JOURNAL OF SOLID STATE CHEMISTRY 32, 181–184 (1980)

High-Resolution Electron Microscope Observations of β''''-Alumina Prepared in a Na_2O–MgO–Al_2O_3 System

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Received March 12, 1979; in final form July 9, 1979

The existence of a β''''-alumina phase in a Na_2O–MgO–Al_2O_3 ternary system is confirmed based on 1-MV high-resolution electron microscopy. The crystal with a composition of $0.8Na_2O{\cdot}2.4MgO{\cdot}7Al_2O_3$ has rhombohedral symmetry with lattice parameters $a = 5.6$ and $c = 48$ Å. The structure is composed of alternate stacking of Na–O planes and spinel-like blocks containing six close-packed oxygen layers. Electron irradiation damage takes place in a manner very similar to that previously reported for β''-alumina.

The phase relations in a Na_2O–Al_2O_3 binary system have so far been widely examined (*1*). Two phases, β- and β''-alumina, are known to exist in this system. Both structures are composed of alternate stacking of Na–O planes and spinel-like blocks. Each spinel-like block contains four cubic close-packed oxygen layers (*2, 3*). The latter phase does not grow large and the single crystals are usually prepared in a ternary system including MgO (*4*). In this ternary system another variant, β''''-alumina, is found (*5*). It has a structure similar to that of β-alumina except that each spinel-like block contains six close-packed oxygen layers. It has, moreover, been suggested (*6*) that there exists a fourth phase, β''''-alumina, similar to β''-alumina but having the thick spinel-like blocks. The hypothetical structure model of this β''''-alumina is shown in Fig. 1. Detailed experimental data on this phase have, however, not been reported so far.

In a Na_2O–MgO–Al_2O_3 system, T. Ohta, M. Harata, and A. Imai (in preparation) have recently prepared a compound of which the powder X-ray diffraction data could be indexed by the β''''-alumina phase. A single crystal of this compound could, however, not be obtained. It is known that high-resolution electron microscope images show the projected potential of a crystal if they are taken satisfying certain (so-called Scherzer's) conditions (*7, 8*). More details are obtained in the images by increasing the accelerating voltage of the microscope (*9*). In the present study, the crystal mentioned above is examined by a 1-MV high-resolution electron microscope in order to confirm its crystal structure.

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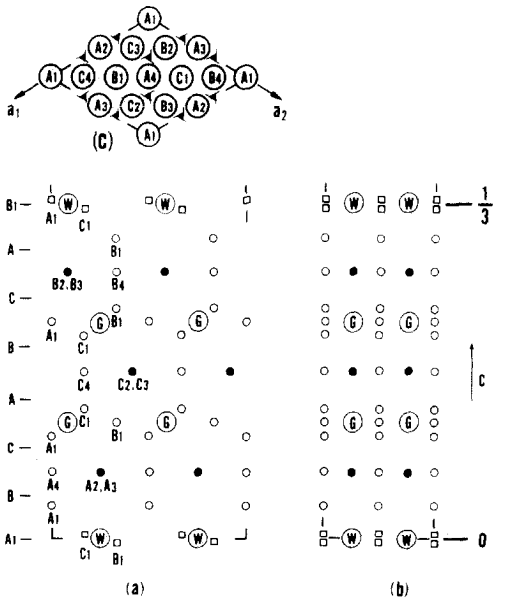

FIG. 1. Schematic representation of the crystal structure of β'''-alumina. The space group is assumed to be $R\bar{3}m$. $a = 5.6$ and $c = 48$ Å. (a) and (b) show the projections normal to the (110) and the (100) planes, respectively. Only one-third of the unit cell is shown. Squares represent sodium atoms. Open and solid circles represent Al atoms which are partially substituted by Mg atoms. At the latter circles cations array twice as densely as compared to those at the former. The positions W and G correspond to the large and small white dots in Figs. 3a and b, respectively. The stacking sequence of the oxygen layers in spinel-like blocks is indicated on the left-hand side of (a). The positions of oxygens in Na–O planes are also shown. (c) shows the atom sites projected in the c direction.

Samples were prepared by a hot press at 1770°C under 300 kg/cm^2 for 1 hr. Details of the preparation will be given elsewhere (T. Ohta, M. Harata, and A. Imai, in preparation). According to the chemical analysis, the product has the composition $0.8Na_2O{\cdot}2.4MgO{\cdot}7Al_2O_3$. A small amount of polycrystal was lightly crushed in CCl_4 in an agate mortar. The fragments obtained were set on a holey carbon film. Observations were made with a 1-MV high-resolution electron microscope (H-1250), constructed especially for crystal structure image observations (*10*). The instrument has a resolving power of 2 Å under the equipment of the specimen tilting stage (±35° tilt). All the following photographs were taken at the underfocus between 500 and 1000 Å using the objective aperture corresponding to 0.56 Å^{-1} in reciprocal space. It has already been shown that images taken under these conditions approximately reflect the atomic arrays in crystals (*11*). In other words, the positions where atoms are arrayed more densely along the direction of projection have the darker contrast.

Electron diffraction patterns corresponding to various reciprocal lattice sections of the crystal were taken. They can consistently be indexed by a hexagonal lattice with $a = 5.6$ and $c = 48$ Å, in accordance with the powder X-ray diffraction data. Systematic absences of the reflections with $-h + k + l \neq 3n$ indicate that the crystal has a rhombohedral symmetry. Figures 2a and b show two examples of the patterns, taken with the incident electron beam normal to the (110) and the (100) planes, respectively. The circles drawn in the patterns indicate the size and the position of the objective aperture used.

