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Re-examination of the crystal structure of $Na_2Al_2B_2O_7$: stacking faults and twinning

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Abstract

The crystal structure of the layered compound $Na_2Al_2B_2O_7$ is re-examined. It is found that stacking faults can be introduced easily in the sequence of $[Al_2B_2O_7]_{\infty}^{2-}$ lamellae. Both rotation and reflection twinning can form in the crystal by introducing appropriate stacking faults. A domain of the $Sr_2Be_2B_2O_7$-type structure might occur at the twin boundary. Single crystal refinement is performed successfully with the twinning model. A similar analysis and discussion is extended to the structures of $Sr_2Be_2B_2O_7$ and $AEAl_2B_2O_7$ (AE = Alkaline earth elements Ca, Sr and Ba).

Keywords: Layered structure; Stacking fault; Twinning

1. Introduction

The compound $Na_2Al_2B_2O_7$ was first reported by Samedov et al. in 1971 [1]. Only an unindexed X-ray powder diffraction pattern was given without any crystallographic information. Several years ago, we also synthesized this compound when we reinvestigated the Na_2O–Al_2O_3–B_2O_3 system [2]. But our attempts to solve its structure from powder diffraction and single crystal data did not succeed. Later on, Corbel et al. [3] reported the structure of $Na_2Ga_2B_2O_7$ and pointed out that $Na_2Al_2B_2O_7$ was isostructural. However, they did not give the details of the structure of $Na_2Al_2B_2O_7$. Moreover, the thermal parameters of O atoms in $Na_2Ga_2B_2O_7$ are non-positive definite, and disorder in O2 position occurs in their structure model. Twinning was suggested but the twin law was not determined. Indeed, the refinement of the $Na_2Al_2B_2O_7$ structure on single crystal data based on the structural model of $Na_2Ga_2B_2O_7$ [3] converged to unacceptably large agreement factors, whereas Rietveld refinements on the powder diffraction data proceeded successfully [2].

In the past few years, several other compounds with similar formulae and building units, such as $Sr_2Be_2B_2O_7$ [4], $CaAl_2B_2O_7$ [5], $SrAl_2B_2O_7$ [6] and $BaAl_2B_2O_7$ [7], were obtained in the exploration of new nonlinear optical materials, low thermal expansive ceramics [8], and luminescence hosts [9]. It is interesting to note that problems frequently occur in the structure determination of these compounds. For example, in the case of $Sr_2Be_2B_2O_7$, one of the isotropic thermal parameters is negative, and the maximum peak in the final difference Fourier map is as high as 5.6 e Å^{-3}. $SrAl_2B_2O_7$ was once proposed as a nonlinear optical material [10,11] but it turned out to be centrosymmetric later [6]. In this paper, the twin laws of the $Na_2Al_2B_2O_7$ structure are deduced from a stacking fault model, and the refinements with such twin laws are reported. Similar analysis is extended to related compounds, and twinning resulting from stacking faults is proposed as the reason for the problems in structure determination of these compounds.

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2. Experimental details

The preparation of $Na_2Al_2B_2O_7$ single crystals was described in a previous publication [2]. Single crystal diffraction data were collected with a Bruker SMART Apex CCD Area Detector diffractometer, and the details of the data collection are given in Table 1. Structure refinement was performed with Shelxl97 [12], and the starting model was taken from Ref. [2].

