# Electron Microscopic Study of Barium Hexaaluminates

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The crystallographic relation between phase I and phase II of barium hexaaluminates, which were conventionally considered as the single compound "barium hexaaluminate ($BaAl_{12}O_{19}$)," was investigated using principally the electron diffraction method. Phase I ($Ba_{0.79}Al_{10.9}O_{17.14}$) was found to have $\beta$-alumina type structure with space group $P6_3/mmc$. On the other hand, phase II ($Ba_{2.34}Al_{21.0}O_{33.84}$) exhibited an $a\sqrt{3} \times a\sqrt{3}$ superstructure, which is probably due to the ordering of excess Ba ions within Ba–O layers. Possible structure models of both phases are presented.

## Introduction

"Barium hexaaluminate" was first described by Toropov (*1*) as having an ideal formula $BaO \cdot 6Al_2O_3$ or $BaAl_{12}O_{19}$ and has been considered to be a single compound with the magnetoplumbite structure (*2*), similar to other hexagonal aluminates containing divalent cations $MAl_{12}O_{19}$ ($M$ = Ca, Sr, Pb, etc.). Recently, however, data contradictory to these concepts began to be published by several researchers. Haberey *et al.* (*3*) reported for the first time the existence of two distinct phases having compositions close to that of so-called barium hexaaluminate, and expressed them as $BaO \cdot 4.6Al_2O_3$ and $BaO \cdot 6.6Al_2O_3$. Kimura *et al.* (*4*) confirmed their results and referred to Ba-poor ($0.82BaO \cdot 6Al_2O_3$) and Ba-rich ($1.32BaO \cdot 6Al_2O_3$) phases as phase I and phase II, respectively. On the other hand, Stevels (*5*), who did not distinguish phase I and phase II, introduced the formula $Ba_{1-x}Al_{10\frac{2}{3}+\frac{1}{3}x}O_{17+x}$ ($-0.2 \le x \le 0.35$), the composition of which covers the range

from phase I to phase II. Other formulae postulated were as follows: Mateika and Lauden (*6*) used $Ba_{1-x}Al_{12+\frac{2}{3}x}O_{19}$ as the formula ($0.1 \le x \le 0.19$) for phase I, and Bartels *et al.* (*7*) introduced $BaAl_{11}O_{17.5}$ and $BaAl_{12}O_{19}$ for two phases. These formulae were deduced only from hypothetical structural models. The discrepancies seem to have been caused by the lack of crystallographic data for the compounds.

Neither the formulae nor the structures and symmetries are as yet established. The symmetry of "barium hexaaluminate" was generally accepted as hexagonal, but Haberey *et al.* (*3*) suggested that phase I exhibits monoclinic (pseudo-hexagonal) symmetry. On the other hand, Stevels (*5*) suggested the presence of a superstructure in $Ba_{1-x}Al_{10+\frac{2}{3}+\frac{1}{3}x}O_{17+x}$. They assumed the superstructure to have a volume threefold over that of a magnetoplumbite type subcell, but the relation between the superstructure and the subcell was not made clear.

The aim of this study was to obtain crystallographic data for barium hexaalumi-

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nates, for elucidating these problems, using mainly the electron diffraction technique.

## Experimental

*Phase I*. Phase I was grown by the floating zone (FZ) method at a rate of 1 mm/hr using a xenon arc lamp as the heat source. Air was chosen for the atmosphere during growth and a heat reservoir of alumina was used in the same manner as already reported by Kitamura *et al*. (*8*). The starting materials were $BaCO_3$ and $Al_2O_3$ (0.85:6.0 in molar ratio), which were mixed and sintered in a usual manner. The grown crystal was 7 mm in diameter and 5 cm in length. It was for the most part transparent and clear without visual imperfections, except for some cracks, of which clear parts without inclusions were selected and examined.

