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Reinvestigation of the crystal structure of barium aluminum borate difluoride, $BaAlBO_3F_2$, *a new nonlinear optical material*

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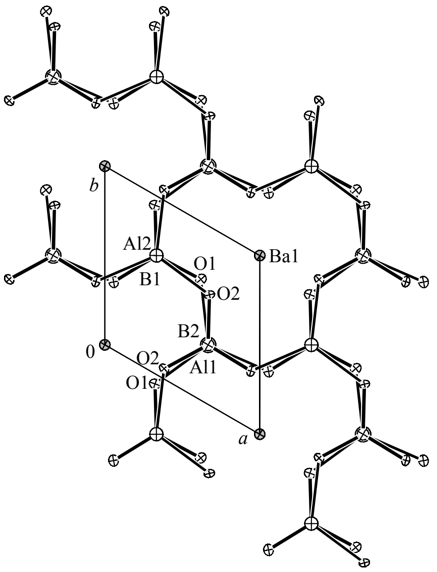

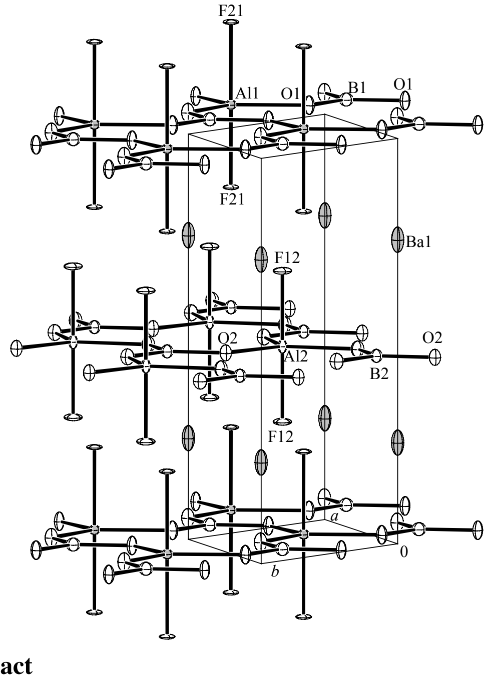

Abstract
$AlBBaF_2O_3$, hexagonal, $P\bar{6}$ (No. 174), $a = 4.8879(6)$ Å, $c = 9.403(1)$ Å, $V = 194.5$ Å^3, $Z = 2$, $R_{gt}(F) = 0.024$, $wR_{obs}(F^2) = 0.036$, $T = 296$ K.

Source of material

Crystals of the title compound were grown by the spontaneous nucleation method from NaF flux. The starting materials BaF_2, Al_2O_3, B_2O_3 and NaF were mixed in the appropriate ratio, then heated in a platinum crucible by using a vertical cylindrical electric furnace until they were completely melted . The temperature was decreased at a rate of 1 K/h from the saturation temperature. After 2 days, the solution was cooled to room temperature at a rate of 30 K/h. Small crystals for X-ray determination were obtained by mechanic fragmentation.

Experimental details

In a preliminary study, the structure was refined in the space group $P6_3$ (No. 173). But, the R-values ($R_1 = 0.061$ and $wR_2 = 0.083$) were significantly larger that those in the present refinement. Moreover, the refinement resulted in unusual B—O distances. Also, a refinement in space group $P3$ failed. Finally, it was stablished that the correct space group is $P\bar{6}$.

Discussion

In recent years, a series of alumino-borate compounds have been structurally characterized: $K_2Al_2B_2O_7$ [1] and $MAl_2B_2O_7$ with M = Ca [2], Sr [3] and Ba [4-6].

A new alumino-borate $BaAlBO_3F_2$ has been investigated in [7], using Rietveld refinement of powder X-ray data and suggested to be isostructural with $BaGaBO_3F_2$. According to this report, the $BaAlBO_3F_2$ compound crystallizes in the hexagonal system with space group $P6_3/m$, $Z = 2$, and $a = 4.882(1)$ Å, $c = 9.398(1)$ Å, $R_{wp} = 0.222$, $c2 = 2.59$. The structure of $BaAlBO_3F_2$ was studied in detail by X-ray analysis on single crystal in our group and we found that $BaAlBO_3F_2$ has a non-centrosymmetric structure.

The structure is composed of (001) layers of corner-sharing AlO_3F_2 symmetric trigonal bipyramids and BO_3 triangles. Ba cations are housed in the two dimensional ($Al_3B_3O_6F_6$) frameworks as shown in both figures. The layers are repeating alternatively (···ABAB···). Co-planar BO_3 groups are normal to the c axis, but the turn of the BO_3 groups has a small divergence in neighboring layers and the B—O bond lengths are different 1.369(4) Å and 1.376(4) Å. In the AlO_3F_2 symmetric trigonal bipyramids, all Al atoms and O atoms lie in the same plane normal to the c axis. The Al—F bond lengths are 1.917(4) Å and 1.751(6) Å. The structure has some similarities with that of the nonlinear optical crystal $KBe_2BO_3F_2$ (KBBF) [8], which reveals the shortest vacuum ultraviolet second harmonic generation output (184.7 nm) [9]. KBBF crystal consisted of corner-sharing BO_3 group where all B and O atoms lie in the same plane normal to the c axis and tetrahedral BeO_3F group, Be atoms are alternately above and below the plane at a distance of 0.5792(4) Å.

