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Redetermination of the crystal structure of dipotassium dialuminum borate, $K_2Al_2B_2O_7$, *a new non-linear optical material*

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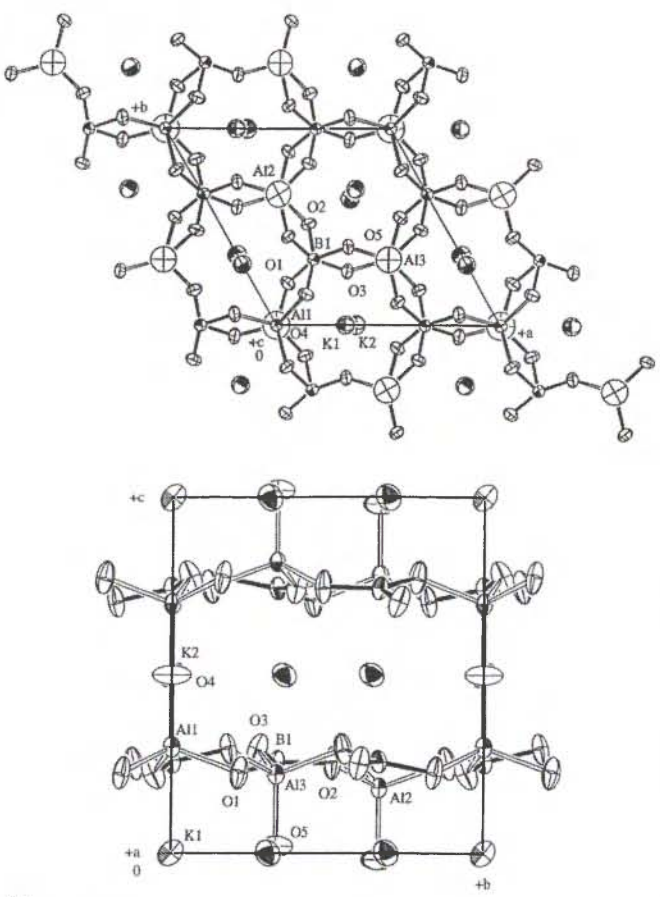

Abstract

$Al_2B_2K_2O_7$, trigonal, $P321$ (No. 150), a = 8.5657(9) Å, c = 8.463(2) Å, V = 537.8 Å^3, Z = 3, $R_{gt}(F)$ = 0.018, $wR(F^2)$ = 0.060, T = 297 K.

Source of material

The $K_2Al_2B_2O_7$ (KAB) crystals were obtained by the top-seeded solution growth (TSSG) method with K_2CO_3 - B_2O_3 - LiCl flux. The starting materials K_2CO_3, B_2O_3, Al_2O_3 and LiCl were mixed thoroughly in the appropriate ratio and then heated in a platinum crucible until they were completely melted by using a vertical cylindrical electric furnace. Crystal growth was carried out at a cooling rate of 0.3~0.5 Kd^{-1} from the saturation temperature. The large crystal was grown in 25 days, and was cut for X-ray determination.

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Discussion

The phase $K_2Al_2B_2O_7$ was studied by Kaduk and Satek [1]. They provided X-ray evidence of the $K_2Al_2B_2O_7$ compound, and the material crystallizes in the hexagonal space group $P321$ with a = 8.55800(2) Å, c = 8.45576(3) Å. FWHM = 0.08° at 30° TT, R-factor: 0.145. However, the crystal class was a mistake as hexagonal insted of trigonal [1]. In fact we found that $K_2Al_2B_2O_7$ (KAB) is a new non-linear optical (NLO) crystal [2]. In this study, the $K_2Al_2B_2O_7$ crystal structure is redetermined by X-ray analysis.

