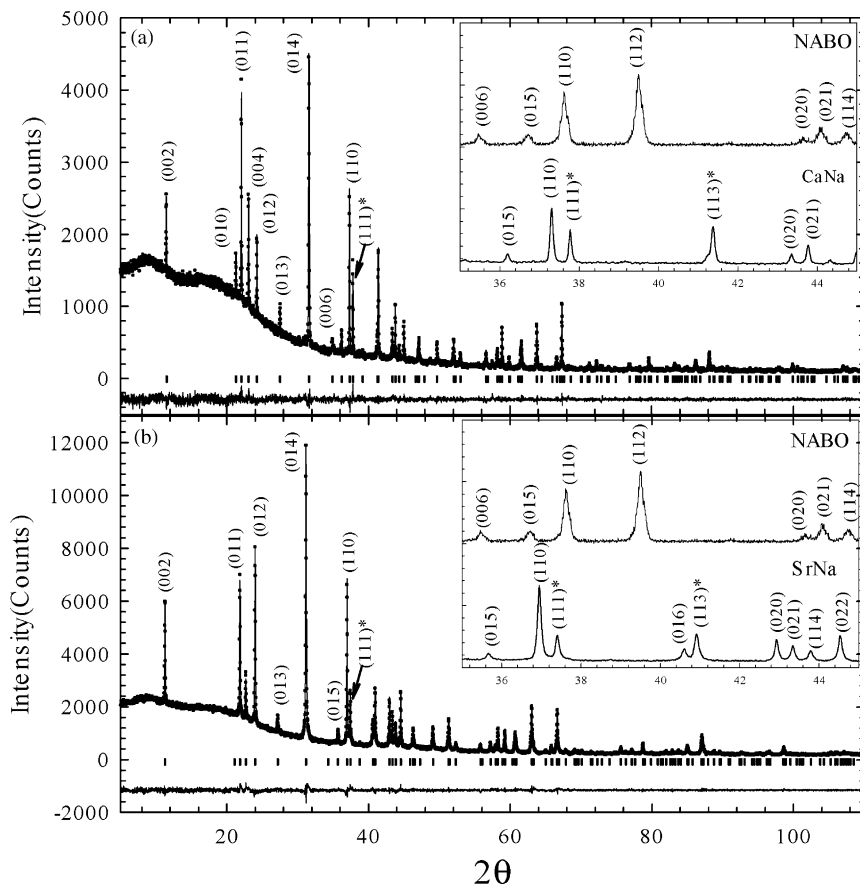


Fig. 1. The XRD patterns of (a)  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  (top) and (b)  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  (the insets show their comparison with that of  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  (NABO), the points are observed data, the lines represent calculated and difference plot, the tick marks are the diffraction peak positions).

the diffraction peaks of the XRD patterns can be indexed with a hexagonal unit cell, and are consistent with space groups of  $P6_3$ ,  $P6_3/m$  and  $P6_322$ . Since a second-harmonic generation (SHG) test with a Nd:YAG laser (at 1064 nm) gives no signal at 532 nm, we tend to select the space group  $P6_3/m$  with inversion symmetry and  $P6_322$  which does not support the SHG effect if Kleinman symmetry is considered [13]. A structure model containing the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer similar to that in  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  was adopted as a starting model. Both space groups,  $P6_3/m$  and  $P6_322$ , were tested at the early stage of the refinement. The structure models with the two space groups only differentiate in the relative orientations of the Al–O1 and B–O1 bonds in the different  $[\text{AlBO}_3]$  layers when projected along the  $c$ -axis. The  $P6_3/m$  model gives a perfect alignment between the two  $[\text{AlBO}_3]$  layers within the double layer but the double layers are twisted against each other, while  $P6_322$  model results in twisted  $[\text{AlBO}_3]$  layers within the double layer, and the Al–O1 and B–O1 bonds between adjacent double layers are perfectly aligned. The excellent agreement between the calculated and observed patterns (Fig. 1a and b) confirmed that  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  actually belong to space group  $P6_3/m$ . Totally 58 parameters, including 1 scale factor and 1 for zero shift, 30 interpolated background, 6 pseudo-Voigt profile with asymmetry and 4 anisotropic broadening, 1 preferred orientation, and 15 structural parameters, are refined simultaneously. The final refinements gave the lattice parameters of  $a = 4.85640(8) \text{ \AA}$ ,  $c = 15.6635(4) \text{ \AA}$  and  $a = 4.81292(10) \text{ \AA}$ ,  $c = 15.4056(4) \text{ \AA}$ , and converged to  $R_{\text{wp}} = 4.30\%$  ( $R_{\text{wp}}^{-\text{Bkd}} = 4.63\%$ ),  $\chi^2 = 1.527$  and  $R_{\text{F}2} = 5.78\%$  for Sr-analog and  $R_{\text{wp}} = 5.04\%$  ( $R_{\text{wp}}^{-\text{Bkd}} = 5.66\%$ ),  $\chi^2 = 1.245$  and  $R_{\text{F}2} = 9.85\%$  for the Ca-analog, respectively. Crystallographic structure details are sum-