3. Results and discussion

A perspective view of the $Na_2Al_2B_2O_7$ structure proposed in Ref. [2] is presented in Fig. 1. In this structure, BO_3 triangles and AlO_4 tetrahedra combine into a $[Al_2B_2O_7]_\infty^{2-}$ lamella, parallel to the *ab* plane. The entire structure is built by stacking these lamellae along the *c*-axis with the sodium atoms located both in and between these layers. The successful Rietveld refinement indicates that this structure model is approximately correct [2]. On the other hand, the unacceptable *R* factors, $R(F) = 0.199$ and $wR(F^2) = 0.559$, in the single crystal refinement imply that the crystal under investigation might be twinned. Sometimes, a crystal, which seems to be trigonal, contains in fact a multiple-twin of several components with lower symmetry. But in this case, a single $[Al_2B_2O_7]_\infty^{2-}$ lamella itself has 3-fold axis (plane group *P*312), which is consistent with the entire structure. So it is more reasonable to assume that the twinning arises from stacking faults of these $[Al_2B_2O_7]_\infty^{2-}$ lamellae. For the convenience of description, we introduce a notation system to represent the stacking sequence of $[Al_2B_2O_7]_\infty^{2-}$ lamellae in the $Na_2Al_2B_2O_7$ structure. The $[Al_2B_2O_7]_\infty^{2-}$ lamellae have two enantiomorphous configurations (shown in Fig. 2) denoted as "+" and "−", respectively. "*A*" and/or "*B*" are used to label the relative projective positions of adjacent lamellae in the *ab* plane. These two kinds of positions rotate by 60° relative to each other around the *c*-axis. Then the structure of $Na_2Al_2B_2O_7$ can be described as "…*A*+/*B*−/*A*+/*B*−/…". Three kinds of stacking faults can occur in the sequence, which are shown in Table 2. By introducing an I-type stacking fault, the lamella rotates by 60° around the *c*-axis relative to the original part of the crystal, resulting in a rotation twin with the twin law (110, −100, 001) or (0−10, 110, 001).

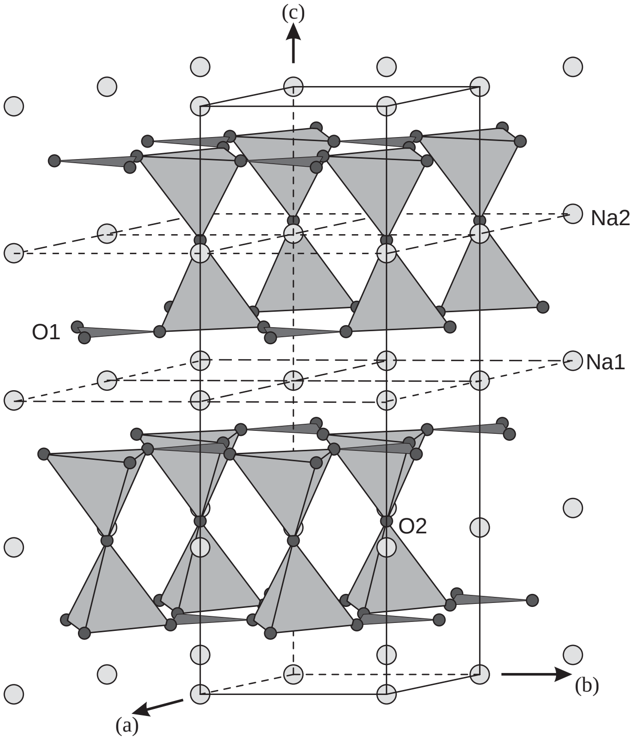

Fig. 1. (a), (b), and (c) A perspective view of the $Na_2Al_2B_2O_7$ structure. Black triangles and gray tetrahedra represent BO_3 and AlO_4 groups, respectively.

Table 1
Crystallographic data and details of data collection for $Na_2Al_2B_2O_7$

