

New Hollandite Oxides: $\text{TiO}_2(\text{H})$ and $\text{K}_{0.06}\text{TiO}_2$

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The topotactic oxidation of the bronze K_xTiO_2 (x close to 0.25), with a hollandite structure, leads to lower x values. By complete oxidation of the parent bronze a new form of titanium dioxide $\text{TiO}_2(\text{H})$ is obtained. Its structure is the iono-covalent framework of hollandite. By heating above 410°C , $\text{TiO}_2(\text{H})$ transforms into anatase. Starting from a single crystal of the precursor bronze it is possible to obtain a partly disintercalated single-crystal product. In this way, $\text{K}_{0.06}\text{TiO}_2$ has been prepared and its structure determined. © 1989 Academic Press, Inc.

Introduction

The type of chemistry called “chimie douce” uses two main routes to obtain new, frequently metastable, materials (1). The first is a hydroxylation–condensation process applied to an insulating host lattice of low dimensionality. This process includes an ion exchange in acidic medium followed by a topotactic dehydroxylation as the temperature is increased. This chemistry is similar to that which, in solution, leads to the formation of polyanions. It can be illustrated, for example, by the synthesis of $\text{Ti}_2\text{Nb}_2\text{O}_9$ starting from KTiNbO_5 (2) or by that of $\text{K}_2\text{Ti}_8\text{O}_{17}$ or $\text{TiO}_2(\text{B})$ from $\text{K}_2\text{Ti}_4\text{O}_9$ (3). The second route uses host lattices which are electronic conductors. The lattice charge is modified by disintercalation which is then a topotactic electron/ion transfer. This redox process leads to metastable host lattices obtained by topotactic

oxidation of a ternary mother phase. In this way, new metastable forms of compounds such as VS_2 (4), FeS_2 (5), CrSe_2 (6), V_2O_5 (7), and MnO_2 (8) have been prepared from LiVS_2 , Li_2FeS_2 , KCrSe_2 , $\beta\text{-CuV}_2\text{O}_5$, and LiMn_2O_4 , respectively. In this paper this latter process is applied to the bronze K_xTiO_2 ($0.13 < x < 0.25$). This phase of hollandite type was first prepared by Lundberg and Andersson (9).

Experimental

The starting material K_xTiO_2 ($0.13 < x < 0.25$) was previously obtained either by hydrogen reduction of the potassium dititanate at 900°C (9) or by electrolysis of a melt containing K_2O and TiO_2 in a molar ratio 1:2 at temperatures ranging between 990 and 1020°C (10). In this work the bronze K_xTiO_2 (with x close to 0.25) is prepared by reaction of potassium metal on titanium dioxide in a nickel tube sealed under vacuum. This tube is preheated at the same tempera-

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ture under an atmosphere of argon before use. The sealed tubes are heated at 1250°C for 2 days. The product obtained in this way is homogeneous, blue-black in color, and well crystallized.

The oxidation is carried out from a slurry containing the powdered bronze in an acidic solution of hydrogen peroxide. The suspension is stirred and heated at 80°C for 2 days in order to ensure a complete reaction. The bronze oxidation may be followed by the color evolution of the slurry from black to light yellowish via blue and green. A partial solubility of the powder is observed. The final product is removed by filtration and dried in air at room temperature. It is light yellowish in color. This hydrated oxide loses its water content by heating at 300°C, leading to the anhydrous compound $\text{TiO}_2(\text{H})$.

When single crystals of bronze are used as starting material, the oxidation reaction proceeds more slowly and is not complete. This topotactic reaction does not destroy the single crystal. The study of $\text{K}_{0.06}\text{TiO}_2$

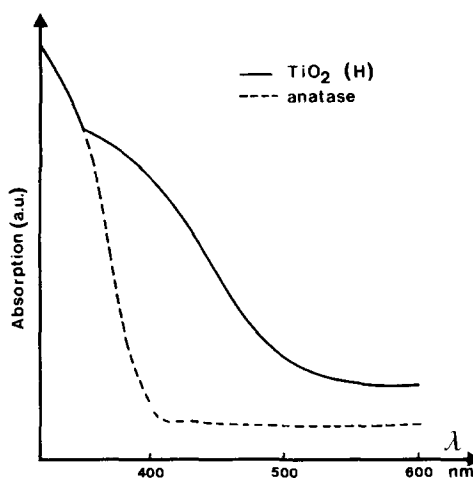


FIG. 1. Reflectance spectra of $\text{TiO}_2(\text{H})$ and $\text{TiO}_2(\text{A})$ anatase.

obtained in this way has been carried out with a CAD 4 diffractometer operating under the conditions given in Table I. For the data reduction, structure solution, and refinement, the SDP-PLUS program chain (1982 version) of Enraf-Nonius has been used (11).

Results

The Hollandite Oxide $\text{TiO}_2(\text{H})$

The final product is light yellow; Fig. 1 shows the reflectance spectra of both $\text{TiO}_2(\text{H})$ and anatase. The onset of absorbance is near 500 nm for $\text{TiO}_2(\text{H})$ compared with 400 nm for anatase form. After heating at 150°C in air, $\text{TiO}_2(\text{H})$ is white and the reflectance spectrum is identical to that of anatase.

