

Superstructure of Barium Lead Hexaaluminate Phase II (BaPb β (II)-alumina) Revealed by High-Resolution Electron Microscopy

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Introduction

Since the discovery of two distinct barium hexaaluminates by Haberey *et al.* (1), several investigations were made on these two compounds—BaO · 6.6Al₂O₃ (Ba phase I) and BaO · 4.6Al₂O₃ (Ba phase II) (2). We (3) revealed the crystal structure of Ba phase I by using X-ray single-crystal diffraction data, with essentially the same results with the independent study by van Berkel *et al.* (4). Ba phase I, having the formula Ba_{0.75}Al_{11.0}O_{17.25} (5), was referred to as Ba β -alumina from structural point of view. On the other hand, several electron microscopic studies have reported an $a\sqrt{3} \times a\sqrt{3}$ superstructure in Ba phase II (6-9). Recently, we also revealed the average structure of Ba phase II ((Ba_{0.8}Pb_{0.2})_{2.34}Al_{21.0}O_{33.84}), which was referred to as BaPb β (II)-alumina, by using X-ray single-crystal diffraction data (10). On the basis of these parameters, a structural model was proposed that consists of perfect cells (Ba_{2.0}Al_{22.0}O_{34.0}) and defect cells ((BaPb)_{3.0}Al_{20.0}O_{35.0}) in a 2 : 1 ratio. The defect cell was supposed

to contain a Ba or Pb ion near in the middle of the spinel block at the site produced by complex defects including triple Reiding defects. Such a defect was observed, for the first time, in the β -alumina related compounds. As the model is based on the parameters of the average structure, it would be necessary to examine it by the other methods. In the present paper, the superstructure of BaPb β (II)-alumina is studied by the combined use of the convergent-beam electron diffraction (CBED) and the high-resolution electron microscopy.

Experimental

The single crystals were grown by the flux method using PbF₂-PbO solvent and the obtained chemical formula was (Ba_{0.8}Pb_{0.2})_{2.34}Al_{21.0}O_{33.84}, showing the replacement of $\frac{1}{4}$ Ba by Pb ions (6). The crystal has a hexagonal symmetry with lattice parameters of $a = 5.6003(5)$ Å and $c = 22.922(2)$ Å (for the subcell). The crystals were lightly crushed in an agate mortar to fragments of several micron size. They were supported

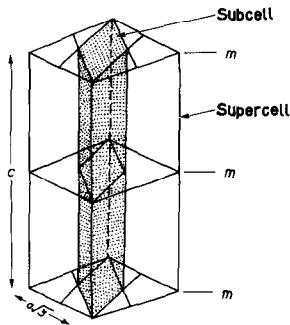


FIG. 1. A schematic depiction of the relation between the supercell and the subcell.

on a holey carbon film and observed by a 400-kV high-resolution analytical electron microscope (JEM-4000EX), operated at 400 kV. The objective aperture size corresponded to about 0.5 \AA^{-1} in reciprocal

space. The images were obtained around 1200 \AA under focus. The direct magnification was 3×10^5 and the exposure time was about 2 sec. The CBED was also observed at 200 kV. The probe diameter was about 200 \AA at the crystal.

Model and Computer Simulation of Images

Computer simulations of the image contrasts are based on the superstructure models reported previously (10). From the positional parameters of the average structure with a dimension $a \times a \times c$, we made an $a\sqrt{3} \times a\sqrt{3} \times c$ supercell model having a $P\bar{6}2m$ space group symmetry (Fig. 1). Figure 2 shows the atomic positions at each z section in the supercell. The defect subcell