Crystal data	
$Na_2Al_2B_2O_7$	Mo*Kα* radiation
$Mr = 233.56$	Cell parameters from 1578 reflections
Trigonal, *P*-31*c* (No. 163)	$\theta = 2.67-33.06$
$a = 4.8010(4)$ Å	$\mu = 0.612\,\mathrm{mm}^{-1}$
$c = 15.2425(16)$ Å	$T = 296(2)$ K
$V = 304.26(5)$ Å^3	Plate, colorless
$Z = 2$	$0.4 \times 0.2 \times 0.02\,\mathrm{mm}^3$
$Dx = 2.549\,\mathrm{Mg\,m}^{-3}$	
Data collection	
Bruker Apex CCD area detector diffractometer	$R_{int} = 0.0411$
ω scan	$\theta_{max} = 33.49°$
Absorption correction: none	$h = -7 \rightarrow 7$
2498 measured reflections	$k = -7 \rightarrow 7$
399 independent reflections	$l = -23 \rightarrow 11$
376 reflections with $> 2\sigma(I)$	
Refinement without O2-disorder	
Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0331$	$\Delta\rho_{max} = 0.585\,\mathrm{e}$Å^{-3}
$wR(F^2) = 0.0961$	$\Delta\rho_{min} = -0.259\,\mathrm{e}$Å^{-3}
$S = 1.095$	Twin law: see the text
399 reflections	BASF [12] = 0.575(5)
23 parameters	
$\omega = 1/[\sigma^2(F_o^2) + (0.0636P)^2 + 0.0643P]$	
Where $P = (F_o^2 + 2F_c^2)/3$	
Refinement with O2-disorder	
Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.0306$	$\Delta\rho_{max} = 0.368\,\mathrm{e}$Å^{-3}
$wR(F^2) = 0.0847$	$\Delta\rho_{min} = -0.250\,\mathrm{e}$Å^{-3}
$S = 1.109$	Twin law: see the text
399 reflections	BASF [12] = 0.575(5)
27 parameters	
$\omega = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.0643P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

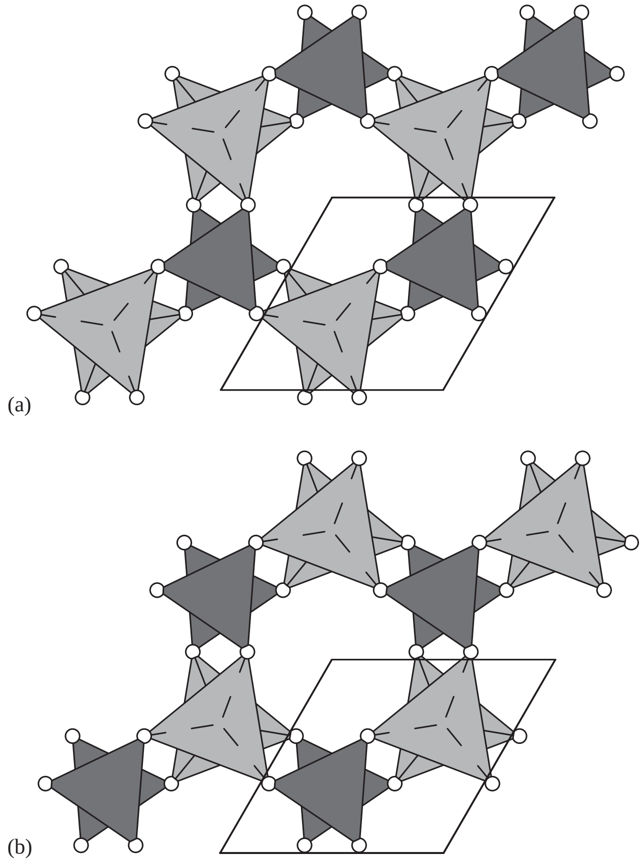

Fig. 2. Two different kinds of $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae in the structure of $Na_2Al_2B_2O_7$: (a) "+"-type and (b) "−"-type.

Table 2
Stacking faults of $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae in the $Na_2Al_2B_2O_7$ structure

Correct sequence	Stacking fault I	Stacking fault II	Stacking fault III	
:	:	:	:	
:	:	:	:	
B−	*A*−	*A*+	*B*+	
A+	*B*+	*B*−	*A*−	Domain 2
B−	*A*−	*A*+	*B*+	
A+	*B*+	*B*−	*A*−	
B−	*A*−	*A*+	*B*+	← Stacking fault
A+	*A*+	*A*+	*A*+	
B−	*B*−	*B*−	*B*−	
A+	*A*+	*A*+	*A*+	Domain 1
B−	*B*−	*B*−	*B*−	
A+	*A*+	*A*+	*A*+	
:	:	:	:	
:	:	:	:	

