

A Structural Model For "Barium Hexagallate"

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A model for the structure of "barium hexagallate" (and by implication Phase II of "barium hexaluminate") has been derived from a comparison of calculated and experimental high-resolution electron microscope images. In the proposed structure Ba is placed in the "spinel" blocks as well as on the mirror planes of the structure. © 1988 Academic Press, Inc.

Introduction

Although $\text{BaAl}_{12}\text{O}_{19}$ was for several years considered to be an analog of magnetoplumbite ($\text{PbFe}_{12}\text{O}_{19}$), it is now well established that this compound actually exists as two distinct phases (I and II). As originally described by Kimura *et al.* (1), Phase I represents a compound which is Ba-poor with respect to the ideal composition and Phase II represents a relatively Ba-rich compound. Three transmission electron microscope studies of this system have been published (2–4), and the high-resolution images obtained in each of these studies revealed the following: (a) The two phases intergrow coherently; (b) Phase I has a well-ordered structure projecting an image with contrast typical of ideal β -alumina or magnetoplumbite structures; (c) Phase II consists of a disordered superlattice structure of dimensions $\sqrt{3}a \times \sqrt{3}a \times c$ relative to a β -alumina or magnetoplumbite-like substructure. The disordering observed in the Phase II structure is due to the random choice of one of three possible origins for the supercell in the structure.

Two structural refinement studies of Phase I have been published (5, 6), and these both report this compound as having composition $\text{Ba}_{0.75}\text{Al}_{11}\text{O}_{17.25}$ with a structure very closely related to that of β -alumina. The structure of a barium lead hexaluminate Phase II compound has been reported by Iyi *et al.* (7), and this paper was the first to indicate that the excess Ba atoms are not positioned on the conduction planes. Instead, Iyi *et al.* determined from their single crystal X-ray data that the excess Ba (or Pb) atoms are positioned in the centers of the spinel blocks at one of the tetrahedral Al sites in place of the tetrahedral Al and apex O atoms. This arrangement occurs in one of every three unit cells, and furthermore, the Ba or Pb atoms in the spinel block are positioned directly on either side of an unoccupied Beevers–Ross (BR) site in one of the two "conduction planes" per unit cell. Surrounding this unoccupied BR site are three interstitial M_2O groups (i.e., Reidinger defects), where these interstitial Al atoms are located between unoccupied Al(1) [i.e., octahedral Al sites—here and throughout we use the

numbering system of Peters *et al.* (8)]. The interstitial oxygen atoms are then located at the same sites as the bridging oxygen atoms of the M_2O_3 group in the magnetoplumbite structure. The other conduction plane apparently has the ideal β -alumina arrangement, resulting in the observed supercell of dimensions $a\sqrt{3} \times a\sqrt{3} \times c$. Iyi *et al.* (7) reported their experimentally determined composition of this structure to be $3[(Ba_{0.8}Pb_{0.2})_{2.34}Al_{21}O_{33.84}]$, which is in close agreement with the ideal formula of $3[(Ba,Pb)_{2.33}Al_{21.33}O_{34.33}]$ per unit cell.

Iyi *et al.* (9) have subsequently published their results of an electron microscope study of barium lead hexaaluminate Phase II. In this paper, the structure described above from their earlier single crystal X-ray diffraction results (7) was used to calculate an image for comparison to an experimental electron micrograph. Based on this comparison, as well as results obtained from a CBED pattern, the structural model described above was confirmed. Following the earlier studies on the barium hexaaluminate system, we had conducted an electron microscope study of $BaGa_{12}O_{19}$ and found structural behavior closely related to that of Phase II barium hexaaluminate (10). At the same time as this work was completed, Zandbergen *et al.* (11) published their results of a similar electron microscope study of $BaGa_{12}O_{19}$. An interesting feature of the barium hexagallate system indicated by both studies is that only one phase with a structure related to that of β -alumina or magnetoplumbite exists in this system; that is, no Phase I analog is present. Zandbergen *et al.* did however report that they observed a second phase in barium hexagallate images, which they assumed to be Ga_2O_3 . Concerning the structure of barium hexagallate (as well as Phase II barium hexaaluminate) Zandbergen *et al.* suggested that in one of the two conduction planes per unit cell, excess Ba atoms replace one-third of the M_2O ($M = Ga$ or

Al) bridging groups and another one third of the M_2O groups are replaced by M_2O_3 . The other conduction plane then has the ideal β -alumina arrangement, resulting in a composition per triple cell of $Ba_7M_{64}O_{103}$.

