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Preparation and Crystal Structure Analysis of Magnetoplumbite-Type $BaGa_{12}O_{19}$

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Single-crystal X-ray analysis has verified preparation of an ideal magnetoplumbite-type phase in the ternary barium hexagallate system. X-ray refinement was carried out by the full-matrix least-squares on F^2 method, to give $R_1 = 4.61\%$ and $wR_2 = 7.76\%$ for 54 parameters and 374 independent reflections with $I > 2\sigma(I)$. Microanalysis data yields a composition of $Ba_{1.07}Ga_{11.95}O_{19}$. The crystal chemistries of the barium hexagallate and barium hexaaluminate systems are compared and discussed. Crystal data for $BaGa_{12}O_{19}$: $M = 1277.98$, space group $P6_3/mmc$ (No. 194), $a = 5.8140(8)$ Å, $c = 23.038(5)$ Å, $V = 674.4(2)$ Å^3, $Z=2$, $D_c = 6.293$ g cm^{-3}, Mo$K\alpha$, $\lambda = 0.71073$ Å, $\mu = 26.532$ mm^{-1}, $2\theta_{max} = 56.74°$. © 1998 Academic Press

INTRODUCTION

Magnetoplumbite ($PbFe_{12}O_{19}$) compounds have structures closely related to that of β-alumina ($NaAl_{11}O_{17}$), which is well known for the high mobility of cations in its lattice. The β-alumina structure consists of slabs of aluminum oxide with the spinel structure ("spinel blocks"), separated by mirror planes ("conduction planes") in which the large cations are located. The magnetoplumbite structure then differs only in the arrangement of cations on the conduction planes (1). Barium hexaaluminate was first reported in 1935 (2) as having the ideal magnetoplumbite-type structure with composition $BaO \cdot 6Al_2O_3$, or $BaAl_{12}O_{19}$. Several years later it was discovered that this composition does not actually exist (3). Instead, it was found that barium hexaaluminate exists as a two-phase material: Phase I is Ba-poor with respect to $BaAl_{12}O_{19}$, and Phase II is relatively Ba-rich. The Phase I material has since been well characterized by single-crystal X-ray diffraction (4, 5), and the Phase II structure has been characterized both by high-resolution transmission electron microscopy (HRTEM) (6) and from single crystal X-ray studies as the Pb-stabilized form (7).

The crystal chemistry of the barium hexagallate system has been largely described by analogy to the hexaaluminate system, since their powder patterns are similar and suggest that neither phase has the ideal magnetoplumbite structure. Only one single-crystal X-ray study on the ternary barium hexagallate system has been published previously (8), in which a Phase I-type structure was observed. Wagner and O'Keeffe (9, 10) published HRTEM studies of $BaGa_{12}O_{19}$ and observed only Phase II-type behavior. A qualitative structural model was proposed for this phase based on images taken along $[1\bar{1}00]$, although Park and Cormack (11) treated the model as quantitative and used it in lattice energy minimization calculations to show that the proposed model did not optimally describe the structure of Phase II barium hexaaluminate (i.e. by analogy) as well as the Ba(Pb) hexaaluminate model proposed by Iyi *et al.* (7).

The purpose of the present work, therefore, was originally to obtain a single-crystal of Phase II-type barium hexagallate for X-ray characterization, in order to verify that its structure is indeed analogous to the Ba(Pb) form of Phase II barium hexaaluminate. Instead of single-phase crystals of the Phase II-type structure, however, it appears that crystals with a magnetoplumbite-type phase and one or more as yet unidentified commensurate phases (but possibly Phase II) have been prepared. This paper is concerned with analysis of the magnetoplumbite-type phase, and it provides the first evidence showing that the Ba–Ga–O system can accommodate the ideal magnetoplumbite-type structure.

EXPERIMENTAL

Sample Preparation

Single crystals were grown from a Bi_2O_3 flux, utilizing the procedure outlined by Habery *et al.* (12) for the preparation of single crystals of $SrGa_{12}O_{19}$. Several different mixtures of $BaCO_3/Ga_2O_3/Bi_2O_3$ were reacted in covered Pt crucibles to a temperature of 1350°C for 5 h, and then cooled to 500°C at a rate of 20°C/h. and finally to room temperature at a rate of 50°C/h. The products usually consisted of only a few (or no) barium hexagallate crystals mixed with mostly Ga_2O_3 crystals and a monoclinic phase recently characterized as $Ba_2BiGa_{11}O_{20}$ (13). The crystal selected for analysis

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was broken from a larger piece and had an irregular shape with approximate dimensions $0.08 \times 0.04 \times 0.02\ mm^3$.

