New Titanium Dioxide Bronze with Partially Ordered Arrangement of Sodium Ions

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Sodium titanium dioxide bronzes were prepared under hydrothermal conditions. The bronzes could be classified into two groups on the basis of their preparation temperatures. One was synthesized below 300°C and had a disordered distribution of sodium ions in a host lattice of chemical composition TiO_2. The other obtained above 350°C took a sodium-ordered arrangement resulting in a superlattice. The ordered phase was shown by heating to change into a sodium-disordered form by way of another sodium-ordered form. It was considered that the first ordered phase was hydrated titanium dioxide bronze and the second ordered phase was a true sodium-ordered dioxide bronze.

Introduction

Titanium dioxide bronze containing sodium ions, $Na_xTi_4O_8$ ($x = 0.8$), was first prepared by heating trititanate in an atmosphere of hydrogen at 950°C (1). At the same time, its crystal structure was determined to have a framework of titanium–oxygen octahedra with very distorted cubic interstitial positions partly occupied by sodium ions in disordered arrangement. Afterward, the mineral freudenbergite ($2, 3$), in which iron ions were substituted partly for titanium ions in $Na_xTi_4O_8$, was pointed out to be isostructural with the dioxide bronze (4). Dioxide bronze was also prepared under hydrothermal conditions to be identified with freudenbergite in structure (5).

Freudenbergite shows that a part of the titanium ions may be replaced by di- or tri-valent cations. Various compounds of the $Na_xTi_4O_8$ type containing Al, Cr, Ni, and so on were prepared by solid state reactions and

they had nonstoichiometric compositions within a wide range (6). On the other hand, no $Na_xTi_4O_8$ ($x \neq 0.8$) has been found so far although the crystal structure could accept at maximum two sodium ions in a single unit cell. Moreover, no reports have been made on structural varieties of $Na_xTi_4O_8$ based on various host structures and arrangements of sodium ions as found for alkali metal tungsten bronzes.

In this report, the description has been given of new bronzes with a superstructure in addition to the $Na_{0.8}Ti_4O_8$-type substructure. It has been revealed by lattice images that new bronzes are based on an ordered array of sodium ions. They had sodium ion arrangements similar to each other in the $Na_{0.8}Ti_4O_8$-type host framework. Either ordered or disordered bronzes could be synthesized selectively by controlling hydrothermal conditions. Chemical relations among the bronzes obtained are discussed. Hereafter, sodium-ordered and disordered bronzes are designated by the letters OB and DB, respectively.

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Experimental

Starting materials were X-ray amorphous titanium dioxide gel containing 20 wt% water and aqueous solutions of NaOH whose concentrations were in the range of 5 M. Sixty milligrams of gel and 50 mm^3 of solvent solution were charged in platinum capsules (35×5 mm). Many capsules were placed together in a Morey-type autoclave. Hydrothermal reactions were processed between 250 and 530°C under the pressures corresponding to 65% fill for 10 to 20 days. The detailed procedures will be reported in another paper on the reproducibility of the hydrothermal reactions in the system TiO$_2$–NaOH$_{aq}$.

Products were investigated by means of the X-ray powder diffraction method and transmission electron microscopy. For electron microscopic examinations, fine crystallites dispersed in carbon tetrachloride were collected on holey carbon films. They were examined in a JEM 100C high-resolution microscope with a top entry goniometer. For the bronze-type products, many diffraction patterns were gathered to determine their unit cells and space groups. High-resolution electron micrographs were taken by through-focusing with 2.8 aberration coefficiency using 100 kV.

DTA–TG measurements were made to investigate chemical relations among the present bronze-type products.

Products

Products are shown on a reaction diagram in Fig. 1 with temperature as ordinate and mole percent of Na$_2$O as abscissa. They were obtained after hydrothermal reactions of 10 days duration. Bronze-type products formed together only with Na$_2$Ti$_9$O$_{19}$ (7, 8) below 450°C and with Na$_2$Ti$_9$O$_{19}$, Na$_2$Ti$_6$O$_{13}$ (9) and Na$_2$Ti$_3$O$_7$ (10) above 450°C. They were prepared alone near 15% below 400°C, and again near 20% with Na$_2$Ti$_9$O$_{19}$ not well
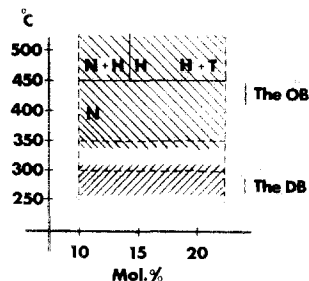