In this study, we have analyzed high-resolution images of barium hexagallate using computer image calculations in an effort to further elucidate the structural properties of the superlattice in this compound, particularly with regard to the positioning of the excess Ba atoms. The results indicate that, in agreement with the findings of Iyi *et al.* (7) for barium lead hexaaluminate, the excess Ba atoms in barium hexagallate are not positioned on the conduction plane as previously assumed. However, for reasons to be discussed later, we also do not find the heavy atoms to be located at the centers of the spinel blocks as do Iyi *et al.*, but rather we suggest a conduction plane arrangement with a triple layer of Ba atoms. In this arrangement, two Ba atoms are positioned in the oxygen layers directly on either side of an anti-BR (aBR) site in alternating conduction planes in one of every three unit cells.

Experimental

Samples of $BaGa_{12}O_{19}$ and $BaGa_2O_4$ (used as a standard for microanalysis) were prepared as described in the previous paper (9). High-resolution images were obtained from a JEM 200CX electron microscope, and EDX spectra were obtained from a Philips 400T microscope equipped with a Tracor Si(Li) detector and a Tracor Northern TN2000 multichannel analyzer system. Images were calculated through application of the multislice method on a VAX 11/750 computer system, using programs written mainly by M. A. O'Keefe. The images thus calculated were written to the input video digitizer of a DeAnza IP8500 image processor, and hard copies were obtained using a Tektronix 4632 Video Hard Copy Unit.

Microanalysis

In our previous paper (10) we reported the Ba:Ga concentration ratio in our barium hexagallate specimen as being near the ideal stoichiometry of 1:12; however, subsequent analysis using more carefully selected samples of standard material indicated that this is not the case. BaGa₂O₄ was again used as a standard, and eight crystals yielded a mean $I_{\text{Ba}}/I_{\text{Ga}}$ ratio of 0.688 ± 0.026 . Assuming that BaGa₂O₄ is stoichiometric and that $I_{\text{Ba}}/I_{\text{Ga}} = k_{\text{Ba-Ga}}(c_{\text{Ba}}/c_{\text{Ga}})$ (12) then gives $k_{\text{Ba-Ga}} = 0.727 \pm 0.027$. The mean $I_{\text{Ba}}/I_{\text{Ga}}$ value obtained from 11 barium hexagallate crystals was 0.143 ± 0.004 , so that we now have a Ba:Ga concentration ratio of $1:9.62 \pm 0.65$ for this compound. We cannot fully explain the difference in the two sets of analyses, but note that the "standard" crystallites were more carefully selected, and measured with a smaller probe, than in the previous work and that the standard deviations for the new analyses are smaller, so that the earlier analyses may have been biased by contamination by small amounts of other phases.

Image Analysis

Image analysis was concentrated on images in the [1100] orientation, since these are the most informative concerning the structural nature of the disordered superlattice in barium hexagallate. Figure 1 shows such an image of barium hexagallate, along with an image calculated from a barium hexagallate compound having the ideal β -alumina structure. It is apparent from the comparison of the two images that the contrast in the experimental image corresponding to superlattice reflections is represented by the splitting of every third white spot along the X-type (labeled) conduction planes into two spots. Another difference between the two images can be seen in the rows indicated by the two long arrows to

the right of the experimental image; here it is seen that two of the three spots observed in the calculated image are now absent. The most significant point to be emphasized, however, is not the difference between the two images, but their similarity. Except for the two differences mentioned above, the experimental image shows identical contrast to that expected from the ideal structure. From these observations, it seems plausible to assume that the superstructure involves only a local change in the arrangement of the Ba and Ga atoms in the vicinity represented by the "anomalous" contrast in the experimental image.