The diffraction patterns of the parent bronze and of the final products are very similar in peak positions but not in intensity. Refined parameters of $\text{K}_{0.25}\text{TiO}_2$ and $\text{TiO}_2(\text{H})$ are respectively $a = 10.180(2) \text{ \AA}$, $c = 2.961(2) \text{ \AA}$, $a = 10.161(3) \text{ \AA}$, $c = 2.970(1) \text{ \AA}$.

X-ray fluorescence analysis shows the to-

TABLE I

UNIT CELL CONSTANTS, DATA COLLECTION, AND REFINEMENT CONDITIONS

| <i>Unit cell constants</i> | |
|---|--|
| Crystal symmetry | Tetragonal |
| a (Å) | 10.182 (1) |
| c (Å) | 2.966 (1) |
| V (Å ³) | 307.4 |
| Z | 8 |
| Space group | $I4/m$ |
| <i>Data collection</i> | |
| Radiation (Å) | $\text{MoK}\alpha$, $\lambda = 0.71069$ |
| Scan mode | $\omega - 2\theta$ |
| Scan angle (°) | $\Delta\omega = 0.90 + 0.50 \tan \theta$ |
| Recording angular range (°) | 1.5–35.0 |
| Number of independent data observed with $\sigma(I)/I < 0.30$ | 349 |
| <i>Refinements</i> | |
| Number of variables | 23 |
| $R = \sum(F_o - F_c) / \sum F_o $ | 0.023 |
| $R_w = [\sum w(F_o - F_c)^2 / \sum w F_o^2]^{1/2}$ | |
| with $w = 1$ | 0.028 |
| Extinction parameter refined | $1.33(3) \times 10^{-5}$ |

TABLE II
DENSITY OF TITANIUM
DIOXIDES

| Structure | Density |
|---------------------------------|---------|
| α -TiO ₂ (12) | 4.33 |
| Rutile (13) | 4.13 |
| Brookite (14) | 3.99 |
| Anatase (13) | 3.79 |
| TiO ₂ (B) (3) | 3.64 |
| TiO ₂ (H) | 3.46 |

tal disappearance of the potassium peaks. Quantitative analysis gives less than 0.2 mole% potassium.

These results allow one to conclude that the redox process transforms potassium bronze into a new titanium dioxide. Its structure is the ionic-covalent framework of the hollandite type. Among all the titanium dioxides, TiO₂(H) has the more open structure (Table II). Like TiO₂(B), which exhibits the ionic-covalent framework of the Wadsley bronze Na_{0.20}TiO₂ (15), this other new form of titanium dioxide TiO₂(H) is metastable.

TGA and X-ray powder diagrams show clearly that removing water from TiO₂(H) · nH₂O does not destroy the hollandite framework which is consequently that of the anhydrous form TiO₂(H) up to 410°C. DSC analysis (Fig. 2) exhibits two peaks: The first is endothermic and is related to the water removal between 70 and 230°C: The second is exothermic and corresponds to the transformation of TiO₂(H) into TiO₂ anatase.

The fact that heating TiO₂(H) leads to anatase instead of rutile is noteworthy because, according to a previous work, the transformation of compounds of hollandite type to rutile has been observed under the electron beam in an electron microscope (16), and the tunnel cations could be blasted away under this beam. It is not clear in that work whether the observed phenomenon was really a transformation or a thermal decomposition. In a formal way, two mechanisms described by Bursill (17) would allow the transformation of a hollandite framework into a rutile one. However, the structural filiation between hollandite and anatase is not so clear. As a matter

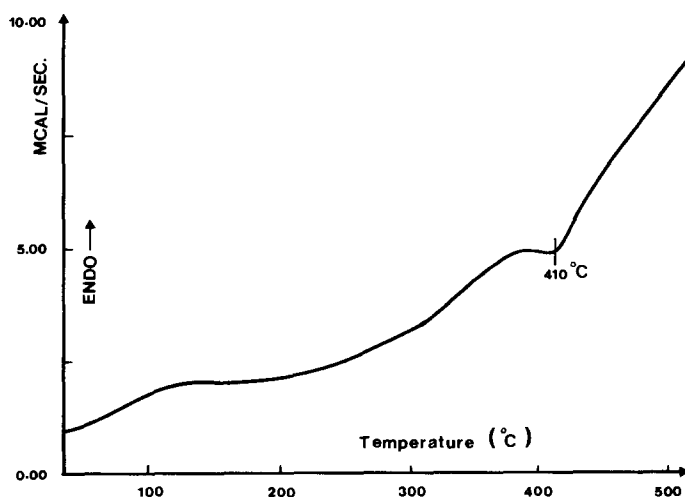


Fig. 2. Differential scanning calorimetry of TiO₂(H).