*Phase II*. For the growth of phase II, the $PbO–PbF_2$ flux (1:1 in molar ratio) was chosen as a solvent. The flux containing a proper amount of raw material was heated to 1200°C and cooled to 700°C at a constant rate. After such treatment, tiny columnar crystals up to $0.2 \times 0.2 \times 0.3$ mm were obtained, which were clear and transparent but contained small particlelike inclusions near one end of the crystal. Crystalline parts containing inclusions were cut off with a razor blade, and the remaining clear crystals without visual imperfections were used for the examination. In this paper the specimen thus prepared is referred to as BaPb-phase II.

Flux-free phase II was obtained by the FZ method using $BaCO_3$ and $Al_2O_3$ (3.12:6.0 in molar ratio) as starting materials. The boule so obtained was a mixture of $BaAl_2O_4$ and phase II, the grain size of which was about 20 $\mu$ or less. This specimen is referred to as Ba-phase II.

Electron diffraction patterns were taken by a high voltage electron microscope (Hitachi-1250), operated at an accelerating voltage of 1 MeV. The powder X-ray diffraction measurements were obtained by a Phillips diffractometer using aluminum powder (#300) as the internal standard material, and lattice parameters were calculated by the least-square computer program. The precession photographs were taken by using 40 kV $\times$ 20 mA Mo$K\alpha$ radiation. The density of phase I was measured by the method of Archimedes. For BaPb-phase II, the density was measured by the flotation method using a heavy aqueous solution of a mixture of thallous formate and malonate, the density of which was determined separately. By means of electron probe microanalyzer (EPMA), the chemical compositions of the specimens were determined, using $Al_2O_3$, $BaAl_2O_4$, and $PbTiO_3$ crystals as standards for Al, Ba, and Pb, respectively.

The growth conditions of barium hexaaluminates will be reported elsewhere in detail.

## Results and Discussion

*Phase I*. Figure 1a–c shows electron diffraction patterns taken on FZ-grown crystal fragments, in which the incident electron beam was normal to the (001), (100), and (110) planes, respectively. By tilting the crystal around the *c* axis to avoid the forbidden reflections due to multiple diffraction, the extinction rule of phase I was obtained, which was consistent with the results of X-ray precession photographs. The crystal is hexagonal and the systematic absent reflections were $l = 2n + 1$ (*n*; integer) for 00*l* and *hhl*. The possible space groups are therefore $P\bar{6}2c$, $P6_3mc$ and $P6_3/mmc$. Since phase I has a structure similar to $\beta$-alumina or magnetoplumbite, it is reasonable to assume that the space group of phase I is $P6_3/mmc$. The lattice parameters were refined by X-ray powder diffraction to be $a = 5.587$ and $c = 22.72$ (Å).

