Crystal structure of bismuth gallium aluminium oxide, $Bi_2(Ga_xAl_{1-x})_4O_9$, $x = 0.4, 0.6, 0.8$

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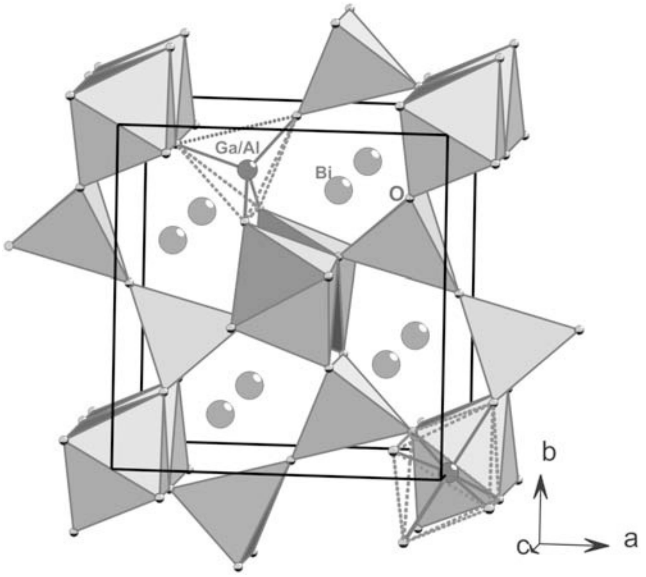

Abstract

$Al_{2.4}Bi_2Ga_{1.6}O_9$, orthorhombic, *Pbam* (no. 55), $a = 7.79697(7)$ Å, $b = 8.16575(7)$ Å, $c = 5.75442(5)$ Å, $V = 366.4$ Å^3, $Z = 2$, $Rw(P) = 0.067$, $R(P) = 0.048$, $R(I) = 0.022$, $T = 293$ K.
$Al_{1.6}Bi_2Ga_{2.4}O_9$, orthorhombic, *Pbam* (no. 55), $a = 7.83752(8)$ Å, $b = 8.20096(8)$ Å, $c = 5.79475(6)$ Å, $V = 372.5$ Å^3, $Z = 2$, $Rw(P) = 0.081$, $R(P) = 0.057$, $R(I) = 0.031$, $T = 293$ K.
$Al_{0.8}Bi_2Ga_{3.2}O_9$, orthorhombic, *Pbam* (no. 55), $a = 7.88345(6)$ Å, $b = 8.24579(6)$ Å, $c = 5.84335(4)$ Å, $V = 379.9$ Å^3, $Z = 2$, $Rw(P) = 0.075$, $R(P) = 0.054$, $R(I) = 0.028$, $T = 293$ K.

Source of material

Solid solution samples of mullite type in the system $Bi_2(Ga_xAl_{1-x})_4O_9$ ($0.0 \le x \le 1.0$) were prepared by glycerine-nitrate method. Equimolar amounts of aluminum nitrate nonahydrate, gallium nitrate heptahydrate, bismuth nitrate pentahydrate were used as reactants. The water content in the reactants was measured using TG (Setaram Setsys evolution 1750). The reactants were dissolved at 353 K in glycerine (metal : glycerine = 1 : 5) and heated at 393 K to form an amorphous gel. The dried gel was heated in an open Pt crucible at 1073 K for about 30 h to get final product. EDXS analysis of the polished samples showed the chemical compositions of the products in good agreement with the nominal compositions.

Discussion

$Bi_2(Ga_xAl_{1-x})_4O_9$ ($0.0 \le x \le 1.0$) is a new solid solution, which is isotype to $Bi_2(Fe_xAl_{1-x})_4O_9$ ($0.0 \le x \le 1.0$) [1,2] and $Bi_2(Fe_xGa_{1-x})_4O_9$ ($0.0 \le x \le 1.0$) [3,4]. M^{3+} (M = Ga/Al) ions are octahedrally (MO_6) and tetrahedrally (MO_4) coordinated with oxygen atoms. MO_6 octahedra are edge-shared along [001] and are inter-linked by dimer (M_2O_7) of MO_4 tetrahedra, forming five-membered rings of two octahedra (MO_6) and three tetrahedra (MO_4). As a result, a channel-like structure is formed. Bi^{3+} ions are located in the channels. The BiO_4 groups alternate with the planes of M_2O_7 units. Structure refinements reveal a preferential occupation of Ga in tetrahedral site (4*h*), which is similar to the results obtained for $Bi_2(Fe_xGa_{1-x})_4O_9$ ($x = 0.50$) [3]. The refinement of the occupation parameters and EDXS analysis of the samples with nominal compositions $x = 0.4, 0.6, 0.8$ give the x values of 0.41(1), 0.59(1), 0.79(1) and 0.39(2), 0.59(2), 0.80(2), respectively. The lattice parameters of $Bi_2(Ga_xAl_{1-x})_4O_9$ system vary linearly (a/Å $= 0.209x + 7.7194$, b/Å $= 0.184x + 8.1036$, c/Å $= 0.202x + 5.6835$) as function of nominal composition, x.

1. Bismuth gallium aluminium oxide, $Bi_2Ga_{1.6}Al_{2.4}O_9$

Table 1. Data collection and handling.