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The distance of neighboring layers d(Be···B) is 5.671 Å, and the vertical distance of nearest two F atoms which belong to neighboring layers is 2.052 Å. The space, which is formed by neighboring layers, was filled with BeO_3F tetrahedral and K cations. However, in the title structure, the distance of neighboring layers d(B···Al) is only 4.70 Å, and the vertical distance of nearest two F atoms is only 1.03 Å. The AlO_3F_2 trigonal bipyramids replace the BeO_3F tetrahedra in $BaAlBO_3F_2$. The number of tetrahedral is doubly increased in $BaAlBO_3F_2$. The results show that the distance between the layers is less in $BaAlBO_3F_2$, and the interlayer space is sufficiently filled. The tendency to cleave along the (001) plane in $BaAlBO_3F_2$ is thus weaker than that of $KBe_2BO_3F_2$. This means that $BaAlBO_3F_2$ crystals would be relatively easier to be grown. It has been identified by the crystal growth experiment. $BaAlBO_3F_2$ is found to have a powder second harmonic generation efficiency about twice than that of KH_2PO_4. This result also confirms that $BaAlBO_3F_2$ is a non-centrosymmetric structure. These properties show that $BaAlBO_3F_2$ is a good candidate for frequency shift to the ultraviolet range.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.10 × 0.10 × 0.10 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	10.37 cm^{-1}
Diffractometer, scan mode:	Rigaku AFC5R, $\omega/2\theta$
$2\theta_{max}$:	118.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	11085, 5733
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 1090
$N(param)_{refined}$:	25
Programs:	SIR92 [10], teXsan [11], DIRDIF-94 [12]

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}
Ba(1)	2g	0	0	0.24974(6)	0.00758(4)	U_{11}	0.00669(6)	$U_{11}/2$	0	0
Al(1)	1e	2/3	1/3	0	0.006(1)	U_{11}	0.004(2)	$U_{11}/2$	0	0
Al(2)	1d	1/3	2/3	1/2	0.0036(9)	U_{11}	0.009(2)	$U_{11}/2$	0	0
F(12)	2h	1/3	2/3	0.3138(6)	0.015(1)	U_{11}	0.002(1)	$U_{11}/2$	0	0
F(21)	2i	2/3	1/3	0.2038(5)	0.0112(9)	U_{11}	0.001(1)	$U_{11}/2$	0	0
O(1)	3j	−0.6750(7)	−1.0575(8)	0	0.0069(8)	0.004(1)	0.016(1)	0.0028(7)	0	0
O(2)	3k	−1.0567(8)	−0.6761(7)	1/2	0.006(1)	0.0082(9)	0.012(1)	0.0034(8)	0	0
B(1)	1c	1/3	2/3	0	0.009(3)	U_{11}	0.008(6)	$U_{11}/2$	0	0
B(2)	1f	2/3	1/3	1/2	0.006(3)	U_{11}	0.008(6)	$U_{11}/2$	0	0

References

1. Hu, Z. G.; Higashiyama, T.; Yoshimura, M.; Yap, Y. K.; Mori, Y.; Sasaki, T.: A new nonlinear optical crystal $K_2Al_2B_2O_7$. Jpn. J. Appl.Phys. **37** (1998) 1093-1094.
2. Chang, K.; Keszler, D. A. : $CaAl_2(BO_3)_2O$: Crystal structure. Mater. Res. Bull. **33** (1998) 299-304.
3. Lucas,F.; Jaulmes, S.; Quarton, M.; Le Mercier, T.; Guillen, F.; Fouassier, C.: Crystal Structure of $SrAl_2B_2O_7$ and Eu^{2+} Luminescence. J. Solid State Chem. **150** (2000) 404-409.
4. Tang, X. P.: Master thesis, Department of Applied Chemistry, University of Science and Technology of China, Hefei, China 1994.
5. Yamada, Kazuhiro: Mitsui petrochemical Ind., Jpn. Kokai Tokkyo Koho Jp. 09.61,864.
6. Ye, N.; Zeng, W.; Wu, B.; Huang, X.; Chen, C.: Crystal structure of barium aluminium borate, $BaAl_2B_2O_7$. Z. Kristallogr. NCS **213** (1998) 452.
7. Park, H.; Barbier, J.: Crystal structures of the new borate fluorides $BaMBO_3F_2$. J. Solid State Chem. **155** (2000) 354-358.
8. Mei, L.; Wang, Y.; Chen, C.; Wu, B.: Crystal structure of $KBe_2BO_3F_2$. Z. Kristallogr. **210** (1995) 93-95.
9. Chen, C. T.; Xu, Z. Y; Deng, D. Q.; Zhang, J.; Wong, G. K. L.: The vacuum ultraviolet phase-matching characteristics of nonlinear optical $KBe_2BO_3F_2$. Crystal. Appl. Phys. Lett. **68** (1996) 2930-2932.
10 Altomare, G.; Cascarano, G.; Giaccovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.: SIR92 - a program for automatic solution of crystal structures by direct methodes. J. Appl. Crystallogr. **27** (1994) 435-436.
11 teXsan. Single Crystal Structure Analysis Software. Version 1.8. Molecular Structure Corporation, 3200 Research Forest Drive, The Woodlands, TX 77381, USA 1997.
12. Beurskens, P. T.; Admiraal, G.; Beurskens, G.; de Gelder, W. P.; Israel, R.; Smits, J. M. M.: The DIRDIF-94 program system, Technical Peport of the Crystallography Laboratory, University of Nijmegen, The Netherlands 1994.