Microanalysis

Microanalysis was performed at the University of California—Davis using a Cameca SX50 electron microprobe with three wavelength dispersive spectrometers, operated at 20 keV with a beam current of 10 nA and a 1 μm spot size. Analyte line intensities $GaK\alpha$, $BaL\alpha$, and $BiL\alpha$ were converted to weight fractions relative to standards $Ga_3Gd_5O_{12}$, $BaSO_4$, and Bi_2Se_3 via standard ZAF corrections. Based on 19 oxygens per formula unit, the composition deduced from the data was $Ba_{1.07}Ga_{11.95}O_{19}$. It should be noted here that the microanalysis results indicated the presence of 0.01 Bi atoms per 19 oxygen atoms, which is too few for Bi to have a significant impact on the structure. Thus this number was incorporated as Ga in the experimental composition and refinement.

Structure Determination

X-ray data were collected at the University of Toledo on a Siemens SMART CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source ($MoK\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Approximately 1.1 hemispheres of intensity data were collected in 1371 frames using ω scans (width of 0.30° and exposure time of 60 s per frame). Unit cell dimensions were determined by a least-squares fit of 2106 reflections with $I > 5\sigma(I)$, and maximum $2\theta = 56.74°$. An empirical absorption correction based on equivalent reflections was performed using SADABS (written by George Sheldrick, University of Göttingen, 1996), which also simultaneously corrected for other effects, such as absorption by the glass capillary. The structure was solved using direct methods and refined by the full-matrix least-squares on F^2 technique. The refinement parameters included correction for secondary extinction, and anisotropic thermal parameters on all atoms. Occupancy factors were refined on all atoms as well. All calculations were performed using Siemens SHELXTL, Ver. 5.05, on a Gateway 2000 PC-90XL computer. Crystal data and refinement results are summarized in Table 1; atomic coordinates and anisotropic and equivalent isotropic displacement parameters are listed in Table 2; and selected bond lengths and angles are given in Tables 3 and 4, respectively.

TABLE 1
Summary of Crystal Data and Refinement Results[a]

Structural formula	$BaGa_{12}O_{19}$
Formula weight	1277.98
Color and habit	Pale green, Irregular Shape
Crystal size (mm^3)	$0.08 \times 0.04 \times 0.02$
Space group	$P6_3/mmc$ (No. 194)
a (Å)	5.8140(8)
c (Å)	23.038(5)
V (Å^3)	674.4(2)
Z	2
ρ_{calc} (g/cm^3)	6.293
$\lambda(MoK\alpha)$ (Å)	0.71073
μ (mm^{-1})	26.532
θ Range for data collection (deg)	3.54 to 28.37
Limiting indices	$-7 \leq h \leq 7,\ -5 \leq k \leq 7,\ -30 \leq l \leq 25$
No. of reflections collected	4241
No. of independent reflections	374
No. of parameters	54
Final R indices [$I > 2\sigma(I)$]	$R_1(F)$[b] $= 0.0461$, $wR_2(F^2)$[c] $= 0.0776$
Final R indices (all data)	$R_1(F)$[b] $= 0.0665$, $wR_2(F^2)$[c] $= 0.0841$
Goodness-of-fit on F^2	1.002
Extinction coefficient	0.0042(7)

[a] According to SHELXTL ver. 5.05 documentation: Refinement on F^2 for all reflections. Weighted R factors, wR_2, and all goodnesses of fit, S, are based on F^2. Conventional R factors, R_1, are based on F, with F set to zero for negative F^2. The observed criterion of $I > 2\sigma(I)$ is used only for calculating R factors, etc., and is not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based of F, and R factors based on all data will be even larger.

[b] $R_1(F) = [\sum||F_o| - |F_c||]/\sum|F_o|$, with $F_o > 4.0\sigma(F)$.

[c] $wR_2(F^2) = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ with $F_o > 4.0\sigma(F)$, and $w^{-1} = \sigma^2(F_o)^2 + (0.0377P)^2 + 0.00P$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$.

