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Two New Long-Period Structures Related to β-Alumina

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Two new ordered forms of "β-alumina" with rhombohedral symmetry have been discovered and their structures deduced from one-dimensional electron microscope images of thick crystals. Referred to a hexagonal cell, their lattice parameters are $a = 5.59$ Å, $c = 169.5$ Å and $a = 5.59$ Å, $c = 339$ Å. A symbolism for describing structures related to that of β-alumina is proposed.

The ceramic materials known collectively as β-aluminas are currently under extensive investigation because of their potential use as solid electrolytes in practical high-energy density batteries based on the sodium–sulfur system. There are two well-known and characterized forms, β- and β″-alumina, with different crystal structures and with different properties (such as ionic conductivity). It is now known that the crystal structure must be carefully controlled in electrolytes that are to be used successfully in long-life batteries. In this report we show that electron microscopy exploiting multiple (dynamic) scattering from thick crystals reveals the existence, in battery electrolytes, of new crystal structures, related to both β- and β″-alumina.

The structure of β-alumina was first described many years ago by Bragg *et al.* (*1*) and has subsequently been refined (*2*). The ideal formula is $NaAl_{11}O_{17}$, although real crystals in practice contain more sodium than indicated by this formula. The structure of a more sodium-rich phase named β″-alumina was subsequently determined by Yamaguchi and Suzuki (*3*). Usually β″-alumina also contains Mg and/or Li to stabilize the structure and a formula $Na_{5/3}Mg_{2/3}Al_{31/3}O_{17}$ has been proposed (*4*).

The essence of the structures is that they are composed of slabs of four oxygen layers arranged as in cubic close packing (*ABCA*) with Al (and Mg or Li in β″-alumina) arranged in octahedral and tetrahedral sites as in spinel ($MgAl_2O_4$). Between these "spinel slabs" are the "conducting layers" of sodium and oxygen ions approximately 11.3 Å apart. The oxygen ions of the conducting layers are also in the positions of cubic close packing (but now with one-fourth of the density) so that the sequence of oxygen layers is, e.g., $C(ABCA)B\ldots$, where the spinel slab is in parentheses.

In β-alumina the conducting planes are mirror planes so that the repeat sequence along the hexagonal **c**-axis is $C(ABCA)B(ACBA)C\ldots$, or, omitting the spinel slabs, $CB\ldots$. The lattice parameters are $a = 5.59$ Å, $c = 22.53$ Å.

In β″-alumina (which is rhombohedral) the sequence along the **c**-axis of the hexagonal cell is $C(ABCA)B(CABC)A(BCAB)C\ldots$, or $CBA\ldots$. The lattice parameters are $a = 5.59$ Å and $c = 33.85$ Å.

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The structures are clearly related as polytypes, and could usefully be described in the notations developed (*5*) for this purpose—thus the stacking of conducting planes in β and β'' would be $2H$ and $3R$, respectively, in the Ramsdell notation and h and c, respectively, in the Jagodzinski notation.

In the present context it is convenient to use yet another notation suggested by Hägg (*6*). Here the spinel slabs are denoted by (−) if the close-packing sequence in the slab is in the order (*ABCA*), i.e., conducting plane sequence *CB*, and by (+) if the sequence is reversed, e.g., slab sequence (*ACBA*), conducting plane sequence *BC*. The β-structure is then symbolized by (+ −) and the β''-structure by $(+)_3$. The subscript indicates the number of times the unit in parentheses must be taken to obtain a repeat unit along the hexagonal c-axis.

Both structures are readily imaged under the electron microscope (*7, 8*). In thick crystals, although the spinel slabs are equivalent in projection, e.g., along [100], one-dimensional (00l) images of β show alternating dark and lighter contrast of the spinel slabs, whereas in β'' images of all slabs have the same contrast (see Fig. 1). This is because a very small misalignment of the crystal of β allows the appearance of "forbidden" reflections such as 001 due to multiple scattering (*9, 10*). The different contrast may be understood as arising because (+) and (−) slabs in a tilted crystal present a slightly different aspect to the beam. This effect has previously been noted and exploited to reveal stacking sequences and disorder in micas (*11*), and is used here to deduce the structures of new members of the β-alumina family.

We have examined, under a JEM 100B microscope, ion-thinned sections of ceramic tubes that contain both β- and β''-regions. An example of a disordered region is shown in Fig. 1 in which we identify dark lines with, e.g., (+) slabs and lighter lines with (−) slabs (the white regions correspond to the conducting planes). At the right of the figure (A) is a region of β'', $(+)_3$; next to this are regions (B, B′) of β (+ −) with an insert (C) of β'' $(-)_3$ which has reverse contrast (in twin orientation) to that at A. One may also see disordered regions such as (− − + +) at D and (+ − + + − + − + + − +) at E.

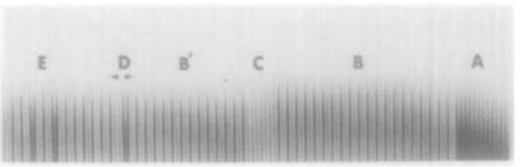

FIG. 1. Electron micrograph of a crystal showing mixed intergrowth of β- and β''-alumina. A and C marke the β''-alumina parts while B and B′ are β-alumina. D and E mark disordered regions.