Interestingly, in such a case, domains 1 and 2 are also correlated to each other by a mirror plane at the boundary of the stacking fault (represented by a dashed line in Table 2), as can be easily seen from Table 2. Then the twinning can also be regarded as a reflection twin with the twin law (100, 010, 00−1). When a II-type stacking fault occurs, domains1 and 2 are correlated by 2-fold axis along [120] or [210] directions, which is a symmetry element of the crystal structure, so no twinning results. In the case of the III-type stacking fault, domains1 and 2 are correlated with each other by a 2-fold axis along [110], which leads to a rotation twin with a twin law (010, 100, 00−1). As can be readily seen from Table 2, a III-type stacking fault just introduces an additional lamella at the twin boundary compared to I-type. In fact, all the twin laws mentioned above are equivalent to each other, and can be described as a reflection twin by a mirror plane perpendicular to [100] with the twin law (−100, 110, 001). Usually, stacking faults occur for good crystal chemical reasons. In this structure, adjacent $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae are connected just via Na1 atoms (Na1–O1 bonds). When a stacking fault occurs, the number and lengths of Na1–O1 bonds at the boundary will remain, only the coordination polyhedron NaO_6 will change, for example, from (distorted) octahedral to trigonal prismatic when a I-type stacking fault occurs. The difference in energy between a NaO_6 octahedral and a trigonal prismatic coordination should be slight, therefore the stacking fault can easily occur in the crystal. With the twin laws mentioned above, the single crystal refinement leads to good *R*-values (see Table 1). The atomic positions, anisotropic displacement parameters and selected interatomic distances and angles are listed in Table 3–5, respectively. The bond valences are calculated with Brown and Altermatt's parameters [13], and presented in Table 6. It is worth noting that the average bond distance $<$Na2–O$>$ is obviously longer (about 0.2 Å) than the expected value as found in the structure of $Na_2Ga_2B_2O_7$ [3], and accordingly, the valence sum of Na2 is much smaller than the expected value. The bond sum of Sr1 in $Sr_2Be_2B_2O_7$, which is in the same coordination as that of Na2 in $Na_2Al_2B_2O_7$, is also found to be much lower than the expected value. A perspective view of $Na_2Al_2B_2O_7$ with displacement

Table 3
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atoms	Site	*x*	*y*	*z*	U_{eq}[a]
Al	4*f*	1/3	2/3	0.63991(4)	0.0148(2)
Na1	2*b*	0	0	0	0.0185(3)
Na2	2*a*	0	0	1/4	0.0423(5)
O1	12*i*	0.9612(2)	0.6029(3)	0.8952(1)	0.0342(4)
O2	2*d*	2/3	1/3	1/4	0.096(2)
B	4*f*	1/3	2/3	0.1040(2)	0.0213(5)
O2[b]	6*h*	−0.3747(7)	0.3747(7)	1/4	0.046(3)

[a] $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$.

[b] The position of O2 in the disordered model. The site occupation factor is 1/3. Both positional and displacement parameters of other atoms keep constant within the accuracy.

Table 4
Anisotropic displacement parameters (Å^2)

Atoms	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al	0.0126(3)	0.0126(3)	0.0191(3)	0.00632(13)	0.000	0.000
Na1	0.0169(4)	0.0169(4)	0.0218(6)	0.0084(2)	0.000	0.000
Na2	0.0303(6)	0.0303(6)	0.0664(13)	0.0151(3)	0.000	0.000
O1	0.0088(4)	0.0114(4)	0.0806(9)	0.0038(3)	0.0025(6)	−0.0079(6)
O2	0.135(4)	0.135(4)	0.0201(15)	0.0673(19)	0.000	0.000
B	0.0094(5)	0.0094(5)	0.0451(15)	0.0047(3)	0.000	0.000
O2[a]	0.063(4)	0.063(4)	0.0224(16)	0.040(3)	−0.005(8)	−0.005(8)

[a] Anisotropic displacement parameters of O2 in the disordered model. Parameters of other atoms keep constant within the accuracy.