RESULTS AND DISCUSSION

An early indication during the course of the experiment that the crystal analyzed in this study has a magnetoplumbite-type structure was given by examining the c/a cell parameter ratio. This can be used as a way to identify structure type, as originally pointed out by Verstegen and Stevels (14). It is generally observed that c/a ratios are lower than 3.98 for magnetoplumbites and above this value for β-aluminas. Table 5 gives the c/a ratios for various Ba compounds, with β-alumina ($NaAl_{11}O_{17}$) and magnetoplumbite ($PbFe_{12}O_{19}$) values shown for comparison. It is seen that the parameters observed in this study are indicative of the magnetoplumbite-type phase. In contrast, the ratio for both Phases I and II barium hexaaluminate suggests that these structures are more closely related to β-alumina, as observed (4–7).

Refinement

Structure solution and refinement of the data set for the crystal analyzed in this study proceeded in a fairly straightforward manner. The initial structure solution determined from the direct methods calculation assigned the Ba position and all five Ga positions expected for the magnetoplumbite-type structure. Following initial refinement of these metal positions, all five of the expected oxygen positions were present as Fourier peaks Q1 to Q5, with the

TABLE 2
Positional, Occupational, and Anisotropic[a] and Equivalent Isotropic[b] Displacement Parameters ($\text{Å}^2 \times 10^4$)

	Position	Number per unit cell	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U(eq)
Ba	2d	1.902(91)	2/3	1/3	1/4	68(6)	U_{11}	103(7)	0	80(5)
Ga(1)	12k	11.511(548)	0.3367(2)	0.1683(1)	0.3916(1)	34(6)	44(5)	77(6)	5(2)	53(4)
Ga(2)	4f	3.789(183)	1/3	2/3	0.4726(1)	22(8)	U_{11}	73(9)	0	39(7)
Ga(3)	4f	3.843(184)	1/3	2/3	0.3107(1)	45(7)	U_{11}	69(8)	0	53(6)
Ga(4)	2a	1.880(91)	0	0	1/2	20(10)	U_{11}	47(13)	0	29(8)
Ga(5)	4e	1.892(93)	0	0	0.2404(3)	30(12)	U_{11}	110(53)	0	58(19)
O(1)	12k	12.565(673)	− 0.1550(7)	0.1550(7)	0.5521(3)	131(33)	U_{11}	141(37)	− 5(13)	133(24)
O(2)	12k	12.168(624)	0.5036(7)	0.0071(14)	0.3515(3)	84(28)	25(34)	150(35)	4(28)	93(19)
O(3)	4f	4.261(264)	1/3	2/3	0.5548(4)	67(47)	U_{11}	161(59)	0	98(36)
O(4)	4e	3.824(224)	0	0	0.3518(4)	74(43)	U_{11}	27(52)	0	58(33)
O(5)	6h	5.869(353)	0.1825(10)	0.3650(19)	1/4	131(49)	60(61)	89(48)	0	101(32)

[a] $U_{12} = \frac{1}{2}U_{22}$; $U_{13} = \frac{1}{2}U_{23}$ by symmetry. The anisotropic thermal parameter is expressed as $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

[b] U(eq) is defined as one-third of the trace of the $\mathbf{U}_{ij}$ orthogonalized tensor.

electron density dropping off significantly from 10.90 to 3.73 $e^-/\text{Å}^3$ at Q6. After all of the atomic positions pertaining to an ideal magnetoplumbite structure had been assigned, the R factors[1] were R_1 $[I > 2\sigma(I)] = 0.0875$ and $wR_2 = 0.2259$. Since a shift in the Ga(5) position from a 2d to a 4e site has been observed previously in magnetoplumbite-type structures (15–17), Ga(5) was at this point refined as a 4e site with half-occupancy. This resulted in a drop in R factors to $R_1 = 0.0636$ and $wR_2 = 0.1402$. Next, gradual refinement of all of the occupancy factors was performed yielding $R_1 = 0.0595$ and $wR_2 = 0.1292$. This represents a relatively small improvement in the R factors, as expected since the experimentally determined composition of $Ba_{1.07}Ga_{11.95}O_{19}$ is close to the ideal composition of $BaGa_{12}O_{19}$, which was used as the starting point for refinement. Examination of the number of atoms per unit cell listed in Table 2 indicates that, within experimental error, the composition calculated from the refinement is consistent with the ideal magnetoplumbite-type composition of $BaGa_{12}O_{19}$ as well. Following refinement of the occupancies, all atoms were refined anisotropically, giving R_1 and wR_2 values of 0.0561 and 0.1209, respectively. The final displacement parameters shown in Table 2 represent in general the relative magnitudes typical for magnetoplumbite compositions (16–18). Following calculation of secondary extinction, the refinement converged to the R values listed in Table 1.