marized in Table 1 and the selected bond lengths and bond angles are listed in Table 2.

In the structure of  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  (Fig. 2a), the sites between two  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layers are statistically occupied by  $\text{Na}^+$  and  $\text{Ca}^{2+}$  or  $\text{Sr}^{2+}$  ions in about 1:1 ratio. These ions are six-fold coordinated to oxygen in a regular octahedron. Bond valence sums (BVS) [14] of these sites give values of about 1.5+ (Table 1), which are ideal for the average valences of  $\text{Ca}^{2+}/\text{Na}^+$  or  $\text{Sr}^{2+}/\text{Na}^+$ . Within the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer, the sites are only half occupied by almost solely the  $\text{Na}^+$  ion which is connected with six O1 and three O2 in a 9-coordinated environment. BVS of the  $\text{Na}^+$  ion here is below 0.5+, indicating that the intra-double layer site is under-coordinated, which is also evidenced by the large anisotropic temperature factors in the  $ab$  plane for the neighboring O2 atoms that are attracted towards the Na atom. The BVS values, on the other hand, also reflect that the  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  ions prefer to occupy the inter-double layer sites with larger BVS, whereas the

Table 2  
Selected inter-atomic distances and angles of  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  (top) and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$

Ca/Na1–O1: 2.423(3) Å × 6	Al–O1: 1.724(3) Å × 3
	Al–O2: 1.675(4) Å × 1
Na/Ca2–O1: 2.959(3) Å × 6	B–O1: 1.382(3) Å × 3
	O1–Al–O1: 107.6(2)°
Na/Ca2–O2: 2.77876(6) Å × 3	O1–Al–O2: 111.3(2)°
	O1–B–O1: 119.997(9)°
Sr/Na1–O1: 2.506(2) Å × 6	Al–O1: 1.715(2) Å × 3
	Al–O2: 1.672(3) Å × 1
Na/Sr2–O1: 2.999(2) Å × 6	B–O1: 1.392(2) Å × 3
	O1–Al–O1: 107.2(2)°
Na/Sr2–O2: 2.80386(5) Å × 3	O1–Al–O2: 111.65(1)°
	O1–B–O1: 119.99(2)°

Table 1  
Crystallographic parameters for  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7^{\text{a}}$  and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7^{\text{b}}$

Atoms	Site	x	y	z	n	$U_{\text{iso}}$	BVS
Ca/Na1	2b	0	0	0	0.461/0.539(6)	0.0213(12)	1.44+
Na/Ca2	2a	0	0	0.25	0.461/0.039(6)	0.0213(12)	0.48+
Al	4f	1/3	2/3	0.6413(2)	1	0.0135(9)	3.13+
B	4f	1/3	2/3	0.1011(7)	1	0.031(4)	2.91+
O1	12i	0.9711(7)	0.5995(6)	0.8993(2)	1	0.0179(11)	1.99–
O2	2d	2/3	1/3	0.25	1	0.073 <sup>c</sup>	1.84–
Sr/Na1	2b	0	0	0	0.492/0.508(1)	0.0200(6)	1.50+
Na/Sr2	2a	0	0	0.25	0.492/0.008(1)	0.0200(6)	0.44+
Al	4f	1/3	2/3	0.6433(2)	1	0.0134(7)	3.19+
B	4f	1/3	2/3	0.1038(6)	1	0.033(3)	2.84+
O1	12i	0.9744(5)	0.5927(4)	0.8971(2)	1	0.0187(8)	1.99–
O2	2d	2/3	1/3	0.25	1	0.085 <sup>d</sup>	1.84–

<sup>a</sup>Space group  $P6_3/m$ :  $a = 4.81292(10) \text{ \AA}$ ,  $c = 15.4056(4) \text{ \AA}$ ,  $R_{\text{wp}} = 5.04\%$ ,  $R_{\text{wp}}^{-\text{Bkd}} = 5.66\%$ ,  $\chi^2 = 1.245$  and  $R_{\text{F}2} = 9.85\%$ .