The density of the phase I crystal was 3.657 g/cm$^3$ and the molar ratio of Al/Ba,
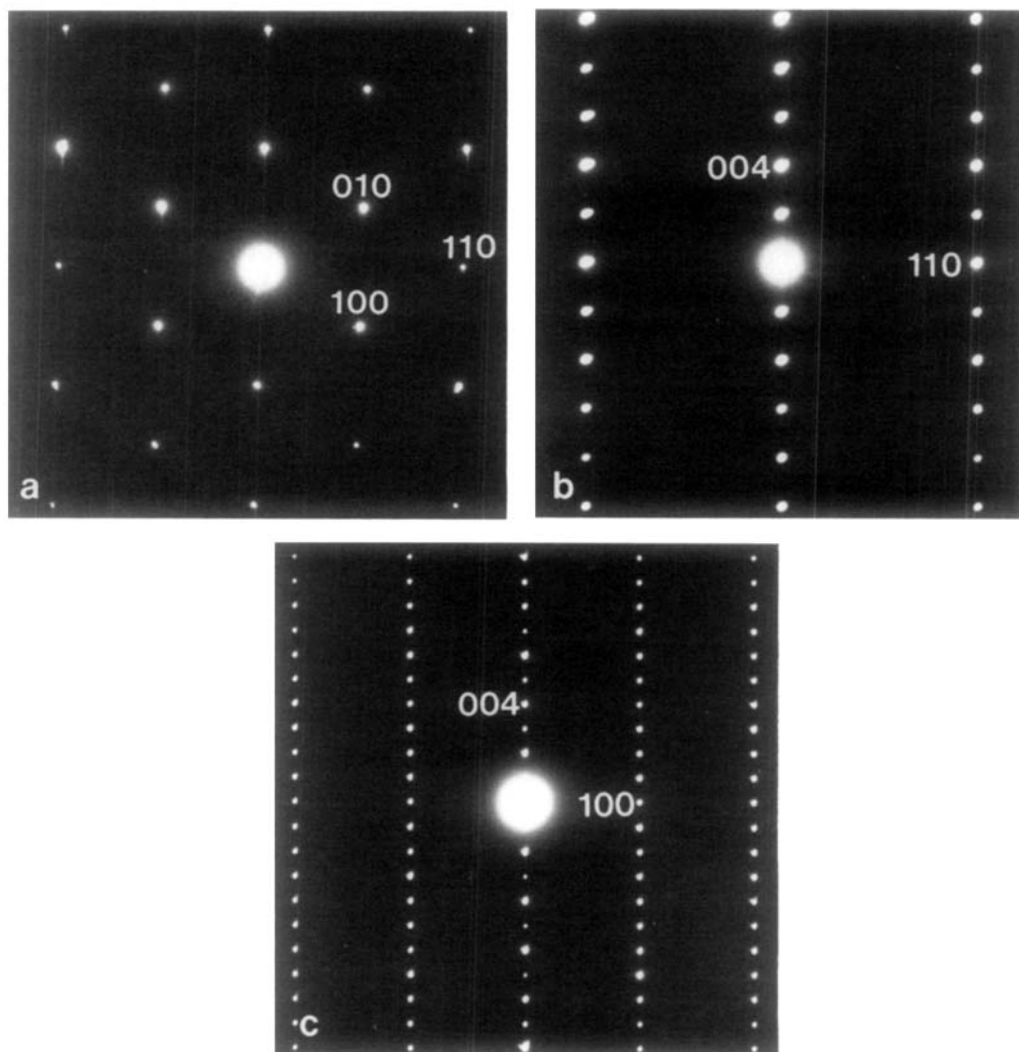
FIG. 1. Electron diffraction patterns from the phase I crystal fragments. The incident beam is normal to the (a) (001), (b) (100), and (c) (110) planes.

determined by EPMA, was 13.8. The formula of phase I was, therefore, calculated to be $Ba_{0.79}Al_{10.9}O_{17.14}$, with molecular units $Z = 2$. The crystallographic data of phase I are summarized in Table I.

The formula of phase I thus obtained suggests a closer relation to the $\beta$-alumina $(M^{1+}Al_{11}O_{17})$ structure than the magnetoplumbite $(M^{2+}Al_{12}O_{19})$, and implies that the large concentration of Ba ion defects as well as Al ion defects (and/or oxygen interstitial (9, 10)) which achieve the charge balance are formed.

The results of Haberey et al. (3) are different from ours both as to diffraction data and as to the space group. They observed $l = 2n + 1$ ($n$; integer) reflections for $hhl$; e.g., 005, 009, and 00.15, by precession photograph and proposed that the symmetry was monoclinic (pseudohexagonal) on the basis of the intensity distribution which was incompatible with hexagonal symme-

TABLE I

CRYSTALLOGRAPHIC DATA OF PHASE I AND PHASE II

| | Formula | Symmetry | Space group |
|---|---|---|---|
| Phase I | $Ba_{0.79}Al_{10.9}O_{17.14}$ | Hexagonal | $P6_3/mmc$ |
| Phase II[a] | $Ba_{2.34}Al_{21.0}O_{33.84}$ | Hexagonal | $P6$ |

| Lattice parameters (Å) | $Z$ | Density (g/cm³) |
|---|---|---|
| $a = 5.587$ $c = 22.72$ | 2 | 3.657 |
| $a = 5.601$ $c = 22.91$ | 1 | — |

[a] For subcell structure.

try. This discrepancy is probably due to their method of sample preparation. They prepared the sample for X-ray diffraction by cooling the melt of phase I composition. As reported by Kimura et al. (4), phase II melts incongruently, so the solidification of the melt having phase I composition leads to a mixture of $Al_2O_3$, phase I, $BaAl_2O_4$, and phase II, which derives from the solid state reaction of phase I and $BaAl_2O_4$. The sample, which Haberey et al. selected as a specimen for X-ray diffraction, could have been such a mixed or inhomogeneous crystal.