Crystal Chemistry

From analysis of powdered barium hexagallate, and by analogy to barium hexaaluminate studies, it has been assumed that the barium hexagallate phase cannot (or is not likely to) have the ideal magnetoplumbite-type structure. The usual explanation is that Ba is too large to fit into the 12-coordinated site of the ideal magnetoplumbite-type structure (19, 20). Examination of the Ba–O bond lengths in Table 3 indicates in fact that Ba is somewhat overbonded in the magnetoplumbite-type structure presented here. Using the equation $v_{ij} = \exp[(r_o - r_{ij})/B]$, where r_o $(= 2.285)$ and B $(= 0.37)$ are empirical parameters taken from Brown and Altermatt (21) and r_{ij} are experimental bond lengths, the summation of bond valences (i.e. v_{ij}) for the 12 bonds around Ba yields a total valence of 2.38. It is important to note that overbonding at the Ba site was also reported in a single-crystal X-ray study of $BaFe_{12}O_{19}$ by Obradors *et al.* (16). They reported that $BaFe_{12}O_{19}$ has the magnetoplumbite-type structure with Ba–O bond lengths of 2.868 Å × 6 and 2.950 Å × 6, which gives a total valence sum of 2.24 for Ba using the method described above.[2] Regarding the Ga–O bond lengths listed in Table 3, these are consistent with corresponding bonds in the Ba β-gallate structure (8). Also, the bond angles given in Table 4 are in good agreement with the relative bond angles for other magnetoplumbite structures (16, 17).

While it appears that the magnetoplumbite structure can exist despite some overbonding at the Ba site, this phase has not been previously observed in powder samples of barium hexagallate, most likely because crystal chemical and thermodynamic factors favor the roomier Ba site and disordering observed in the Phase II-type structure. It should be noted that the crystal examined in the present study was broken from a larger piece, for which the cell parameters

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[1] Unless stated otherwise, these and all subsequent R_1 and wR_2 values reported herein are based on $I > 2\sigma(I)$.

[2] Note that Obradors *et al.* (16) reported a valence sum of 2.31 around Ba, but they used a different method than the one used here.

TABLE 3
Interatomic Distances

	Number of bonds	Distance (Å)
	Polyhedron 12-Coordinated	
Ba –O(2)	6	2.858(6)
–O(5)	6	2.911(1)
	Octahedral Coordination	
Ga(1)–O(1)	2	2.085(4)
–O(2)	2	1.892(4)
–O(3)	1	2.071(6)
–O(4)	1	1.927(5)
Ga(3)–O(2)	3	1.955(7)
–O(5)	3	2.065(7)
Ga(4)–O(1)	6	1.969(7)
	Tetrahedral Coordination	
Ga(2)–O(1)	3	1.884(7)
–O(3)	1	1.893(10)
	Polyhedron 5-Coordinated	
Ga(5)–O(4)	1	2.124(11)
–O(4)′	1	2.567(11)
–O(5)	3	1.851(10)

TABLE 4
Bond Angles[a] (deg)

Octahedral Coordination	
O(1)–Ga(1)–O(1)′	80.81(36)
–O(2)	90.64(26)
–O(3)	88.89(20)
–O(4)	84.83(22)
O(2)–Ga(1)–O(3)	86.26(20)
–O(4)	99.13(23)
O(2)–Ga(3)–O(2)′	98.81(24)
–O(5)	90.19(18)
O(5)–Ga(3)–O(5)′	79.14(28)
O(1)–Ga(4)–O(1)′	86.71(27)
–O(1)″	93.29(27)
Tetrahedral Coordination	
O(1)–Ga(2)–O(1)′	111.30(18)
–O(3)	107.57(19)
Polyhedron 5-Coordinated	
O(5)–Ga(5)–O(4)	96.88(19)
–O(4)′	83.12(19)
–O(5)′	118.59(8)

[a] Primes (′, ″) represent symmetrically equivalent atoms at different positions.