FIG. 1. The formation range of sodium titanium dioxide bronzes in the hydrothermal system, TiO$_2$–NaOH$_{aq}$. Dioxide bronzes are obtained in the range between 10 and 22.5% Na$_2$O above 250°C. N, H, and T represent Na$_2$Ti$_9$O$_{19}$, Na$_2$Ti$_6$O$_{13}$, and Na$_2$Ti$_3$O$_7$, respectively, which are produced together with dioxide bronzes.

crystallized. The bronze-type products could be separated into two groups on the basis of their hydrothermal preparation temperatures. One (DB type) was synthesized below 300°C and the other (OB type) above 350°C. Their X-ray powder patterns, which indicated that both phases kept the Na$_{0.8}$Ti$_4$O$_8$-type structure as a basic construction of their crystals, could be distinguished mutually by slight shifts between corresponding reflections other than 00l. A clear crystallographic distinction between them was found with their diffraction patterns in the (001) reciprocal lattice planes as shown in Figs. 2a and b. A large part of the crystallites hydrothermally prepared at 300 and 350°C gave diffraction patterns with the Na$_{0.8}$Ti$_4$O$_8$-type main reflections (see Fig. 2b), very weakened superreflections (see Fig. 2a), and diffuse scatterings around the super spots.

The bronzes were obtained as white or yellowish powders of fine tabular crystallites less than several micrometers in size. When about 200 mm^3 solvent solutions were charged, the OB-type crystallites grew up to 15 μm in average size near 450°C. It was difficult to grow the crystals further because they could not be transported in NaOH$_{aq}$ solutions with various positive or negative
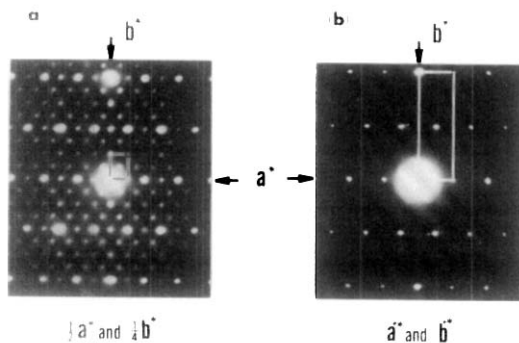
FIG. 2. Electron diffraction patterns. Patterns (a) and (b) are the (001) reciprocal lattice planes of the sodium-ordered (OB) and disordered (DB) phase crystallites, respectively. The rectangle in (b) corresponds to the $Na_{0.8}Ti_4O_8$-type subcell of the DB phase whose periods are represented as a'^* and b'^*. The small face-centered rectangle in (a) is a supercell of the OB phase with $\frac{1}{2}a^*$ and $\frac{1}{4}b^*$, where a^* and b^* are the reciprocal lattice constants of the $Na_{0.8}Ti_4O_8$-type subcell of the OB phase.

temperature differences between nutrient and growth zones. Usually, higher sodium titanates were unilaterally transported under these conditions. In case of the compositions of freudenbergite, the crystals grew up to about 450 μm by the transportation method in $NaOH_{aq}$ solutions (11).

Thermal Phase Change

An endothermic phase change with about 0.8% weight loss took place on heating the OB-type crystallites in air. The weight loss continued uniformly from near 350 to 580°C with heating speeds of 10 to 20°C/min. The white substance cooled to room temperature had also the $Na_{0.8}Ti_4O_8$-type powder pattern and the (001) reciprocal lattice plane with such superreflections as found for the OB crystallites. Hence, it was called the OB'-type compound. These superreflections disappeared completely for the white compound cooled to room temperature after holding the OB' phase near 740°C above 1 hr. This compound maintains a clear powder pattern indicating the $Na_{0.8}Ti_4O_8$-

type structure and is assigned to a disordered form (DB') of the OB' phase. Further heating of the DB' phase brought about decomposition into $Na_2Ti_6O_{12}$ and TiO_2 (rutile) below 900°C with the above heating speeds. The DB-type product showed no phase change below 900°C and, near this temperature, there occurred similarly decomposition into hexatitanate and rutile.

Ordered Arrangement of Sodium Ions

Superreflections observed in Fig. 2a form a C-centered superlattice with the periods $\frac{1}{2}a^*, \frac{1}{4}b^*$, and c^*, where a^*, b^*, and c^* are the reciprocal lattice constants of the $Na_{0.8}Ti_4O_8$-type subcell. The OB'-phase crystals have also a similar superlattice, but the b-axis is slightly shorter than that of the OB. The absent reflections including superreflections indicate possible space groups, $C2$, Cm, and $C2/m$. The lattice parameters of the subcells in the OB and OB' crystallites are shown in Table I in comparison with those of the DB and DB' crystallites.