*Phase II.* Ba-phase II and BaPb-phase II yielded the same electron diffraction and X-ray powder diffraction patterns. The BaPb-phase II crystals contained Pb ions, and the molar ratio of Ba : Pb : Al was determined to be $1.0 : 0.25 : 11.2$ by EPMA. On the other hand, the molar ratio of Ba : Al for Ba-phase II was $1.0 : 8.8–8.9$. These data indicate that $Pb^{2+}$ substitutes for 20% of $Ba^{2+}$; these two specimens were confirmed to have the same structure. The density, measured for BaPb-phase II, ranged from 3.88 to 3.89 g/cm³, which were averaged to give 3.884 g/cm³. The lattice parameters of the Ba-phase II and the BaPb-phase II were determined by X-ray powder diffraction to be $a = 5.601$, $c = 22.91$ (Å) and $a = 5.600$, $c = 22.91$ (Å), respectively. The formula for

the BaPb-phase II then, is calculated to be $(Ba_{0.80}Pb_{0.20})_{2.34}Al_{21.0}O_{33.84}$. Since the molar ratio of (Ba + Pb)/Al for the BaPb-phase II and of Ba/Al for the Ba-phase II are almost equal, the formula of the Ba-phase II can be written as $Ba_{2.34}Al_{21.0}O_{33.84}$. The crystallographic data are listed in Table I.

Figure 2 shows the electron diffraction patterns of Ba-phase II. The indexed spots are the fundamental reflections of the $\beta$-alumina type subcell. In the diffraction pattern (a), taken with the incident electron beam normal to the (001) plane, some weak extra spots are observed. They are situated at $h = m/3$ and $k = n/3$, where $m$ and $n$ are integers. In the diffraction pattern (b), taken with the incident beam normal to the (100) plane, continuous extra reflections elongated along the $c^*$ direction are also observed, while in (c), taken normal to the (110) plane, no extra spots are present. Such streaks were generally observed for the specimens of phase II. The diffuse reflections also appear in the powder diffraction patterns as broad reflections in the range of 28 to 31° for $2\theta$ values. These results suggest the presence of an $a\sqrt{3} \times a\sqrt{3}$ superstructure. The lattice relationships between the $\beta$-alumina-type subcell and the supercell are $A_1 = a_1 - a_2$, $A_2 = a_1 + 2a_2$, and $C = nc_0$ ($n$; integer), where $A_1$, $A_2$, and $C$ are lattice vectors for the supercell, and $a_1$, $a_2$, and $c_0$, for the subcell. The $c$ axis length of the supercell is not well defined because the extra reflections are elongated along the $c^*$ direction as continuous streaks. If the $c$ axis length is equal to the subcell, the superstructure cell volume will be threefold that of the subcell, as reported by Stevels (5).