In the lower part of Fig. 1 is an atomic plot which is projected in exactly the same way as the calculated image. From this atomic plot, the following features of the calculated image (and thus the experimental one) become apparent: (a) the Ba atoms are in reverse contrast; (b) the tetrahedral and octahedral gallium atoms located at the centers of the spinel blocks are also in reverse contrast; (c) the octahedral layers of Ga atoms between the conduction planes and the centers of the spinel blocks are in normal contrast. The question which must therefore be asked concerning the anomalous contrast on the experimental image is whether the two white spots appearing on either side of the X-type conduction plane at intervals of $3d_{11\bar{2}0}$ are in reverse or normal contrast. If they are in reverse contrast, the two spots most likely represent two barium atoms so that the conduction layer now consists of three barium layers instead of one. If on the other hand these anomalous spots are in normal contrast, they represent "holes" in the structure probably caused by missing octahedral gallium atoms at the Ga(1) position.

Assuming first that the anomalous spots described above are in normal contrast, there are two possibilities regarding the positioning of the excess Ba atoms: (1) they are distributed on the conduction planes; or

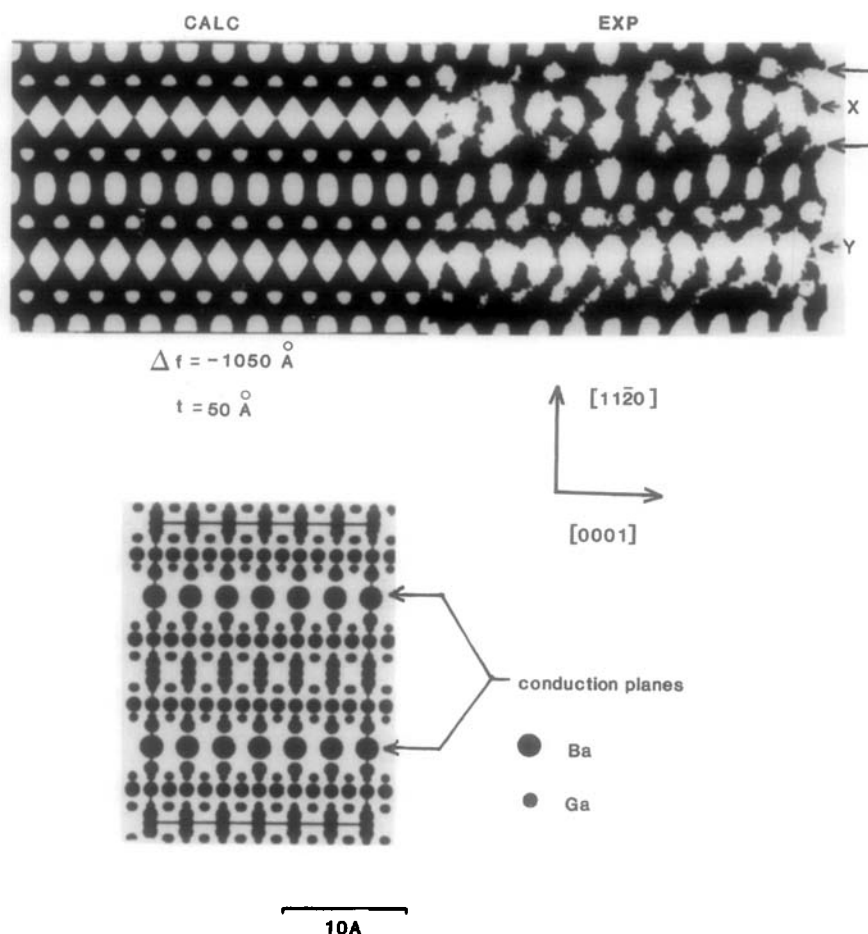


FIG. 1. Top: calculated image for barium aluminate with the β -alumina structure (left) compared with an experimental image from "barium hexagallate" (on the right). Bottom: the projected structure used in the calculations; atom sizes in proportion to atomic number.