Figures 3a and b show the 1-MV high-resolution electron microscope images taken with the incident beam normal to the (110) and the (100) planes, respectively. The image contrast may reasonably be interpreted in terms of the structure model of β'''-alumina, shown in Figs. 1a and b; the large white dots in Fig. 3a correspond to the central sites of two adjoining sodium ions in the Na–O planes (the sites W in Fig. 1a), while the small ones correspond to those of two tetrahedral cations in the spinel-like blocks (G in Fig. 1a). Similarly, the large and small white dots in Fig. 3b correspond to positions W and G in Fig. 1b, respectively. Similar interpretations were successfully applied to the 1-MV electron microscope images of β''-alumina, with the help of the computer simulations of image contrast (*12*). The Na–O planes, seen as the rows of large white dots in the images,

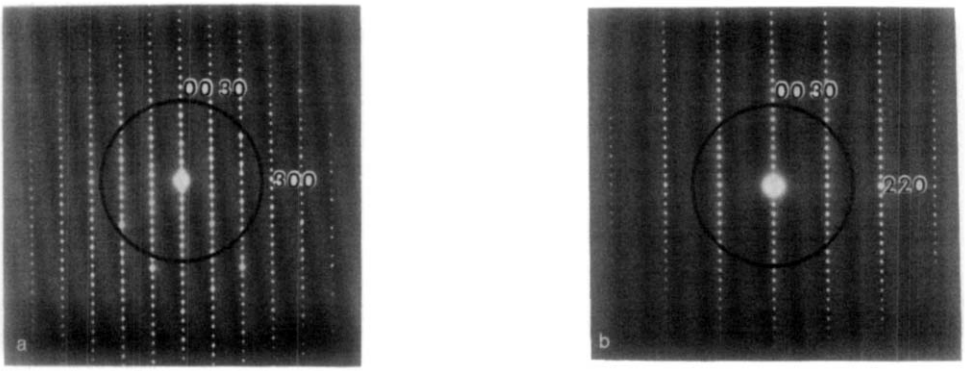

FIG. 2. Electron diffraction patterns of β'''-alumina taken with the incident beam normal to the (110) and the (100) planes in (a) and (b), respectively.

are mutually separated by about 16 Å along the c direction, in accordance with each spinel-like block consisting of six close-packed oxygen layers. It is also clear from Fig. 3a that the dimension of the unit cell in the c direction is three times that of such a spinel-like block.

Under somewhat more intense electrons the crystal suffers from irradiation damage as shown in Fig. 4; some of the Na–O planes are released and accordingly two neighboring spinel-like blocks come in contact. The thickness of a newly formed block is about 30 Å, i.e., it includes 12 oxygen layers. Similar phenomena have already been observed for MgO-stabilized β''-alumina (*13–15*). In our preliminary experiments, such phenomena are not observed in β-alumina. The observations must therefore contribute more evidence to the above conclusion that the present crystal has almost the same crystal structure as the β''-alumina phase except for differences in the number of oxygen layers in each spinel-like block.

Acknowledgments

The authors wish to express their deep gratitude to Drs. A. Imai and M. Harata (Toshiba Research and Development Center) and to Drs. K. Kato and Y. Bando (NIRIM) for valuable discussions and to Mr. Y. Sekikawa (NIRIM) for help in the HVEM experiments.

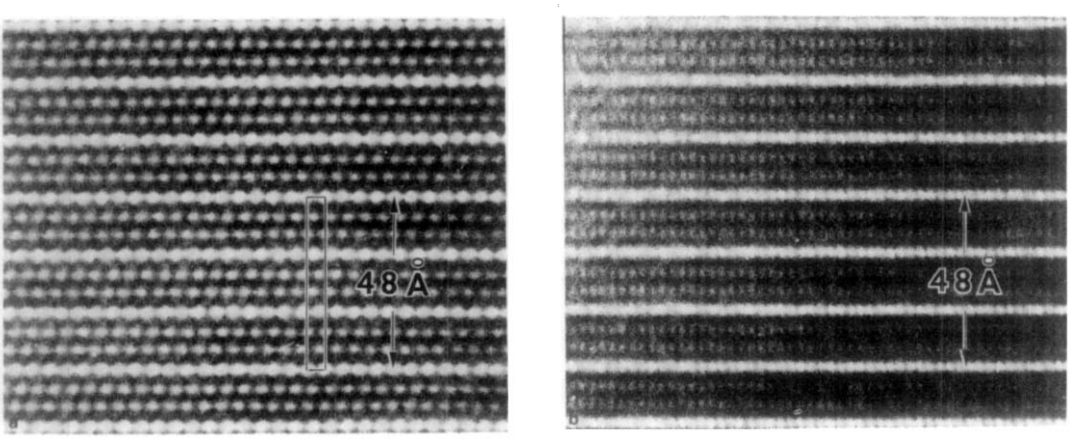

FIG. 3. One-megavolt structure images of β'''-alumina taken with the incident beam normal to the (110) and the (100) planes in (a) and (b), respectively.

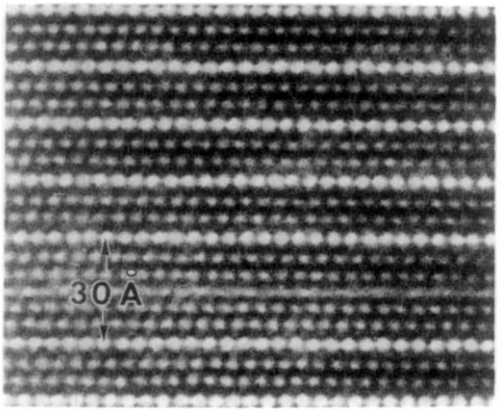

FIG. 4. The thick block formed in a β''-alumina crystal by electron irradiation.

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