Table 5
Selected inter-atomic distances and angles in the structure model without O2-disorder

3 × Al–O1:1.739(1) Å
1 × Al–O2: 1.6780(6) Å
O1–Al–O1: 110.96(6)°
O1–Al–O2: 107.93(6)°
6 × Na1–O1: 2.422(1) Å

3 × B–O1: 1.358(1) Å
O1–B–O1: 119.993(6)°
6 × Na2–O1: 2.866(2) Å
3 × Na2–O2: 2.7719(2) Å

Table 6
Bond valences in the structure model without O2-disorders

	Al	B	Na1	Na2	Valence sums
O1	0.725	1.036	0.188	0.057	2.006
O2	0.855			0.073	1.929
Valence sums	3.03	3.108	1.128	0.561	

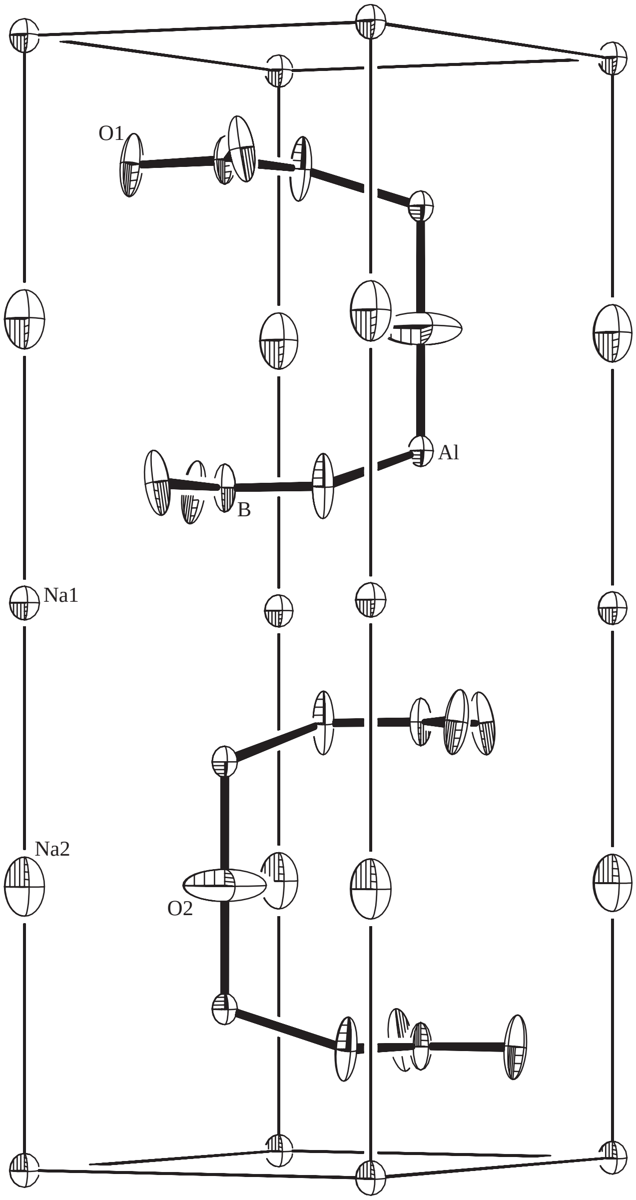

Fig. 3. A perspective view of Na$_2$Al$_2$B$_2$O$_7$ with displacement ellipsoid drawn at 50% probability.