<sup>b</sup>Space group  $P6_3/m$ :  $a = 4.85640(8) \text{ \AA}$ ,  $c = 15.6635(4) \text{ \AA}$ ,  $R_{\text{wp}} = 4.30\%$ ,  $R_{\text{wp}}^{-\text{Bkd}} = 4.63\%$ ,  $\chi^2 = 1.527$ ,  $R_{\text{F}2} = 5.78\%$ .

<sup>c</sup> $U_{11} = U_{22} = 0.107(7)$ ,  $U_{33} = 0.004(8)$ ,  $U_{12} = 0.054(3)$ ,  $U_{13} = U_{23} = 0$ .

<sup>d</sup> $U_{11} = U_{22} = 0.120(5)$ ,  $U_{33} = 0.016(8)$ ,  $U_{12} = 0.060(3)$ ,  $U_{13} = U_{23} = 0$ .

intra-double layer sites with much smaller BVS are solely occupied by the  $\text{Na}^+$  ion.

The difference between present structure and that of  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  (Fig. 2b) centers at the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layer; the two  $[\text{AlBO}_3]$  layers within each double layer are twisted against each other in  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ , but are perfectly aligned on top of each other in the present structure. Comparing with all the other structures containing the  $[\text{M}_2\text{B}_2\text{O}_7]$ ,  $M = \text{Be}, \text{Al}$  double layers, we can classify them according to where the disorientation occurs. Table 3 lists the relative orientations among four successive  $[\text{AlBO}_3]$  layers in the unit cells of the compounds containing the  $[\text{M}_2\text{B}_2\text{O}_7]$  double layer. From the table, we found that in SBBO and BABO, the layers between the double-layers are perfect aligned and in the present structure they are twisted but perfectly alignment occurs within the double layer.

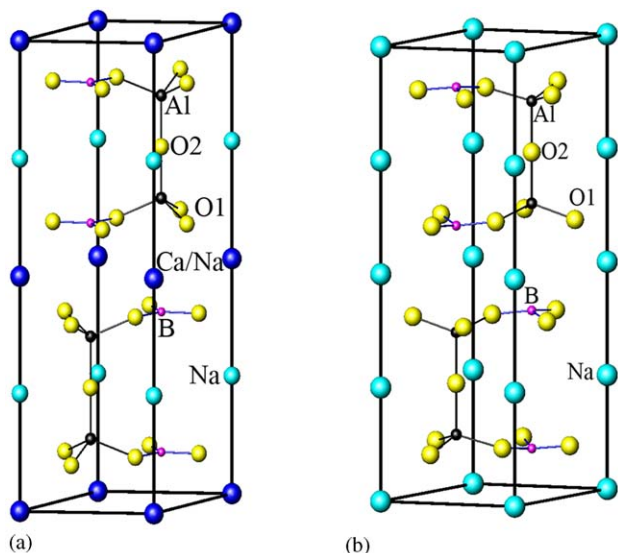


Fig. 2. The refined structure of (a)  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and (b) the structure of  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$  (the small purple balls are B atoms, the black balls are Al atoms, the larger blue balls are Ca/Na atoms, the lighter blue balls are Na atoms and the smaller yellow balls are O atoms).

As it has already been observed by Kang and Keszler [9], introducing a small amount (2%) of Na changed the  $\text{CaAl}_2\text{B}_2\text{O}_7$  structure, but instead of the  $P6_322$  structure proposed by them it more likely changed to the present structure with  $P6_3/m$  symmetry. Fig. 3 shows the structure of  $\text{CaAl}_2\text{B}_2\text{O}_7$  with a hypothetical Na doping. One can see that the introduction of  $\text{Na}^+$  ion into the sites within the double layer will not only form a normal  $\text{NaO}_9$  coordination polyhedron but also build an abnormally short Na–B contact with a distance of 2.37 Å. This distance is within the range of chemical bonding, which is not possible between two positively charged ions. It is the strong Coulomb repulsion between  $\text{Na}^+$  and  $\text{B}^{3+}$  ions that forces the  $\text{BO}_3$  group on top of the  $\text{Na}^+$  ion (Fig. 3) moves away from its position. This short Na–B contact cannot be avoided in doping, whatever the small amount of Na in the

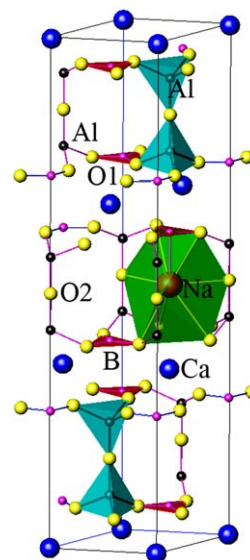


Fig. 3. A hypothetical structure of Na-doped  $\text{CaAl}_2\text{B}_2\text{O}_7$  (only half of the unit cell along  $c$ -axis is shown here; the large brown ball within the green polyhedron is the Na atom, the small purple balls are B atoms, the black balls are Al atoms, the larger blue balls are Ca atoms and the smaller yellow balls are O atoms).

