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Diffusion Process of Sodium Ions in the Transition of the Bronze-Type Sodium Titanium Dioxide

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Sodium-ordered Na_xTiO_2 is transformed into its disordered form by way of a new ordered form. All forms have the same crystal structure framework and monoclinic symmetry. When **a**, **b**, and **c** represent the lattice vectors of *C*-centered unit cells in the disordered form, the starting ordered form has a *C*-centered lattice of 2**a**, 4**b**, and **c**, and the new ordered form has a primitive lattice of **a**, **b**, and **c**. Sodium ions make one-dimensional diffusion along the **b** axis in the first phase change and two-dimensional diffusion parallel to the **ab** plane in the subsequent transformation. Two stages of diffusion correspond to two kinds of interstitial paths in the framework. Crystallites of the starting ordered arrangement are often divided into many domains with respect to the sodium arrangement. The present diffusion mechanism suggests that the initial arrangement changes directly into the final disordered one in the vicinity of domain boundaries.

Introduction

The fundamental structure of Na_xTiO_2 determined by Andersson and Wadsley (*1*) is projected, using idealized octahedra, along the **b** and **c** axis in Fig. 1a and b, respectively. The framework is built up from doubled layers of TiO_6 octahedra edge-shared in a zigzag manner. These double layers are parallel to (001) planes, and adjacent layers are bridged by vertices of octahedra. Sodium ions occupy at the same weight all of the cubooctahedral sites in the framework, that is, they form a disordered arrangement.

An ordered arrangement of sodium ions was first revealed with high-resolution lattice images of a hydrated Na_xTiO_2-type compound prepared under hydrothermal conditions (*2*). DTA measurements for the hydrate (*2*) showed that it changed into an anhydrate with the same ordered arrangement while undergoing about 0.8% weight loss from near 350 to 580°C, and further heating at 740°C above 1 hr converted the ordered anhydrate into a disordered one of itself. In this work, a new phase with an intermediately ordered arrangement between the ordered and the disordered anhydrate was found, and the intermediate arrangement suggests a route of the present order–disorder transition. The route can be explained by the disordering process, or the diffusion process, which is considered on the basis of structural properties of interstitial paths. In the last section, brief explanations are offered for the relation between diffuse scatterings and domain structures

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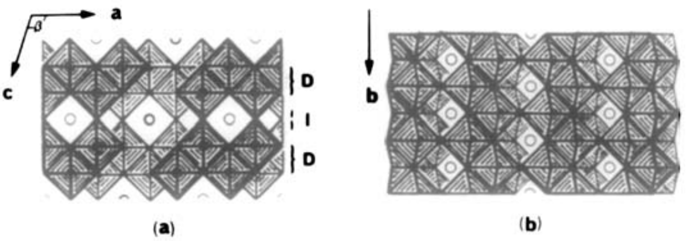

FIG. 1. The Na_xTiO_2-type fundamental crystal structure. (a) and (b) are the figures projected along the *b* and the *c* axis, respectively, where TiO_6 octahedra are idealized. "D" and "I" represent a double layer of TiO_6 octahedra and an interlayer, respectively. Sodium ions occupy the positions in cubooctahedra shown by circles in both figures.

observed in the sodium-ordered arrangement, and for the effect of domains on the transition.

Experimental

The ordered anhydrate was obtained by heating at 580°C the hydrate which was hydrothermally synthesized according to the previous procedure (*2, 3*). In order to observe *in situ* the order–disorder transition of the anhydrate, trials of electron beam heating were made for the ordered anhydrate crystallites. Those direct observations, however, could not succeed because there were no effects of the beam heating on the compound. Considering that it takes above 1 hr for sodium ions to complete a

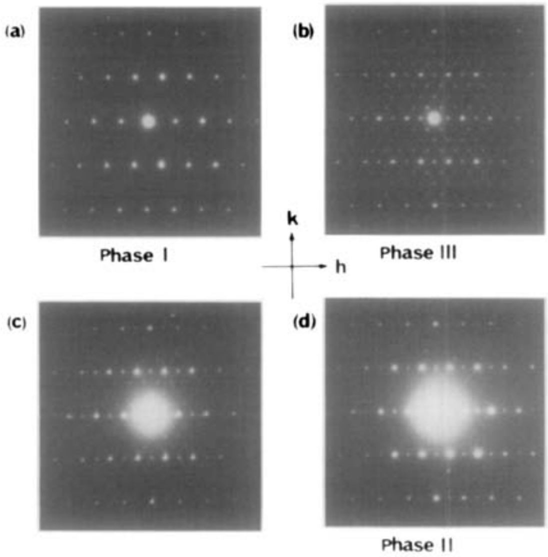

FIG. 2. Electron diffraction patterns on (*hk*0) reciprocal lattice sections. (a) is scattered from the disordered form (Phase I) corresponding to the fundamental structure and (b) from the ordered one (Phase III); many superlattice reflections are observed in addition to the fundamental reflections. In (c), diffraction intensities of the superlattice reflections with $k \neq 4n$ (*n* equal to integers) are reduced and those disappear in (d), resulting in a new ordered form (Phase II) with a primitive lattice. Reticulate lines hatched in (e) show diffuse scatterings observed in the present work and often for Phase III in the previous work (*2*).