TABLE IIIa
FRACTIONAL ATOMIC COORDINATES

| Atom | Position | Occupancy factor | x | y | z | B_{eq} (\AA^2) |
|------|----------|------------------|------------|------------|---------------|------------------------------------|
| K | 2a | 0.243(6) | 0 | 0 | $\frac{1}{2}$ | 4.8(3) |
| Ti | 8h | 1 | 0.35210(4) | 0.16935(5) | 0 | 0.708(6) |
| O(1) | 8h | 1 | 0.1569 (2) | 0.2075 (2) | 0 | 0.62(3) |
| O(2) | 8h | 1 | 0.5404 (2) | 0.1643 (2) | 0 | 0.68(3) |

Note. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B_{\text{eq}} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i a_j$.

of fact, investigations using transmission electron microscopy reveal that parent and product oxides exhibit quite different morphologies. The former, $\text{TiO}_2(\text{H})$, occurs as plate-like crystals, whereas the latter forms a felt-like mass of very thin acicular crystals.

The Hollandite Bronze $\text{K}_{0.06}\text{TiO}_2$

As already mentioned, previous syntheses of the hollandite bronze K_xTiO_2 , using high-temperature methods, lead to x values ranging from 0.13 to 0.25. The disintercalation process described above allowed us to obtain single crystals corresponding to lower x values. These crystals are suitable for structure determination. The X-ray dif-

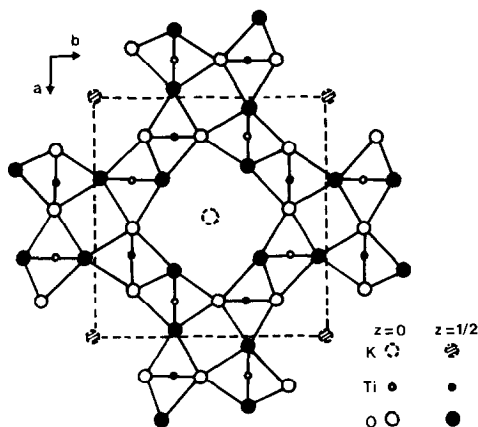


FIG. 3. Projection of the hollandite structure of $\text{K}_{0.06}\text{TiO}_2$ on (001).

TABLE IIIb
THERMAL PARAMETERS

| Atom | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|------|--------------|--------------|--------------|--------------|--------------|--------------|
| K | 0.0038(3) | β_{11} | 0.32(3) | 0 | 0 | 0 |
| Ti | 0.00172(3) | 0.00193(3) | 0.0173(3) | 0.00068(5) | 0 | 0 |
| O(1) | 0.0016(1) | 0.0014(1) | 0.018(2) | 0.0003(2) | 0 | 0 |
| O(2) | 0.0012(1) | 0.0020(1) | 0.021(2) | 0.0000(2) | 0 | 0 |

Note. The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

fraction patterns do not exhibit any extra spots or diffuse streaks in (001) reciprocal planes as usually observed for hollandite oxides with partly occupied channels (18-22).

The structure was refined in the $I4/m$ space group. In the final stages of refinement anisotropic temperature factors were assigned to all atoms and corrections for secondary extinction and anomalous dispersion were applied. This refinement converged to $R = 0.023$ and $R_w = 0.028$. The final Fourier difference map is featureless with maxima and minima in the range $\pm 0.35 \text{ e}\text{\AA}^{-3}$. Table III presents the final atomic coordinates and thermal parameters (a structure factor table is available upon request). A list of bond distances along with their standard deviations is given in Table IV.

The potassium cations are randomly distributed in the center of the pseudo-cubic cavity inside the channel (Fig. 3). There is a large anisotropic vibration along [001]. The root-mean-square amplitude in this direction is 0.378 \AA compared to 0.14 \AA in the

TABLE IV
BOND DISTANCES (\AA)

| | | | |
|--------|---------------------|---------|---------------------|
| K-O(1) | $3.035(3) \times 8$ | Ti-O(1) | $1.945(2) \times 2$ |
| K-O(2) | $3.442(4) \times 4$ | Ti-O(1) | $2.025(3)$ |
| | | Ti-O(2) | $1.988(2) \times 2$ |
| | | Ti-O(2) | $1.918(3)$ |

perpendicular plane. A refinement carried out with potassium in $(0, 0, z)$ instead of $(0, 0, \frac{1}{2})$ leads to $z = 0.424(3)$ and $B = 1.9(1) \text{ \AA}^2$ for R and R_w equal to 0.024 and 0.028, respectively. In this case an extremum of 0.87 e\AA^{-3} is observed in the Fourier difference map. This result in relation to the random distribution of potassium shows that it is difficult to get a realistic picture of the location of these cations in the channel. Electron microscopy studies may improve the knowledge of such phenomena.

Conclusion

The oxidation of potassium bronzes K_xTiO_2 of hollandite type allows the preparation of bronzes having a low potassium content. Such small x values cannot be obtained from syntheses at high temperature. When all the potassium cations are removed, the disintercalation process leads to a new form of titanium dioxide. This form of hollandite type transforms into anatase at 410°C . The potential applications of $\text{TiO}_2(\text{H})$ in the area of catalysis, energy storage, and photochemistry will be investigated.

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