(2) they are located at the centers of the spinel blocks and so are represented in reverse contrast by the bright white spots at the corresponding positions in the experimental image of Fig. 1. As an initial consideration, the first possibility seems to be the more likely of the two, since structural refinement studies of β -alumina compounds (8, 13) have indicated that Al(1) sites are vacant while excess cations are distributed on the conduction plane. However, the experimental image of Fig. 1 as well as image calculations we have obtained suggest that

this is not the case for the barium hexagallate structure. The second possibility then seems quite feasible, since here the arrangement of the excess Ba atoms in barium hexagallate agrees with that reported by Iyi *et al.* (7) for the excess Ba (or Pb) atoms in barium lead hexaaluminate. We do not accept this hypothesis directly, however, as it is possible that ternary barium hexagallate is not isostructural with barium lead hexaaluminate. This is indicated by the results obtained from applying the valence sum principle of Zachariasen (14) to the

bond lengths reported by Iyi *et al.* for the 12-coordinated spinel-block Ba position in barium lead hexaaluminate.

For the valence sum analysis we use for the bond valences the equation, $v_{ij} = \exp[(R_0 - R_{ij})/b]$, and take the values reported by Brown and Altermatt (15) for the empirical constants b and R_0 (= bond length for unit bond valence) for Ba–O and Pb–O bonds. Inserting the bond lengths reported by Iyi *et al.* (7) for the 12-coordinated spinel-block Ba position and then summing for both Ba and Pb atoms at this position yields the results shown in Table I. As the results indicate, with the reported atomic coordinates, the Ba atoms would be severely overbonded so that they are probably not at this site. On the other hand the bond valence sum for Pb atoms is close to the ideal valence of 2, suggesting that this site is actually a Pb position.

Thus it is possible that in the ternary (Ba only) compound the excess Ba atoms are located at positions other than the centers of the spinel blocks, and we therefore assume that the anomalous spots of Fig. 1 described earlier represent Ba atoms in reverse contrast at such a position. The X -type planes of Fig. 1 would then consist of a triple layer of Ba atoms with two Ba atoms on either side of the conduction plane at intervals of $3d_{11\bar{2}0}$.

Figures 2 and 3 compare images calculated using a layered-barium model to experimental images taken under different conditions of thickness and defocus, and the match is seen to be reasonably close for a variety of different images so that this superstructure model is probably at least qualitatively correct. In the structural model used in the calculations, the excess Ba atoms were positioned on the $z = 0.65$ and $z = 0.85$ planes directly above and below the (aBR) site of the conduction plane at $z = 0.75$. Thus the layered Ba atoms have replaced three Ga(1) atoms and one O(4) atom, and in fact are located at the O(4)

TABLE I
VALENCE SUMS OF Ba AND Pb ATOMS AT THE
INSIDE-SPINEL BLOCK SITE REPORTED BY IYI
et al. (7)

M -O dist. reported by Iyi <i>et al.</i> (7) (Å)	No. of bonds	Σv_{ij} at inside-spinel block site	
		$M = \text{Ba}$	$M = \text{Pb}$
2.819	6	1.42	0.89
2.604	3	1.27	0.79
3.011	3	0.42	0.26
Total:	12	3.11	1.95

position. Since microanalysis indicates that the Ba : Ga concentration ratio is $1 : 9.62 \pm 0.65$, and since the ideal β -alumina-like composition of this compound would be $(\text{Ba}_6\text{Ga}_{66}\text{O}_{102})^{+6}$ per triple cell, it is apparent that there are seven Ba atoms per triple cell. Therefore in our supercell model we have replaced one of three Ba (per triple cell) atoms at the BR site on the anomalous conduction plane by a bridging $M_2\text{O}_3$ group which consists of two face-shared octahedra, as found in the magnetoplumbite structure. In addition, two Ga atoms have been positioned on the conduction plane near this face-shared octahedral $M_2\text{O}_3$ group. The resulting compound used in the calculations thus has composition $\text{Ba}_7\text{Ga}_{64}\text{O}_{103}$.