ellipsoids drawn at 50% probability is given in Fig. 3. All the ellipsoids of strongly bonded atoms are elongated perpendicular to the bonds as expected. Root-mean-square displacements (rmsd) along the principal axes of the ellipsoids are given in Table 7. The amplitudes of displacement along a bond should be close to each other for the two atoms connected by the bond, which, in fact, perfectly holds for all atoms and bonds except for that between Na2 and O2. The rmsd in the (001) plane of O2 is unusually large (0.367 Å), which is about two times as large as that of Na2 (0.174 Å). Therefore an O2-disordered model as reported in Ref. [3] was applied in the refinement. With four additional parameters, *R*-values decreased further from 0.0331 to 0.0306. The position of O2 refined to (−0.3747(7), 0.3747(7), 0.25) with a site-occupation-factor 1/3. All the positional and displacement parameters of other atoms keep constant within the accuracy. The inter-atomic distances and angles in the disordered model are given in Table 8. The new position of O2 shifts from the original one (2/3, 1/3, 0.25) by about 0.344 Å, which is comparable with the rmsd in the (001) plane of O2 (in the structure model without disorders). However, the amplitudes of displacement of O2 are still rather large. In Ref. [3], the O2-disorder was suggested to correlate with unrecognized twinning. As an alternative, the disorder could be related with the very low valence sum of Na2. The shift of O2 from (2/3, 1/3, 0.25) to

(−0.3747(7), 0.3747(7), 0.25) influences the valence sum of Al and O2 only slightly and raises that of Na2.

We examined our $Na_2Al_2B_2O_7$ crystals with TEM and found the electron diffraction patterns were in perfect accordance with the unit cell determined by X-ray techniques (see Fig. 4). Unfortunately, it is impossible to get high-resolution images in order to confirm our model directly, because the sample decomposes quickly in the strong electron beam.

$[Be_2B_2O_7]^{2-}_{\infty}$ lamellae in $Sr_2Be_2B_2O_7$ have the same configuration as those in the $Na_2Al_2B_2O_7$ structure; however, they stack along the *c*-axis in a different way. With the same notation system, the structure of $Sr_2Be_2B_2O_7$ can be described as "$\ldots A+/A-/A+/A-/\ldots$". It is interesting to note that when a I-type stacking fault occurs in the $Na_2Al_2B_2O_7$ crystal, a layer (one unit cell in thickness) of $Sr_2Be_2B_2O_7$-type structure forms at the twin boundary. On the other hand, the $Sr_2Be_2B_2O_7$ crystal also could be twinned by introducing a stacking fault. When the stacking sequence changes into "$\ldots A+/A-/A+/A-/A+/B-/B+/B-/B+/\ldots$" from "$\ldots A+/A-/A+/A-/\ldots$", a rotation twin is obtained and a layer of $Na_2Al_2B_2O_7$-type structure appears at the twin boundary. Other kinds of stacking faults do not yield new types of twinning.

Table 7
Root-mean-square displacements (rmsd) along the principal axes of the displacement ellipsoids

Atoms	Without O2-disorders			With O2-disorder		
	rmsd 1 (Å)	rmsd 2 (Å)	rmsd 3 (Å)	rmsd 1 (Å)	rmsd 2 (Å)	rmsd 3 (Å)
B	0.097	0.097	0.212	0.098	0.098	0.212
O1	0.093	0.107	0.287	0.094	0.108	0.287
O2	0.142	0.367	0.367	0.148	0.218	0.263
Na1	0.130	0.130	0.148	0.130	0.130	0.148
Na2	0.174	0.174	0.258	0.174	0.174	0.256
Al	0.112	0.112	0.138	0.113	0.113	0.138

Table 8
Selected inter-atomic distances and angles in the disordered structure model

3 × Al–O1: 1.739(1) Å
1 × Al–O2: 1.713(1) Å
O1–Al–O1: 110.92(6)°
O2–Al–O1: 97.1(2)°
O2–Al–O1: 109.45(7)°
O2–Al–O1: 116.8(2)°
3 × B–O1: 1.359(1) Å
O1–B–O1: 119.994(6)°
6 × Na1–O1: 2.421(1) Å
6 × Na2–O1: 2.867(2) Å
2 × Na2–O2: 2.617(2) Å
1 × Na2–O2: 3.116 (2) Å