Figure 2 shows a diffraction pattern and image taken from another crystal that was

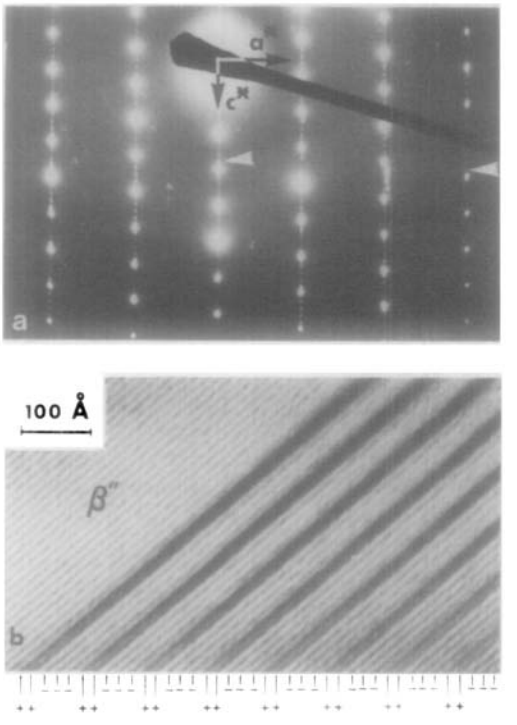

FIG. 2. Electron micrograph (b) and the corresponding electron diffraction pattern (a) showing the intergrowth of β''-alumina and the $15R(5)$ type. The diffraction spots of the supercell marked with arrows in (a) are (0042) and (3042). The Hägg notation of the polytype is shown in the lower part of (b).

partly β'' and partly a new ordered structure. The $h0l$ diffraction pattern shows strong spots due to β'', but also clearly shows a commensurate supercell with the same a, but with a c-axis five times as long. The extinctions for $h+l \neq 3n$ for the supercell show that this also has rhombohedral symmetry as β'' and thus must be for a $15R$ polytype. There are possible two distinct stacking sequences, with Jagodzinski symbols $(hhhhc)_3$ and $(cchch)_3$. In the Hägg notation these are $(-+--++)_3$ and $(+++---)_3$, respectively. The contrast in the image, three lighter and two darker fringes alternating, shows clearly that the second alternative is the correct one.

In Fig. 3, we illustrate the new structure. The conducting planes marked h are similar to those in β-alumina and those marked c are similar to those in β''-alumina. The length of the c-axis can be determined from the $ACB\ldots$ sequence to be 15 layers or approximately $15 \times 11.3 = 169.5$ Å.

Figure 4 shows an image of a structure with a repeat unit twice that of the $15R$ structure. Using the same interpretation of contrast, the Hägg sequence is determined to be $(++---++--)_3$ or, translated into Jagodzinski notation, $(ccchchchch)_3$. Note that the proportion of c to h layers (3:2) is the same in this polytype as in the $15R$ polytype. The necessity for the subscript 3 is determined by examining the stacking sequence of the conducting planes, which is

$$ACBACABACA, BACBABCBAB,$$
$$CBACBCACBC, A\ldots.$$

This is a $30R$ sequence as the symbols in each set of 10 (separated by commas) are related by the transformations $A \rightarrow B \rightarrow C \rightarrow A$. The length of the c-axis of this structure is therefore approximately $30 \times 11.3 = 339$ Å. This structure is illustrated in Fig. 5.

The discovery of these new structures raises the question of suitable nomenclature. There have already been reported structures

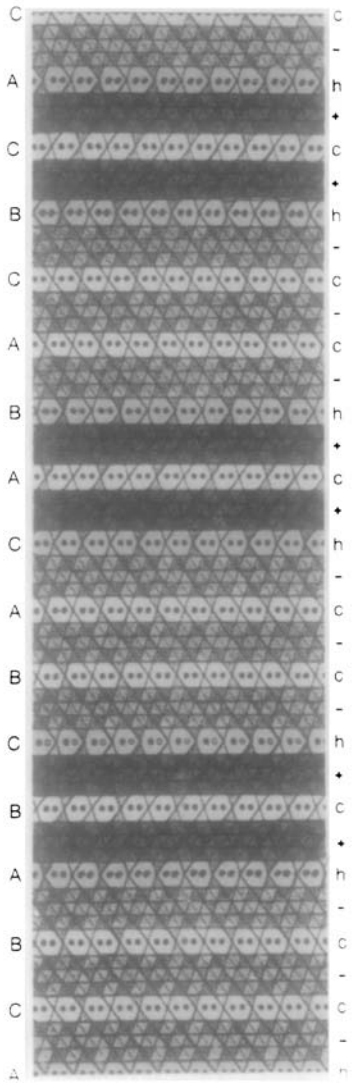

FIG. 3. The structure of the β-alumina type $15R(5\dagger$ projected on the 110 plane. The Hägg notation of the spinel slabs (+ or −) is shown to the right together with the Jagodzinski notation of the conducting planes (h or c).