It should be noted that the same image contrast would be obtained from models placing the layered Ba atoms above and below either the Beever's–Ross or O(5) (i.e., bridging oxygen) sites, since exact positions cannot be ascertained from the projected image. We have chosen to position the layered Ba atoms on either side of the aBR site because this involves a minimum change in local structure about the anomalous site, as this is a feature of the superstructure suggested by the electron micrographs.

Conclusion

Two basic properties regarding the crystal chemistry of the disordered superstruc-

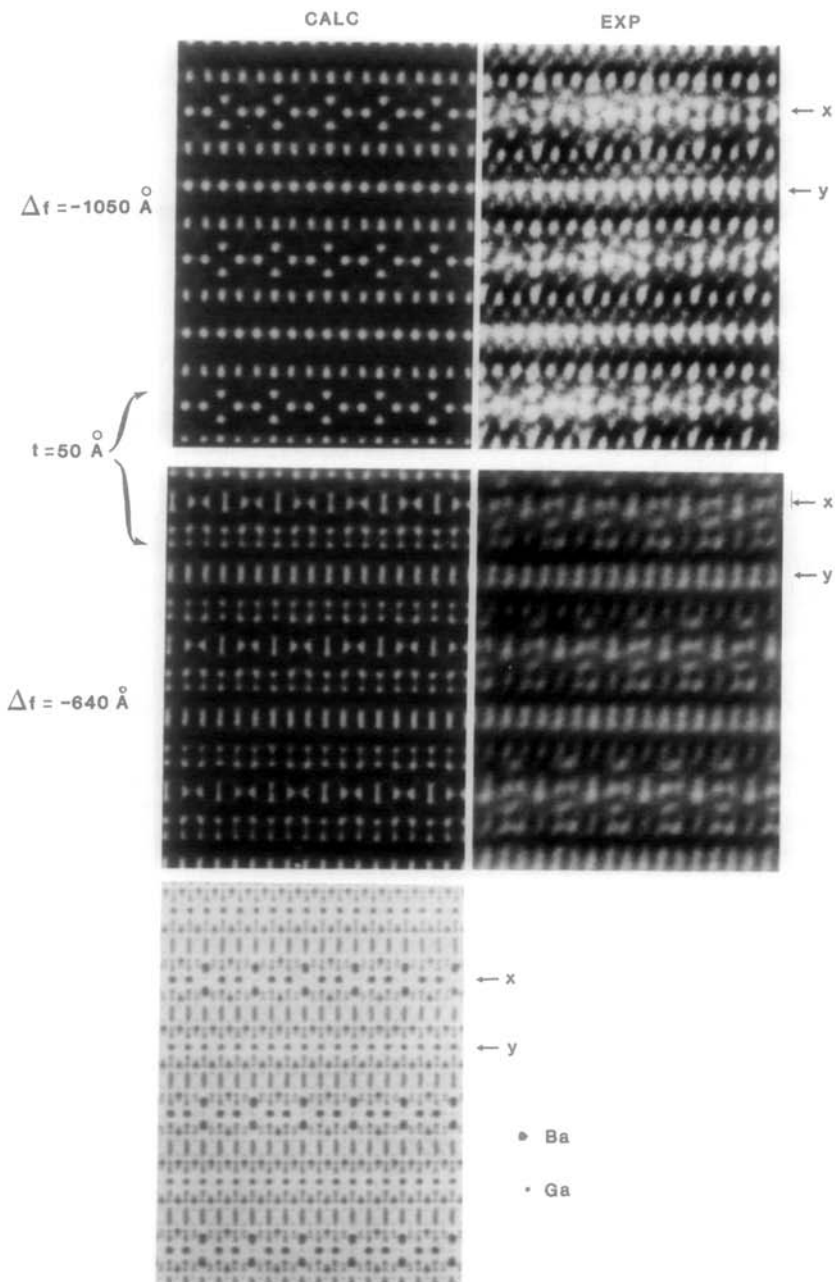


FIG. 2. Calculated and experimental images for barium hexagallate at two different amounts of defocus. The projected structure used to calculate the images is shown at the bottom with atom sizes in proportion to atomic number.