The different stacking of $[M_2B_2O_7]^{2-}_{\infty}$ (M = Be, Al) lamellae in $Sr_2Be_2B_2O_7$- and $Na_2Al_2B_2O_7$-type structures only leads to a difference in the coordination of alkali or alkaline-earth cations between the lamellae. The structures of $Sr_2Be_2B_2O_7$ and $Na_2Al_2B_2O_7$ indicate that Sr favors trigonal prismatic coordination while Na prefers octahedra. However, a small energy gain in the system might lead to a different stacking sequence of these lamellae, and then twin boundaries and even domains of different structure type will occur in the crystal. This may be regarded as intergrowth of $Sr_2Be_2B_2O_7$- and $Na_2Al_2B_2O_7$-type structures if such kind of stacking fault occurs frequently and successively in the crystal. However, the success of the twin model in the refinement suggests reasonably large domains.

We transformed the single crystal data to a "powder pattern" (project the three-dimensional data to one-dimensional), and calculated the powder patterns of both $Na_2Ga_2B_2O_7$-type and hypothetical $Sr_2Be_2B_2O_7$-type $Na_2Al_2B_2O_7$. Comparison among them reveals that the transformed "powder pattern" agrees very well with the $Na_2Ga_2B_2O_7$-type structure model, and the content of $Sr_2Be_2B_2O_7$-type phase is undetectable. The positional parameters of the hypothetical $Sr_2Be_2B_2O_7$-type $Na_2Al_2B_2O_7$ were derived from $Na_2Ga_2B_2O_7$-type structure by inserting a mirror plane between adjacent $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae.

The structure of $Sr_2Be_2B_2O_7$ has been questioned [10] because of the poor quality of the structure determination and the inconsistency between the structure and nonlinear optical properties. However, we prefer to

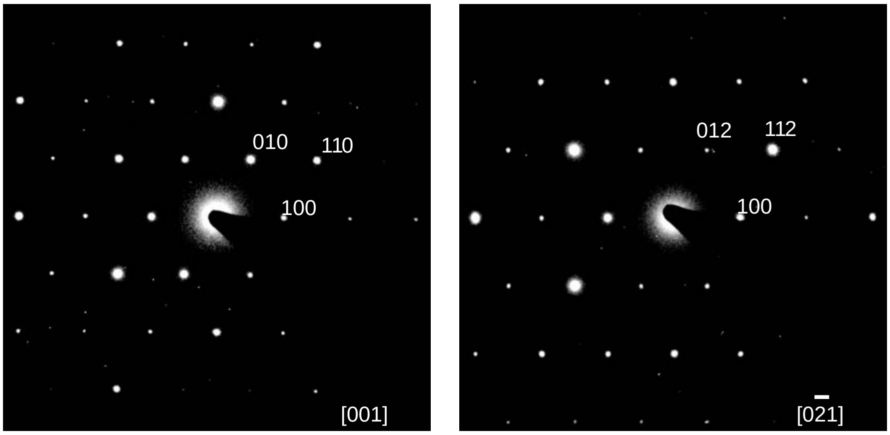

Fig. 4. Electron diffraction patterns of $Na_2Al_2B_2O_7$ recorded along the [001] and [0$\bar{2}$1] directions.