In addition to the presence of a superstructure, it should be pointed out that the fundamental odd number reflections such as $l = 2n + 1$ ($n$; integers) for $00l$ and $hhl$ are present, as observed in Fig. 2b and c. This was also confirmed by X-ray precession photographs. The reasonable space group
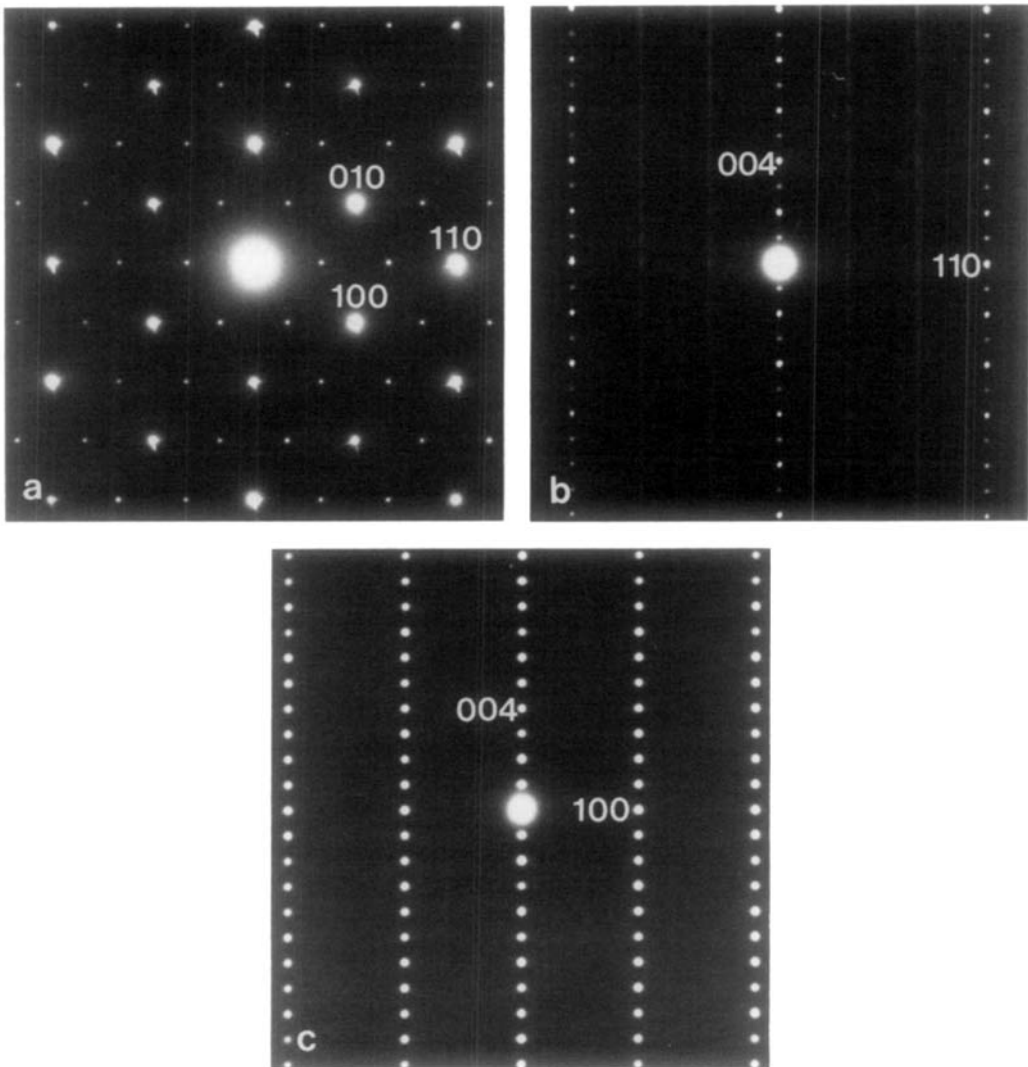
FIG. 2. Electron diffraction patterns from the phase II crystal fragments. The incident electron beam is normal to the (a) (001), (b) (100) and (c) (110) planes. The indices are based on the $\beta$-alumina-type subcell.

is, therefore, $P\bar{6}$ or $P6$. The space group $P\bar{6}$ is more likely for the subcell of phase II, because the structure is closely related to the $\beta$-alumina type.

An interesting imperfection in phase II crystals was observed by the 1-MV electron microscope. Figure 3 shows an electron micrograph of the phase II crystal from a very thin part of the crystal region. The incident electron beam was parallel to the [100] direction of the subcell. It is clear that the crystal is not perfect and that it contains anti-phase boundaries (APB) with the displacement vector of $1/2c$. The size of anti-phase domains varies, but the APB structure was observed in every specimen.