The lattice image in Fig. 3a was taken with an OB-type crystal fragment at 1200 to 1300 Å underfocus. Fifty-eight beams (6 main and 52 superreflections) were allowed to contribute to the image. The image contrast consists of weak and strong white maxima, which are arrayed closely along [010]. Geometric relations among white maxima are explained in Fig. 3b. A strong

TABLE I

LATTICE PARAMETERS OF THE DISORDERED PHASES AND THOSE OF THE SUBCELLS OF THE ORDERED PHASES

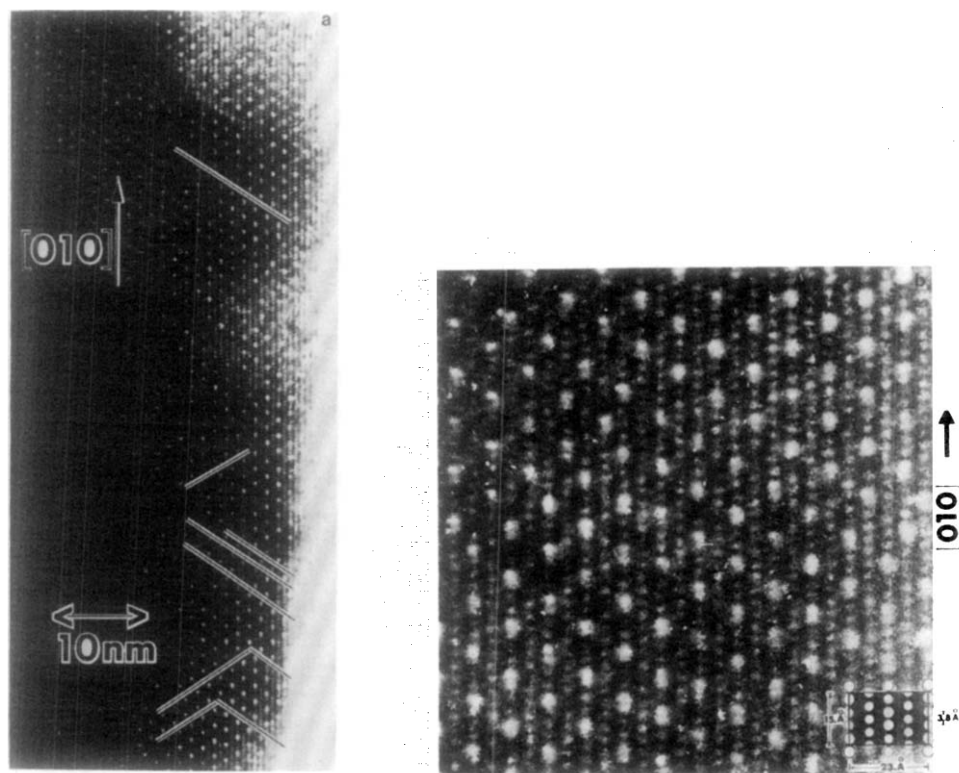| Phases	DB	DB'	OB	OB'
d (Å)	12.22 ± 0.01	12.19	12.17	12.17
b (Å)	3.837 ± 0.005	3.829	3.850	3.828
c (Å)	6.448 ± 0.007	6.429	6.432	6.427
β (°)	107.5 ± 0.1	107.2	107.1	107.0

FIG. 3. High-resolution electron micrographs of sodium-ordered titanium dioxide bronze (the OB). Image (a) was taken with the corresponding diffraction pattern in Fig. 2a at about 1250 Å underfocus with $Cs = 2.8$ mm. For an array of strong white maxima, antiphase boundaries are observed along several white lines. A part of image (a) is enlarged in (b) to explain geometric relations among white maxima. The inset shows a unit of the two-dimensional arrangement of white maxima. Large and small circles represent strong and weak white maxima, respectively.

maximum is accompanied by one of slightly less or comparable brightness and they form a strong pair. The strong pairs take a face-centered array in this projection, but antiphase boundaries are found at some places for an array of these pairs. Weak maxima similarly have a smaller face-centered relation among themselves than among the strong pairs. The inset in Fig. 3b represents a unit of two-dimensional arrangement of white maxima in this projection. The distances between strong pairs are related to the periods given by the super-lattice and those among weak maxima to the periods by the sublattice.