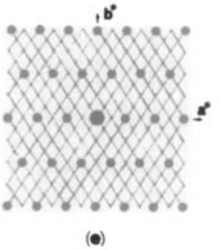

FIG. 2—*Continued.*

disordering state in the framework at 740°C, some crystallites of the ordered anhydrate were heated at 720°C for 20 min and some at 650°C for 15 hr, and both ashes were cooled to room temperature (RT). For the white powder samples cooled from 580, 650, 720, and 740°C to RT, crystalline fragments were examined in an electron microscope with a top entry goniometer (100 kV, Type H-500, Hitachi Co., Ltd.), and many diffraction patterns were taken from a number of fragments to check the processes of disappearance of superlattice reflections.

Results

Sodium disordering in the present order–disorder transition was characterized by disappearance of superlattice reflection in (*hk*0) reciprocal lattice sections because no additional modulation was found out in the direction along the c^* axes. The (*hk*0) section in Fig. 2a is obtained for the sodium-disordered form (hereafter, Phase I), cooled from 740°C to RT, and contains only main reflections corresponding to the fundamental structure. The diffraction pattern in Fig. 2b is given by the anhydrous sodium-ordered Na_xTiO_2 (Phase III) brought from 580°C to RT. Compared with Fig. 2a, extra reflections can be seen besides the main ones. Figures 2c and d are the patterns which were commonly observed for the samples heated at 720°C, but not for the crystallites heated at 650°C. In the former, some superlattice reflections are selectively weakened. These diffraction spots disappear in Fig. 2d, which means an occurrence of a new order state (Phase II) simpler than that in Phase III.

Phase II has a primitive superlattice, the lattice vectors of which are **a**, **b**, and **c** when the *C*-centered lattice of Phase I is represented by the vectors **a**, **b**, and **c**. For the *C*-centered lattice of Phase III, these are 2**a**, 4**b**, and **c**. Reticulate diffuse scatterings as illustrated in Fig. 2e were observed for some diffraction patterns corresponding to Fig. 2c, which were considerably weaker than the superlattice reflections.

Sodium-Ordered Arrangement in Phase II

Cubooctahedral sites are located between adjacent double layers (see Fig. 1a). In every interlayer, these sites are in an arrangement connected with the translation vectors $\pm(\mathbf{a} \pm \mathbf{b})/2$. When the ions statistically occupy all these positions at the same weight, we get a sodium-disordered phase like Phase I, showing only main reflections as in Fig. 2a, because the sodium arrangement has the translation vectors equivalent with that of the framework. On the other hand, when the ions are ordered, both vectors are different from each other and extra diffraction spots appear in addition to the main ones. For example, additional reflections in Fig. 2b are based on the ordered arrangement schematically drawn in Fig. 3a. For Phase II, which keeps the Na_xTiO_2 framework, this kind of superlattice reflection changes a fundamental unit cell into a primitive one similar in size. Such a change is attained by the situation that the ions occupy two cubooctahedral sites in a unit cell at different weights. Figure 3b illustrates a possible configuration of sodium ordering, where A sites have a half lighter weight than B sites. The occupancy at A is evaluated as an averaged value among vacant and filled sites arrayed on each line along the *b* axis in Fig. 3a, as is explained later.

Discussion

White ashes cooled from 580, 650, 720, and 740°C to RT keep the Na_xTiO_2-type crystal structure framework and DTA curves above 580°C have no changes which indicate reconstruction of the framework into the other type before the anhydrate decomposes into hexatitanate and rutile near 900°C. On the other hand, the electron diffraction patterns show that the ashes have a different arrangement of sodium ions from each other. The changes to be considered, therefore, are order–disorder transformations for the ions between 580 and 740°C. In this case, the route III → II → I is regarded to be the simplest process for the present sodium disordering. Considering that the transition is based on rearrangement of sodium ions in the same crystal structure framework, the ions are thought to undergo diffusion in two stages during the whole process. The route is believed to be possible because we can get a reasonable explanation of these stages from structural viewpoints as is described later.

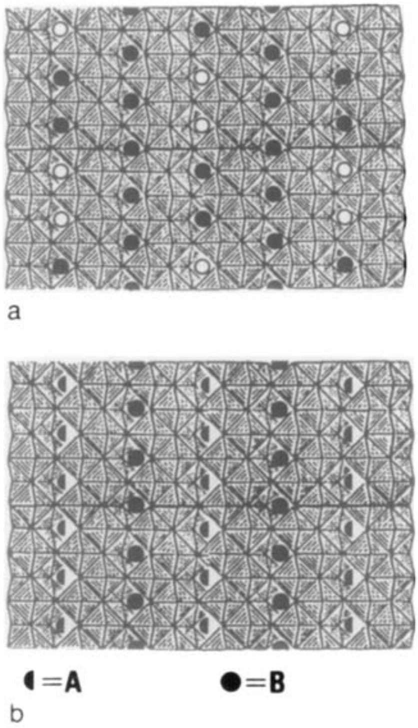

FIG. 3. Ordered arrangements of sodium ions and a domain figure. Sodium-ordered arrangements of Phase III and II are schematically illustrated in (a) and (b), respectively. Both are projected along their c axes. Black, white, and half-black circles represent filled, vacant, and a half-filled cubooctahedral site, respectively. (c) depicts the sodium-ordered arrangement in Phase III, which is divided into domains. The domain boundaries are indicated by "B."