On the basis of the diffraction study and other observations, one of the possible su-
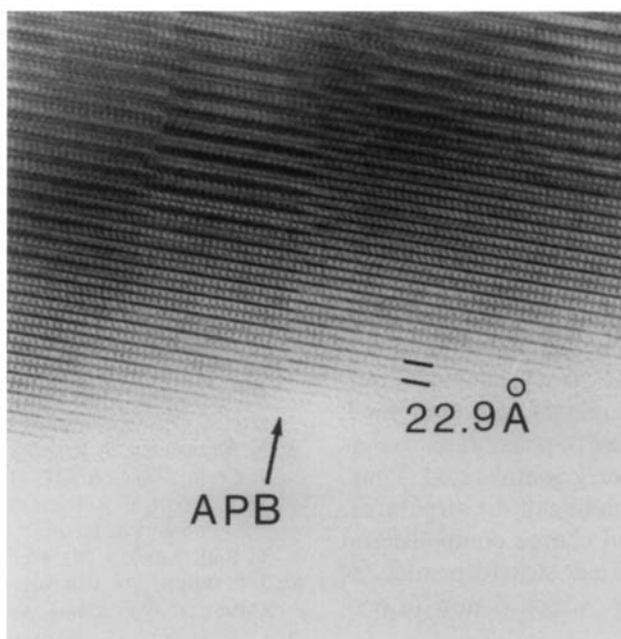
FIG. 3. Electron micrograph of phase II projected along [100] direction, revealing the existence of an anti-phase boundary (APB).

perstructure models is shown in Fig. 4. Ba ions would be situated at the BR (Beevers–Ross) sites (*11*) of the $\beta$-alumina-type subcell owing to its low potential energy (*12*), but, even if all BR sites were fully occupied, the postulated formula for phase II requires an approximate $\frac{1}{3}$ excess of Ba ions in the $\beta$-alumina-type subcell. It is therefore likely that the superstructure is formed by the ordering of such excess Ba ions within the Ba–O layers. The excess Ba ions may enter into anti-BR sites to avoid interactions with Ba ions at BR sites. As shown in Fig. 4a, three kinds of the anti-BR sites for each Ba–O layer are present in the lattice of the superstructure. One concludes that excess Ba ions occupy one kind of the anti-BR sites, and these excess Ba–O layers are confined in every second Ba–O layer, as shown in Fig. 4b. The extra reflections are accompanied by continuous streaks along the $c^*$ direction. This proba-
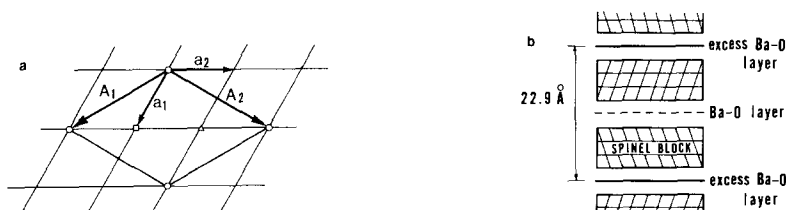


FIG. 4. (a) Lattice relation between subcell and superstructure cell (supercell) of phase II projected on the $c$ plane. The $a_1$ and $a_2$ are lattice vectors of subcell, and $A_1$ and $A_2$ are those of supercell. Three kinds of anti-BR sites are shown by the symbols (O △ □). (b) Probable model of phase II. In Ba–O layers, Ba ions are situated at BR sites and in excess Ba–O layers, $\frac{1}{3}$ of the anti-BR sites are occupied, other than BR sites.

bly occurs because the stacking sequence of the ordered layers containing the excess Ba ions ("excess Ba–O layers") is considerably disordered, and because there is no correlation of the occupied anti-BR sites between excess Ba–O layers. It has already been reported by several authors (*13–16*) that in the $\beta$-alumina structure the cations do not occupy the ideal BR or anti-BR sites but, more or less, deviate from these sites. This is, probably, also the case with barium hexaaluminates. The structural model outlined above is preliminary and simplified.

The actual structure of phase II as well as of phase I could be very complicated. Thus, for a better understanding of the structures, e.g., cation sites and charge compensation mechanism, a detailed structure analysis should be necessary, which is now in progress.

### Acknowledgments

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