ture of barium hexagallate have been revealed by this paper: (a) excess Ba atoms are not located on the conduction planes as

previously assumed (11), but are positioned in the spinel blocks, and (b) barium hexagallate is apparently not isostructural with

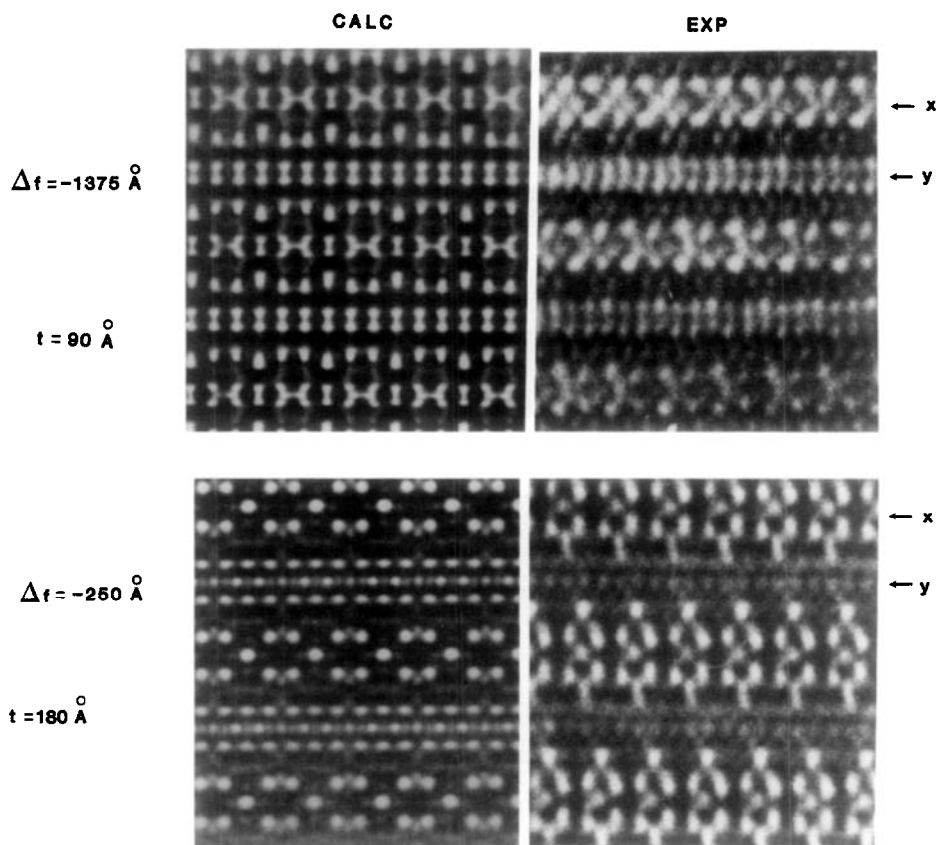


FIG. 3. Calculated and experimental images using the same model as used for Fig. 2, but for slightly thicker crystals.

barium lead hexaaluminate, probably due to the presence of Pb atoms in the latter structure. We have suggested that the excess Ba atoms in barium hexagallate are positioned midway between the spinel-block centers and alternating conduction planes, as this is the most reasonable model providing image calculations that match the experimental images fairly closely. A valence sum analysis utilizing the Ba-O distances reported by Iyi *et al.* (7) for the central spinel-block site indicated that Ba atoms are actually too crowded at this position in a hexaaluminate matrix, although it would appear that the site is well suited for Pb

atoms. Thus barium hexaaluminate is probably not isostructural with barium lead hexaaluminate and possibly has the structure that we have proposed for barium hexagallate.

We emphasize that our main purpose in this paper has been to propose a qualitative arrangement for the excess Ba atoms in barium hexagallate, as a more rigorous structural analysis is not possible utilizing the transmission electron microscopy method. Indeed, from the results presented here, it seems that the detailed structures of both barium hexagallate and barium hexaaluminate will remain unresolved until suf-

ficiently large single crystals of these compounds are successfully prepared and refined by conventional methods.

Acknowledgments

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