Powder:	white, particle size < 63 μm
Wavelength:	1.78896 Å
μ:	23.7 cm^{-1}
Diffractometer:	Stoe STADI P
$2\theta_{max}$, stepwidth:	114.98°, 0.02°
$N(hkl)_{measured}$:	185
$N(param)_{refined}$:	29
Programs:	DIAMOND [5], TOPAS [6]

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

Atom	Site	Occ.	x	y	z	U_{iso}
Bi	4*g*		0.3287(1)	0.1677(1)	0	0.0177(3)
Ga(1)	4*e*	0.313(9)	½	½	0.2606(6)	0.0228(12)
Al(1)	4*e*	0.687	½	½	0.2606	0.0228
Ga(2)	4*h*	0.499(7)	0.1490(3)	0.3377(4)	½	0.0164(10)
Al(2)	4*h*	0.501	0.1490	0.3377	½	0.0164
O(1)	4*g*		0.356(1)	0.423(1)	0	0.0127(4)
O(2)	4*h*		0.366(1)	0.409(1)	½	0.0114(3)
O(3)	8*i*		0.130(1)	0.206(1)	0.251(1)	0.0254(3)
O(4)	2*d*		0	½	½	0.0215(5)

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2. Bismuth gallium aluminium oxide, $Bi_2Ga_{2.4}Al_{1.6}O_9$

Table 3. Data collection and handling.

Powder:	white, particle size < 63 μm
Wavelength:	1.78896 Å
μ:	23.7 cm^{-1}
Diffractometer:	Stoe STADI P
$2\theta_{max}$, stepwidth:	114.98°, 0.02°
$N(hkl)_{measured}$:	186
$N(param)_{refined}$:	29
Programs:	DIAMOND [5], TOPAS [6]

Table 4. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
Bi	4*g*		0.3280(1)	0.1685(1)	0	0.0224(4)
Ga(1)	4*e*	0.50(1)	½	½	0.2600(7)	0.0253(3)
Al(1)	4*e*	0.50	½	½	0.2600	0.0253
Ga(2)	4*h*	0.673(9)	0.1487(4)	0.3370(5)	½	0.0184(11)
Al(2)	4*h*	0.327	0.1487	0.3370	½	0.0184
O(1)	4*g*		0.354(2)	0.421(1)	0	0.0177(4)
O(2)	4*h*		0.367(2)	0.409(1)	½	0.0165(4)
O(3)	8*i*		0.131(1)	0.207(1)	0.252(1)	0.0342(3)
O(4)	2*d*		0	½	½	0.0355(6)

3. Bismuth gallium aluminium oxide, $Bi_2Ga_{3.2}Al_{0.8}O_9$

Table 5. Data collection and handling.

Powder:	white, particle size < 63 μm
Wavelength:	1.78896 Å
μ:	23.7 cm^{-1}
Diffractometer:	Stoe STADI P
$2\theta_{max}$, stepwidth:	114.98°, 0.02°
$N(hkl)_{measured}$:	191
$N(param)_{refined}$:	29
Programs:	DIAMOND [5], TOPAS [6]

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	Occ.	*x*	*y*	*z*	U_{iso}
Bi	4*g*		0.3270(1)	0.1699(1)	0	0.0190(4)
Ga(1)	4*e*	0.764(9)	½	½	0.2598(4)	0.0234(11)
Al(1)	4*e*	0.236	½	½	0.2598	0.0234
Ga(2)	4*h*	0.810(8)	0.1482(3)	0.3373(4)	½	0.0139(9)
Al(2)	4*h*	0.190	0.1482	0.3373	½	0.0139
O(1)	4*g*		0.353(2)	0.420(1)	0	0.0215(4)
O(2)	4*h*		0.366(1)	0.405(1)	½	0.0241(4)
O(3)	8*i*		0.132(1)	0.208(1)	0.248(1)	0.0291(3)
O(4)	2*d*		0	½	½	0.0367(6)

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References

1. Fischer, R. X.; Schneider, H.: Crystal chemistry of mullite and related phases. In: Mullite (Eds. H. Schneider, S. Komarneni), p.1-140. Wiley-VCH, Weinheim 2005.
2. Voll, D.; Beran, A.; Schneider, H.: Variation of infrared absorption spectra in the system $Bi_2Al_{4-x}Fe_xO_9$ (x = 0 - 4), structurally related to mullite. Phys. Chem. Minerals **33** (2006) 623-628.
3. Müller-Buschbaum, H.; de Beaulieu, D. Ch.: Zur Besetzung von Oktaeder- und Tetraederpositionen in $Bi_2Ga_2Fe_2O_9$. Z. Naturforsch. **B33** (1978) 669-670.
4. Giaquinta, D. M.; Papaethymiou, G. C.; Davis, W.M.; Zur Loye, H.-C.: Synthesis, structure, and magnetic properties of the layered bismuth transition metal oxide solid solution $Bi_2Fe_{4-x}Ga_xO_9$. J. Solid State Chem. **99** (1992) 120-133.
5. Brandenburg, K.: DIAMOND. Visual crystal structure information system, Version 3.2, Crystal Impact,Bonn Germany 1998.
6. TOPAS.: Version 4.2, Bruker AXS GmbH, Karlsruhe, Germany 1999.