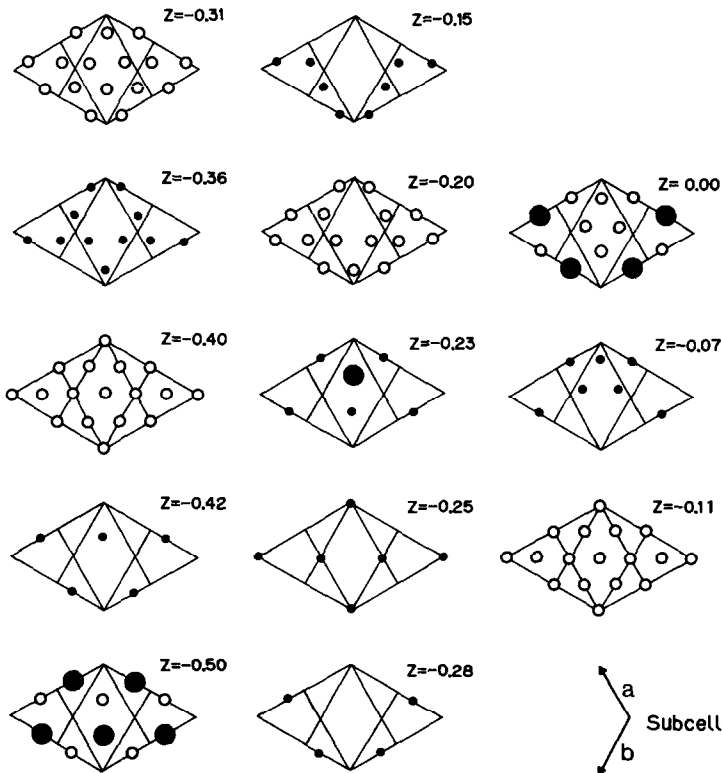


FIG. 2. The arrangement of atoms at each z section of the $a\sqrt{3} \times a\sqrt{3} \times c$ superstructure. Large filled circles show Ba (or Pb) ions; small filled and open circles are Al and oxygen ions, respectively.

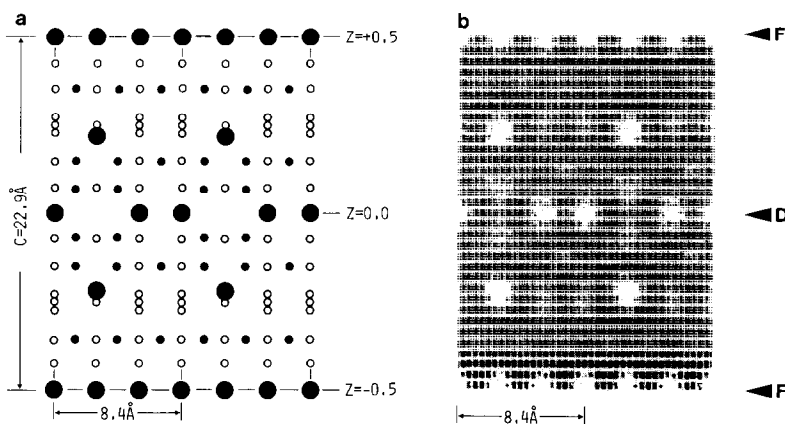


FIG. 3. (a) The superstructure model projected on the (110) plane of the supercell. Large filled circles indicate Ba (or Pb) ions. Others are Al ions. Oxygens are omitted. (b) shows the calculated image on the basis of the structure model under the condition of 1200 Å under focus with 77.6 Å crystal thickness. F and D stand for the fully occupied Ba–O layer and the defect Ba–O layer, respectively.

((BaPb)_{3.0}Al_{20.0}O_{35.0}) is situated in the middle of the supercell, with two perfect subcells (Ba_{2.0}Al_{22.0}O_{34.0}) on its sides. The ideal chemical formula is (BaPb)_{2.33}Al_{21.33}O_{34.33}. The $z = 0.0$ mirror plane contains a Ba deficiency and three interstitial oxygens due to the triple Reidinger defects (the defect Ba–O layer); there is no Ba deficiency at the $z = -0.5$ section (the fully occupied Ba–O layer). Two kinds of the Ba–O layers stack alternately along the c direction, with being separated by the spinel blocks. The triple Reidinger defects in the single mirror plane, together with defects of the Al and oxygen in the spinel block, form a 12-coordinated site inside of the spinel block, where a Ba or a Pb ion is situated ($Z = -0.23$ in Fig. 2). Thus, excess Ba ions are accommodated beyond 2.0 per unit formula. The supercell projected on the (110) plane is depicted in Fig. 3a. Amplitudes of scattered waves were calculated by using the program (supplied by Arizona State University) based on the multislice method (11). The dynamical interactions of 614 waves were taken into account. A simulation of an image (Fig. 3b) was accomplished under the conditions; an incident beam was

along the [110] direction of the supercell, the slice thickness was 9.7 Å, a spherical aberration coefficient of the objective lens was 3.3 mm, a radius of the objective aperture in reciprocal was 0.5 Å⁻¹, a semi-angle of illumination was 1.0 mrad, a half width of Gaussian chromatic spread of defocus was 50 Å, and crystal thickness was 77.6 Å.