The basic structural features of KAB crystal contains K cations, BO_3 groups and AlO_4 groups. The planes of all the BO_3 groups are approximately parallel to the c axis. The whole atomic arrangement can be described as being formed from layers of AlO_4 tetrahedra and BO_3 triangles having a composition $Al_2(BO_3)_2O$. By condensation via the "free" oxygen corners of the AlO_4 tetrahedra, a three dimensional $Al_2(BO_3)_2O$ framework is formed which houses the K ions. The B–O bond lengths in the BO_3 groups range from 1.372(1) Å to 1.368(1) Å, with the O–B–O angles range from 120.6(1)° to 119.18(8)°. These B–O bond lengths and O–B–O bond angles are quite typical for BO_3 group. Likewise, the Al–O bond lengths in the distorted tetrahedral AlO_4 groups range from 1.7557(8) Å to 1.6995(4) Å, with the O–Al–O bond angles range from 110.64(3)° to 108.28(3)°. The Al–O–Al bond angle between the $Al_2(BO_3)_2O$ layers is 180°, with the Al–O bond lengths are shorter than the Al–O bond lengths within the layers. KAB possesses a space arrangement similar to $Sr_2B_2Be_2O_7$ (SBBO) [3]. In the SBBO structure, the nearly planar $(Be_3B_3O_6)_\infty$ network with all BO_3 groups perpendicular to the c axis, and the three terminal oxygen atoms of the BO_3 are linked with Be atoms. The second harmonic generation (SHG) coefficient come from BO_3 groups. Compared with SBBO, the major NLO active group of KAB is also the BO_3 group with its three terminal oxygen atom of BO_3 group to be linked with Al atoms. Because the orientation of BO_3 between the adjacent layers is not identical, the SHG coefficient of KAB is expected to be weaker than that of SBBO.

Table 1. Data collection and handling.

Crystal:	colorless sphere, diameter 0.30 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	156 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC5R, $\omega/2\theta$
$2\theta_{max}$:	79.9°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3672, 2246
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2168
$N(param)_{refined}$:	63
Programs:	PATTY [4], DIRDIF94 [5], SHELXL-93 [6], TEXSAN [7]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K(1)	3*e*	0.30912(4)	0	0	0.01842(7)	0.0183(1)	0.0202(1)	$U_{22}/2$	0.0052(1)	0.00259(6)
K(2)	3*f*	0.35847(4)	0	1/2	0.01858(7)	0.0203(1)	0.0177(1)	$U_{22}/2$	0.0061(1)	0.00305(6)
Al(1)	3*e*	0	0	0.29918(5)	0.00846(9)	U_{11}	0.0127(2)	$U_{11}/2$	0	0
Al(2)	2*d*	1/3	2/3	0.18278(6)	0.0075(1)	U_{11}	0.0117(2)	$U_{11}/2$	0	0
Al(3)	2*d*	2/3	1/3	0.22152(6)	0.0084(1)	U_{11}	0.0115(2)	$U_{11}/2$	0	0
O(1)	6*g*	0.15703(9)	0.21362(9)	0.2261(1)	0.0087(2)	0.0102(3)	0.0325(4)	0.0018(2)	0.0040(3)	–0.0046(3)
O(2)	6*g*	0.39833(9)	0.51554(8)	0.2524(1)	0.0130(2)	0.0078(2)	0.0331(4)	0.0056(2)	0.0007(2)	–0.0045(3)
O(3)	6*g*	0.45151(9)	0.2732(1)	0.2934(1)	0.0092(2)	0.0128(2)	0.0286(4)	0.0068(2)	0.0071(2)	0.0031(2)
O(4)	1*b*	0	0	1/2	0.0441(8)	U_{11}	0.0113(7)	$U_{11}/2$	0	0
O(5)	2*d*	2/3	1/3	0.0196(2)	0.0376(5)	U_{11}	0.0117(4)	$U_{11}/2$	0	0
B(1)	6*g*	0.3350(1)	0.3339(1)	0.2569(1)	0.0078(4)	0.0080(4)	0.0154(4)	0.0037(2)	0.0018(3)	0.0008(2)

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