based on wider spinel slabs named β'''- (*12*) and β''''-alumina (*13*)—any further proliferation of superscripts would clearly be absurd. As a convenient shorthand we suggest using a modification of the Ramsdell notation, although this is not entirely unambiguous (there are, for example, two possibilities for $15R$). In this notation in addition

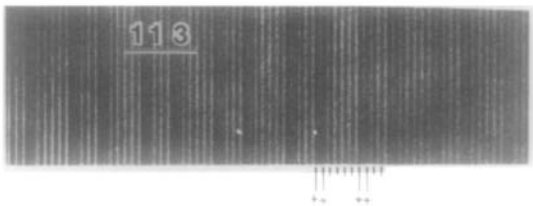

FIG. 4. Electron micrograph of a β-alumina type $30R(5)$ crystal. One-third of the c-axis is marked as 113 Å.

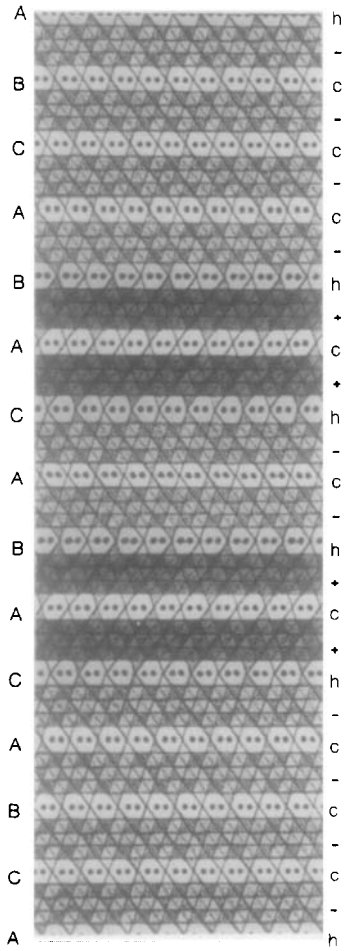

FIG. 5. The structure of the β-alumina type $30R(5)$ represented as in Fig. 3. Only one-third of the c-axis repeat is shown.

to the Ramsdell symbol we add in parentheses the number of polyhedral layers in a slab, i.e., the number of cation layers between conducting planes (*14*), five in the case of β- and β''-alumina and the compounds reported here. Thus β is $2H(5)$, β'' is $3R(5)$, and the new structures are $15R(5)$ and $30R(5)$. In the same notation β'''-alumina is $2H(7)$ and β''''-alumina is $3R(7)$.

When β''-alumina loses sodium, new disordered structures are formed with spinel slabs with widths corresponding to $4n+1$ (here n is an integer) polyhedral layers and slabs with $n=1$, 2, 3, 4, and 5 have been observed (*14*). Sometimes these are ordered corresponding to, for example, structures such as $3R(9)$. A symbol $rX(s)$ gives directly the number of oxygen layers in the c-axis of a structure as rs. The corresponding c-axis repeat is approximately $rs \times 2.2$ Å.

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References

1. W. L. BRAGG, G. GOTTFRIED, AND J. WEST, *Z. Kristallogr.* **77**, 255 (1931).
2. C. R. PETERS, M. BETTMAN, J. W. MOORE, AND J. D. GLICK, *Acta Crystallogr. Sect. B* **27**, 1826 (1971).
3. G. YAMAGUCHI AND K. SUZUKI, *Bull. Chem. Soc. Japan* **41**, 93 (1968).
4. W. L. ROTH, F. REIDINGER, AND S. LAPLACA, *in* "Superionic Conductors" (G. C. Mahon and W. L. Roth, Eds.), p. 223, Plenum, New York (1976).
5. A. R. VERMA AND P. KRISHNA, "Polymorphism and Polytypism in Crystals," pp. 83–91, Wiley, New York (1966).
6. G. HÄGG, *Ark. Kemi Mineral. Geol. B* **16**, 1 (1943).
7. D. J. M. BEVAN, B. HUDSON, AND P. T. MOSELEY, *Mater. Res. Bull.* **9**, 1073 (1974).
8. L. C. DEJONGHE, *J. Mater. Sci.* **12**, 497 (1977).

9. J. M. COWLEY AND A. F. MOODIE, *Acta Crystallogr.* **12**, 360 (1959).
10. J. GJØNNES AND A. F. MOODIE, *Acta Crystallogr.* **19**, 65 (1965).
11. S. IIJIMA AND P. R. BUSECK, *Acta Crystallogr. Sect. A* **34**, 709 (1978).
12. M. BETTMAN AND L. L. TURNER, *Inorg. Chem.* **10**, 1442 (1971).
13. N. WEBER AND A. VENERO, *Bull. Amer. Ceram. Soc.* **49**, 498 (1970).
14. J. -O. BOVIN, *Acta Crystallogr. Sect. A* **35**, 572 (1979).