were found to be $a = 5.832$ Å and $c = 23.543$ Å. Comparison to data listed in Table 5 indicates that these parameters are somewhat larger than the parameters obtained for the magnetoplumbite-type chunk analyzed in this paper but are very similar to those given for the Phase II-type $BaGa_{12}O_{19}$ compound from Ref. 19. Zandbergen *et al.* (19) obtained the cell parameters for their sample using X-ray powder diffraction and completed further studies using HRTEM in which Phase II-type behavior was revealed. No Phase I-type specimens were reportedly observed in this study, although the HRTEM technique does not of course necessarily preclude their existence. However, it seems reasonable to conclude by comparison of cell parameters that the larger parent crystal is an intergrowth of mostly a β-alumina-type phase (possibly Phase II) with a magnetoplumbite-type phase as represented by the sample analyzed in the present work. It should be mentioned here that no isolated crystals of the magnetoplumbite-type phase were observed in any of the samples prepared in this study. Nevertheless, the data presented herein provide the first quantitative evidence that the magnetoplumbite structure can exist in the ternary barium hexagallate system.

Since a magnetoplumbite-type phase has not previously been observed in the ternary hexaaluminate system, despite the fact that the two crystal systems are largely considered analogous, a brief examination of how the overall crystal

TABLE 5
Cell Parameters *a* and *c* and *c/a* of Selected Magnetoplumbite/β-Alumina-Type Compounds

Ideal composition	a (Å)	c (Å)	c/a	Reported structure type	Reference
$NaAl_{11}O_{17}$	5.594	22.53	4.03	β-Alumina	22
$PbFe_{12}O_{19}$[a]	5.895	23.090	3.917	Magnetoplumbite	JCPDS Card 41-1373
$BaFe_{12}O_{19}$	5.892	23.183	3.935	Magnetoplumbite	16
$BaGa_{12}O_{19}$	5.8140	23.0382	3.963	Magnetoplumbite	this study
$BaGa_{12}O_{19}$-Phase I[b]	5.859	23.192	3.958	β-Alumina	8
$BaGa_{12}O_{19}$-Phase II[a]	5.820	23.534	4.04	β-Alumina	19
$BaAl_{12}O_{19}$-Phase I	5.588	22.769	4.075	β-Alumina	4
$BaAl_{12}O_{19}$-Phase I	5.582	22.715	4.069	β-Alumina	5
$(Ba,Pb)Al_{12}O_{19}$-Phase II	5.6003	22.922	4.093	β-Alumina	7

[a] Cell parameters for these compounds were obtained from X-ray powder diffraction; all others were from single-crystal X-ray diffraction studies.
[b] See footnote 3 regarding the anomalously small c/a ratio observed for this phase.

chemistries of the two systems do compare seems worthwhile. Phase I- and Phase II-type structures have been observed in each of the two systems. The ternary Phase I compounds in both systems have been well characterized from single-crystal X-ray data as β-alumina-types, with respective compositions $Ba_{0.75}Al_{11}O_{17.25}$ (4, 5) and $Ba_{0.65}Ga_{10.80}O_{16.84}$ (8). These two Phase I structures are very similar but differ from each other with respect to their proposed charge compensation mechanisms. Such a mechanism is necessary due to the excess positive charge present in the ideal β-alumina-type composition of $BaR_{11}O_{17}$ (R = Al or Ga). For barium hexaaluminate, charge compensation is achieved by replacement of every fourth Ba atom with O (4, 5), whereas the principle compensation mechanism for the hexagallate compound is reported as Ga(2) vacancies in the center of the spinel blocks (8).[3]

The subtle differences in the structures of the respective Phase I compounds, as well as the observation that the gallate system can accommodate the magnetoplumbite-type phase, leads one to wonder whether any differences are present in the corresponding Phase II structures. The only quantitative structural analysis reported to date for a Phase II compound in either system was the study by Iyi *et al.* (7) on Ba(Pb) hexaaluminate (reported composition $(Ba_{0.80}Pb_{0.20})_{1.17}Al_{10.5}O_{16.92}$), which is assumed to be identical to the structures of the ternary Ba hexaaluminate and Ba hexagallate Phase II compounds (7, 11). To verify that the ternary structures are indeed identical to the quaternary Ba(Pb) hexaaluminate structure, however, and to elucidate any subtle differences between them, quantitative structural studies should be performed directly on the ternary systems. This will be the focus of future work.

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[3] Given that the structure and ternary composition reported for this phase are correct, it is possibly due to relaxation at the vacancies in the center of the spinel blocks that the c axis (and therefore the c/a ratio) reported in Table 5 for Ba β-gallate is anomalously small.