The crystal structure viewed along the c-axis of $Na_{0.8}Ti_4O_8$ is illustrated in Fig. 4a using the data reported by Andersson and Wadsley (1). Shaded areas represent titanium–oxygen octahedra joined by shar-ing edges along the b-axis. A sodium ion occupies every position, shown by solid circles, statistically by 80%. These positions are located on a face-centered lattice, whose periods are in good agreement with the dis-tances between the weak white maxima (see Fig. 3b). Ions equivalent with each ion in a unit cell occur every 6.45 Å along the c-axis. These equivalent ions are superimposed on each projected position. But, at each sodium
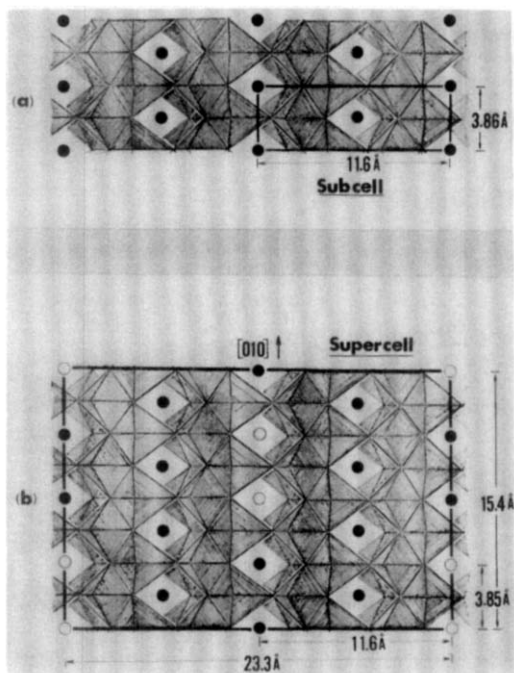
FIG. 4. The mode of sodium-ordered arrangement projected along the c-axis in the OB and OB' crystal structures. (a) shows the crystal structure of $Na_{0.8}Ti_4O_8$ viewed parallel to its c-axis. The rectangle indicates the size of the unit cell, that is, the subcell of bronzes keeping the $Na_{0.8}Ti_4O_8$-type host lattice. (b) contains eight subcells, four and two arraying along [010] and nearly [11 0 6], respectively. Open circles represent sodium-excluded positions. Numerical values in (b) were obtained for the OB phase.

position, a factor of 0.8 is multiplied. The total scattering power for electrons summed up along the c-axis at each sodium position does not reach one-half of the total power at each titanium position. Therefore, sodium positions can be estimated kinematically to become brighter than their surroundings within the first contour line on an image contrast projected along the axis. Furthermore, it is expected, based on this idea that sodium ions are almost or completely excluded from the positions corresponding to the strong white maxima. Figure 4b shows a structure model to explain the image contrast. The model contains eight subcells,

four and two arraying along and normal to [010], respectively. Two sodium-excluded positions form a pair (shown by open circles) and pairs are located on the basis of a face-centered relation with the periods $2a$ and $4b$.

Consequently, the origin of the superstructure is concluded to be due to a partially ordered arrangement of sodium ions.

Discussion

The present hydrothermal syntheses showed that the OB phase occurred in a higher temperature range than the DB. This curious result can be explained by the fact that both phases are not polymorphous with each other because of the difference between their chemical compositions. First, the OB phase undergoes a weight loss in order to change into the OB'. The weight loss is inferred to be due to an escape of water molecules from the crystal structure of the OB. The value of 0.8% gives an estimation that three water molecules are released from each supercell in the crystal. Second, the OB phase may be estimated to be about 25% less in sodium content than the DB because the former contains four sodium-excluded positions in one supercell.

Hydrogen atoms forming the water molecules released are thought to be incorporated in the framework as water molecules rather than protons or hydronium ions. The weight loss does not recover in spite of annealing the OB' and the DB' phases, and also both prime phases do not have any colors other than white although the existence of oxygen defects often results in dark colors for oxide compounds containing titanium atoms as a main component. For example, if protons are largely favored by the OB, about three oxygen defects appear in each supercell with 64 formulas of TiO_2 through water releasing. These defects, if any, would capture oxygen atoms by annealing and, as a result, the weight loss would almost be made up. Therefore, the OB phase is considered to be

hydrated sodium-ordered bronze, and the OB' phase to be a true sodium-ordered dioxide bronze.

It has not been decided yet which of the two disordered phases, DB and DB', is approximate to $Na_{0.8}Ti_4O_8$ reported by Andersson and Wadsley (1). Providing the DB is approximate to the phase ($Na_{12.8}Ti_{64}O_{128} = 16 \times Na_{0.8}Ti_4O_8$), the chemical formulas would be nearly $Na_{9.6}Ti_{64}O_{128} \cdot 3H_2O$ for the OB and $Na_{9.6}Ti_{64}O_{128}$ for the OB' and the DB'. In case the DB' corresponds approximately to the known phase, the OB would have a formula near to $Na_{12.8}Ti_{64}O_{128} \cdot 3H_2O$, and the DB, to $Na_{16}Ti_{64}O_{128}$; that is, all sodium positions are occupied.

Acknowledgments

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