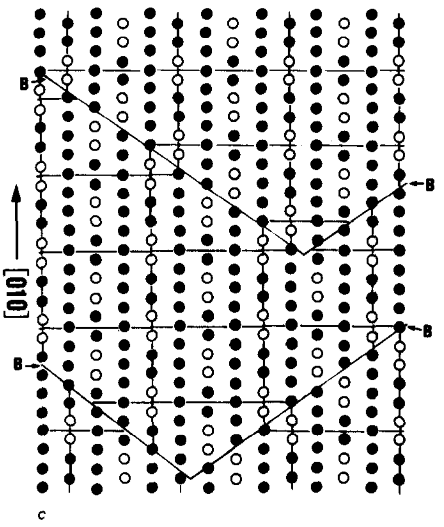

FIG. 3—*Continued.*

For the present structure, we find eight interstitial paths linking each cubooctahedra with eight others around it. These can be classified into three groups according to their structural features. The first group contains two paths parallel to the b axis, the second contains four paths found in an interlayer, and the third has two paths which pierce a double layer. The first paths have about 15% larger cross section and about 40–50% shorter length than the others. On the other hand, between the second and the third groups, there are little differences for both properties, but the former is surrounded by vertex-shared octahedra and the latter by edge-shared ones. From these points, the first seems to be much more effective for diffusion than the others and the second to be more flexible than the third. The ions are therefore considered to use the first paths in the phase change from III to II, and subsequently, the second paths in the change from II to I. The former brings about one-dimensional diffusion along the *b* axis, by which we can convert the *C*-centered cell in Fig. 3a into the primitive cell in Fig. 3b. The latter results in two-dimensional diffusion in the interlayers, by which the primitive cell can be changed into the fundamental *C*-centered cell as in Phase I. This conversion scheme is consistent with the transition route from III to I suggested from the observations. For lack of thermodynamical data, we cannot discuss the stability and a stability field of each anhydrate. Nevertheless, Phase I would be more stable than II and III above at highest 740°C, and Phase II more stable than III above near 720°C. Moreover, possible cooling of I and II to RT must be due to that even at RT Phase III is less stable than II and I, and Phase II is less stable than I and/or that high energy barriers against sodium migration exist between I and II and II and III. In the former case, an essential cause would be that the hydrated sodium-ordered Na_xTiO_2 can be prepared under special atmosphere of hydrothermal conditions (*2*), and in the latter, we could imagine the effect of bottlenecks with considerably smaller diameters compared with 4.8 Å (*6*) on sodium migration as the energy barriers.

These compounds are a typical example in which geometrical properties may be a measure to judge an effectiveness of interstitial paths in diffusion. The measure can be extended to sodium nonatitanates (*3*) with the framework similar to Na_xTiO_2, whose structures are composed of Na_xTiO_2-type double layers and bridging layers interleaved every two double layers. It was revealed by 1-MV high-resolution electron microscopy (*4*) that sodium ions in the bridging layers tend to migrate on electron beam irradiation although those in the other paths do not. Easy migrations can be qualitatively understood on structural grounds in that the ions are placed in tunnels with a slightly larger cross section, a half shorter site–site distance, and a half lighter occupancy, compared with those of cubooctahedra tunnels.

Reticulate diffuse scatterings were similarly detected for Phase III before the transition. Therefore, they are related to an arrangement of sodium ions but bear no direct relation to the transition. Such scatterings indicate that structural mistakes lie at random along [110] and [1$\bar{1}$0] of Phase III's structure, or along [210] and [2$\bar{1}$0] of the fundamental structure (*5*). The present mistakes are inferred to be caused by many domain boundaries, such as those observed along both directions at 50 to 400-Å intervals in the sodium arrangement, as shown in the previous work (*2*). Figure 3c is an example of the arrangement with the boundaries. Whenever one of these is crossed, the arrangement is shifted by $(\mathbf{a} + \mathbf{b})/2$ or $(\mathbf{a} + 3\mathbf{b})/2$ from a regular position, that is, continuous arrays of filled-sites along the *b* axis change into discontinuous ones and vice versa. A uniformity in period is kept only within each domain. Accordingly, for crystallites which are divided into many coherent domains by boundaries placed at random parallel to the above directions, such diffuse scatterings would be observable. One-dimensional diffusion through these boundaries makes the ions move from continuous arrays in one domain to the discontinuous ones in the neighboring domain, and vice versa. In the vicinity of boundaries, therefore, site occupancies tend to be averaged along the boundaries as well as the *b* axis. If domains are relatively smaller in size than a mean length by which the ions move in the one-dimensional diffusion, then it may be difficult to find Phase II. The present boundaries are similar to "antiphase boundaries" (7).

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