Results and Discussion

The selected area electron diffraction patterns suggest that the crystal has hexagonal symmetry with lattice parameters of the supercell $a' = 11.8$ Å and $c' = 22.9$ Å, which holds the relation of $a' = \sqrt{3}a$ and $c' = c$ with the lattice parameters a, b of the subcell. Since the superstructure spots are accompanied with the streaks along the c axis, the length of the c axis for the supercell is assigned to be the same as that of the subcell. The lack of systematic absences indicates that the possible space groups are either $P6$, $P\bar{6}$, $P6/m$, $P6m2$, $P\bar{6}2m$, $P6mm$, $P622$, or $P6/mmm$.

Figure 4 shows a CBED pattern taken along the [001] zone axis. It is clear that a

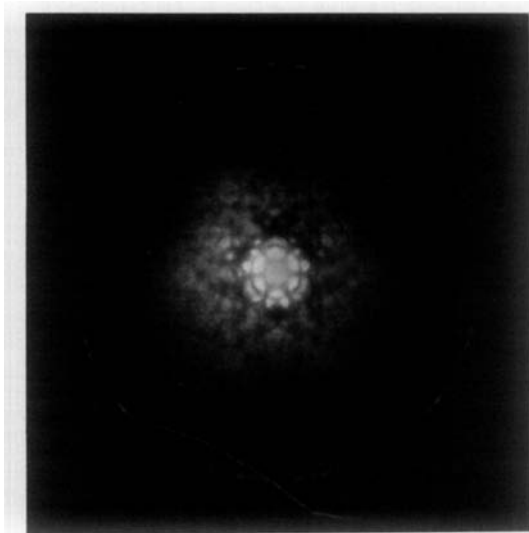


FIG. 4. A CBED pattern taken along the [001] zone axis, showing the whole pattern symmetry.

$3m$ symmetry is present in the whole pattern including a 1st Laue zone. This indicates the point group $\bar{6}m2$ (12), which corresponds to the space group of either $P\bar{6}m2$ or $P\bar{6}2m$. The space group was determined to be $P\bar{6}2m$ on the basis of the plane group symmetry appearing in the structure images shown later. The result agrees with the space group of the model described in the preceding section.

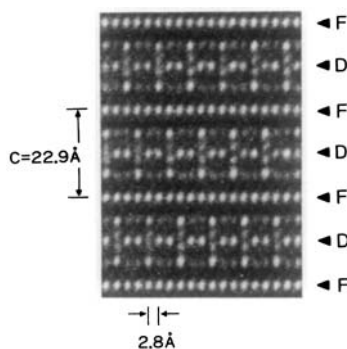


FIG. 5. A high-resolution electron microscopic image of BaPb β (II)-alumina taken along the [110] direction of the supercell. The image corresponds to the calculated image of Fig. 3b.

Figure 5 shows a crystal structure image of BaPb β (II)-alumina, taken along the [110] direction of the supercell. The image consists of bright white dotted lines with interval of 22.9 Å along the c axis. Between them, other white dots with the threefold periodicity normal to the c axis are observed.

Figures 3a and b show the projection of the structure model of the supercell on the (110) plane, which is deduced from the X-ray diffraction (10), and the corresponding calculated image, respectively. It is clear that the observed image contrast agrees well with the calculated one. The bright white spots correspond to the sites of Ba ions. It should be noted that the arrangements of the white dots in the observed image indicate the presence of the two mirror planes both normal and parallel to the c axis in each block of the unit cell. This consists with the space group $P\bar{6}2m$ of the supercell.

There are some disorders in the subcell arrangements. A defect Ba-O layer can take three kinds of positions (10). Stacking disorders of the alternate defect Ba-O layers lead to the elongated lines along the c direction at the superstructure spots (6). Another kind of the disorder, which disturbs threefold periodicity, can be observed in the [110] direction of the supercell as shown in Fig. 6. Other defects, the "anti-

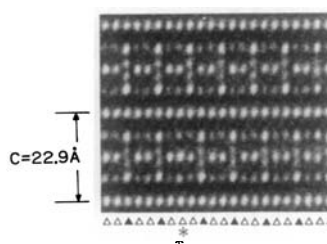


FIG. 6. Electron micrograph projected on the (110) plane of the supercell, showing a disorder in the subcell arrangement perpendicular to the c axis. An asterisk indicates the disorder. F and D stand for the fully occupied Ba-O layer and the defect Ba-O layer, respectively.

phase boundary" in Ba β (II)-alumina and the intergrowth between Ba β - and Ba β (II)-aluminas, were already discussed in the previous paper (10). Now that the structure model was confirmed by the present study, the proposed mechanisms for them become more reliable.

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