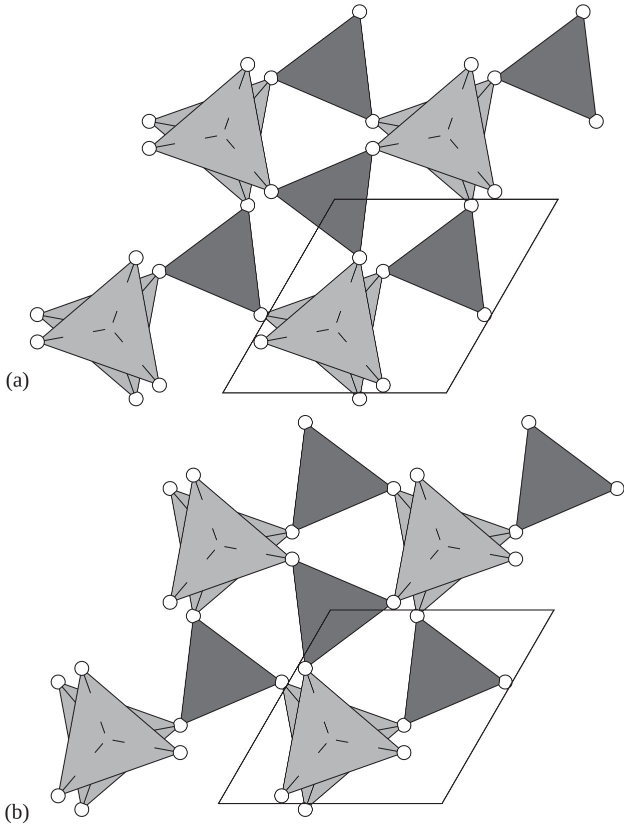

Fig. 5. Two different kinds of $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae in the structure of $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$: (a) "+"-type and (b) "−"-type.

argue that the structure is approximately correct, the negative thermal parameter and large residual peak in the final difference Fourier map just arise from stacking faults (twinning) in the crystal investigated. In a review paper [14], Chen mentioned that they could not grow $Sr_2Be_2B_2O_7$ crystals of optical quality for unknown reasons. Here we suggest that stacking faults (twinning) could be one of the reasons.

A similar analysis can be extended to $CaAl_2B_2O_7$, $SrAl_2B_2O_7$ and $BaAl_2B_2O_7$. Two kinds of $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae are found in $CaAl_2B_2O_7$, $SrAl_2B_2O_7$, which are shown in Fig. 5. They are enantiomorphs of each other, and denoted as "+" and "−", respectively, as before. A, B and C are used to label the projected relative positions of adjacent lamellae in the ab plane, as in cubic close packing. Then the structure of $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$ can be described as "$\ldots A+/B-/C+/A-/B+/C-/A+/B-/C+/A-/B+/C-\ldots$". Interestingly, Sr cations adopt octahedral coordination in $SrAl_2B_2O_7$ rather than trigonal prismatic as found in $Sr_2Be_2B_2O_7$. $BaAl_2B_2O_7$ consists of only one kind of $[Al_2B_2O_7]^{2-}_{\infty}$ lamella, which is isomorphic with the "+"-type in $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$. Its structure may be characterized as "$\ldots A+/B+/C+/A+/B+/C+/\ldots$". Under the condition that the number and lengths of $AE-O$ (AE = alkaline earth cations) bonds remain, no stacking fault can be introduced in $BaAl_2B_2O_7$. With the same premise, only one kind of stacking fault is possible to occur in $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$ crystals; namely, a "+" lamella might be replaced by a "−" one at the same position, or vice versa. For example, a "$B+$" lamella might appear at the position where a "$B-$" should be in the "correct" stacking sequence. When this happens, the coordination polyhedra of AE cations will change into slightly distorted trigonal prisms from octahedra.

4. Conclusion

The structure of $Na_2Al_2B_2O_7$ consists of $[Al_2B_2O_7]^{2-}_{\infty}$ lamellae stacked along the c-axis in a special way, and Na^+ cations located both in and between these lamellae. Stacking faults easily occur in this structure because the number and lengths of Na–O bonds at the boundary do not have to change when a stacking fault is introduced. Some kind of stacking fault will lead to twinning in the crystal, which can be described as both rotation twinning and reflection twinning. In some cases, a domain of $Sr_2Be_2B_2O_7$-type structure can form at the twin boundary. Similarly, a $Sr_2Be_2B_2O_7$ crystal could be twinned by introducing a fault in stacking the $[Be_2B_2O_7]^{2-}_{\infty}$ lamellae, and the twin boundary can be regarded as a domain of $Na_2Al_2B_2O_7$-type structure. With the premise that the number and lengths of $AE-O$ (AE = alkaline earth cations) bonds remain, no stacking fault can be introduced in $BaAl_2B_2O_7$, in contrast to $CaAl_2B_2O_7$ and $SrAl_2B_2O_7$ crystals.

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