Table 3

The relative orientations of Al/Be–O1 and Al/Be–O1 or B–O1 bonds in different  $[\text{AlBO}_3]$  layers of the compounds with  $[\text{M}_2\text{B}_2\text{O}_7]$  double layers<sup>a</sup>

	$\text{CaAl}_2\text{B}_2\text{O}_7$	$\text{SrAl}_2\text{B}_2\text{O}_7$	$\text{BaAl}_2\text{B}_2\text{O}_7$	$\text{Ca}_{0.5}\text{NaAl}_2\text{B}_2\text{O}_7$	$\text{Sr}_{0.5}\text{NaAl}_2\text{B}_2\text{O}_7$	$\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$	$\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$
S.G.	$R\bar{3}c$	$R\bar{3}c$	$R32$	$P6_3/m$	$P6_3/m$	$P\bar{3}1c$	$P\bar{6}c2$
$a$	4.810(6) Å	4.893(1) Å	5.001(2) Å	4.81292(10) Å	4.85640(8) Å	4.8010(4) Å	4.683(3) Å
$c$	46.633(5) Å	47.78(1) Å	24.378(3) Å	15.4056(4) Å	15.6635(4) Å	15.2425(16) Å	15.311(7) Å
A1	—	—	—	—	—	—	—
A2	20.94°	27.58°	37.99°	0°	0°	41.56°	41.9°
B3	42.69°	35.18°	1.87°	43.34°	40.34°	46.39°	0°
B4	20.94°	27.58°	37.99°	0°	0°	41.56°	41.9°
Al/C5	42.69°	35.18°	1.87°	43.34°	40.34°	46.39°	0°
Reference	[9]	[10]	[5]	Present	Present	[8]	[1]

<sup>a</sup>A, B or C represents A, B or C double layer in the unit cell, the number follows represents the sequence of the  $[\text{AlBO}_3]$  layer.

$\text{CaAl}_2\text{B}_2\text{O}_7$  structure, which explains the otherwise unusual behavior of a tiny composition variation ( $x = 0.01$ ) changes the structure completely in the solid solution  $\text{Ca}_{1-x}\text{Na}_{2x}\text{Al}_2\text{B}_2\text{O}_7$  system.

#### 4. Conclusion

In this work, we synthesized the compounds of  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  by solid-state reaction and determined their structure from X-ray powder diffraction data.  $\text{NaCa}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  and  $\text{NaSr}_{0.5}\text{Al}_2\text{B}_2\text{O}_7$  were found to crystallize in a new structure type with space group  $P6_3/m$ . Similar to  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ ,  $A'\text{Al}_2\text{B}_2\text{O}_7$  ( $A' = \text{Ca}, \text{Sr}, \text{Ba}$ ) and SBBO, the basic structure unit in present compounds was found to be the  $[\text{Al}_2\text{B}_2\text{O}_7]^{2-}$  double layers. The differences among them center at the relative alignment of the  $[\text{AlBO}_3]$  layers in the  $ab$  plane; in  $\text{Na}_2\text{Al}_2\text{B}_2\text{O}_7$ ,  $\text{CaAl}_2\text{B}_2\text{O}_7$  and  $\text{SrAl}_2\text{B}_2\text{O}_7$ , the  $[\text{AlBO}_3]$  layers between both inter- and intra-double layers are twisted; in SBBO and BABO those between the intra-double layers are twisted but the inter-double layer ones are perfectly aligned; whereas in the present case it is the intra-double layer ones that are perfectly aligned but those between inter-double layers are twisted. Since good NLO materials in the borate series require good alignment of the  $\text{BO}_3$  groups, if the alignment can happen between both the inter- and intra-double layers, much higher NLO effects may be produced. It is thus hoped the understanding of the interactions of the cations on the alignment of neighboring  $[\text{AlBO}_3]$  layers may help in tailor designing new NLO crystals.

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