Synthesis, Structural Change upon Heating, and Electronic Structure of Ramsdellite-Type TiO_2

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Polycrystalline samples of TiO_2(R) with the ramsdellite-type structure were synthesized by a soft chemical technique using ramsdellite-type $Li_{0.5}TiO_2$ as a parent compound. The structural stability and phase transition of TiO_2(R) upon heating were investigated by XRD and DSC measurements. In the heating process between 423 and 723 K, a novel intergrowth form of TiO_2 between the rutile and ramsdellite-type structures, similar to the γ-MnO_2 structure, has been found for the first time. From the results of the UV−vis absorption measurements, we found that the band gap energy (3.34 eV) for TiO_2(R) was revealed experimentally to be the largest among those for the known TiO_2 compounds; the gap energy changed abruptly to 3.04 eV in the intergrowth phase of the ramsdellite and rutile domains after introduction of the rutile character. These findings were very consistent with those obtained by the FLAPW calculations.

Introduction

Titanium dioxide (TiO_2) is an important industrial material that is a major component of paint, pigment, and cosmetics and that acts as a support for catalysts. Recently, TiO_2 has also received much attention, mainly because of its potential use in environmental photocatalytic processes.[1,2] Its promising applications include energy renewal and storage and the total destruction of organic compounds in polluted air and water.

Several TiO_2 polymorphs have been reported to date. Rutile, anatase, and brookite are the well-known naturally occurring TiO_2 polymorphs, and there are many studies on their synthesis, chemical stability, and electrochemical and physical properties, including photocatalysis. In addition, by means of a soft chemical method using topotactic reactions of the host alkali titanium oxides, some metastable polymorphs of titanium dioxide, TiO_2(B), TiO_2(H), and TiO_2(R), were produced in previous studies.[3−7] TiO_2(B) has been prepared by hydrolysis of $K_2Ti_4O_9$ followed by heating at 773 K[3] and has the host framework of the Wadsley bronze Na_xTiO_2 with $0.20 < x < 0.25$.[8] This phase has also been found in natural anatase crystals as intergrown lamellae.[9,10] TiO_2(H) and TiO_2(R) have been prepared by topotactic oxidation of the parent materials, hollandite-type potassium titanate bronze K_xTiO_2 ($0.13 < x < 0.25$) and ramsdellite-type Li_xTiO_2 ($x = 0.5$), respectively.[4−7,11] However, there are few experimental reports on the chemical and physical properties of these metastable TiO_2 polymorphs because of the complicated synthetic procedures. The unusual physical properties of the high-pressure polymorphs of TiO_2 have recently been suggested by theoretical calculations.[12−14] For example, the narrowest band gap in the fluorite-type TiO_2 has recently been calculated using first-principle calculations.[12]

TiO_2(R) has a ramsdellite-type structure, the basic framework of which is the TiO_6 double rutile chain,[15] as shown in Figure 1a. The lithium ions, located at the central sites of the tunnel structure, can be completely de-intercalated from the parent $Li_{0.5}TiO_2$ by means of chemical and electrochemical oxidation.[6,7] Recently, the electrochemical lithium insertion and extraction properties of TiO_2(R) have been precisely investigated to see if TiO_2(R) is a good candidate electrode material for lithium-ion batteries.[7,16] However, the chemical and structural stability upon heating and the electronic

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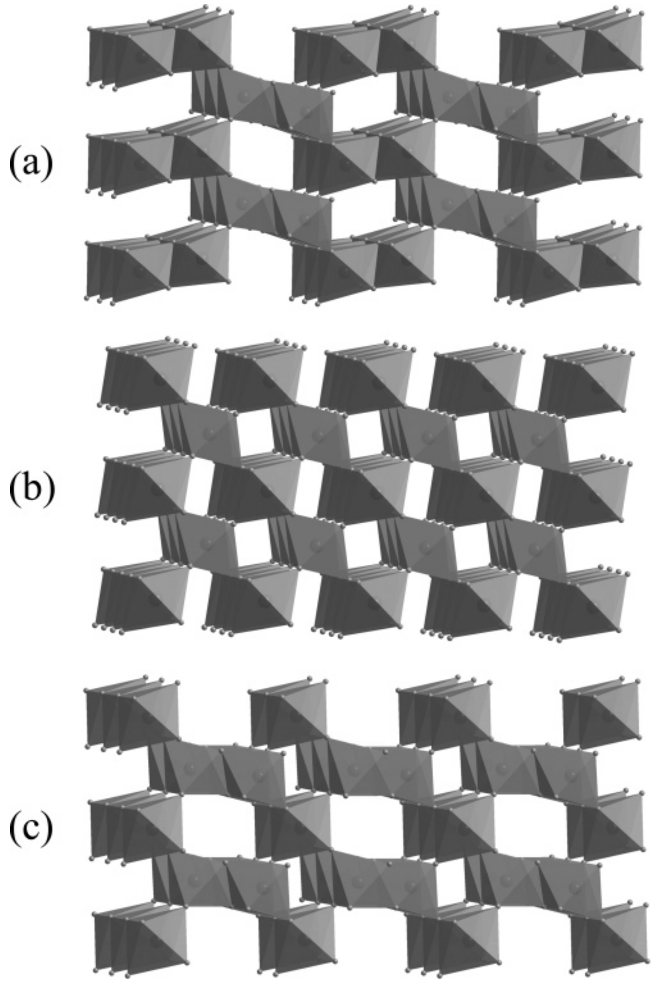

Figure 1. Crystal structures of (a) ramsdellite-type TiO_2, (b) rutile, and (c) the hypothetical intergrowth with ramsdellite and rutile (1:1) domains.

structure of TiO_2(R) have never been investigated experimentally and/or theoretically.

In the present study, we will report the structural stability and phase transition of TiO_2(R) upon heating. In the heating process between 423 and 723 K, a novel intergrowth form of TiO_2 between rutile and ramsdellite-type structures, similar to the γ-MnO_2 structure, has been found for the first time. The optical absorption spectra of the TiO_2(R) before and after the heat treatment were measured, and the results were compared with the theoretical calculations.

Experimental Procedures

Sample Synthesis. TiO_2(R) was prepared by a soft chemical technique using ramsdellite-type $Li_{0.5}TiO_2$ as a parent compound.[6,7] The starting $Li_{0.5}TiO_2$ was prepared by heating pelletized mixtures of $Li_4Ti_5O_{12}$, TiO_2 (99.9%), and Ti metal (99.9%) powder with the $LiTi_2O_4$ composition, as reported previously.[17,18] Spinel-type $Li_4Ti_5O_{12}$ was, as a first step, synthesized by the solid-state reaction of lithium carbonate (99.99%) and titanium dioxide (99.9%). The mixture was pressed into pellets, preheated in air for 20 h at 873 K, fired for 15 h at 1223 K, and then ground and reheated for 48 h at 1173 K. Additional Li_2CO_3 was needed to obtain a single phase because of the volatilization of Li_2O produced by the decomposition of Li_2CO_3.[17] The product was identified as a single phase of spinel-type $Li_4Ti_5O_{12}$ (JCPDS-ICDD #49-207) by X-ray powder diffraction. A mixture of $Li_4Ti_5O_{12}$, TiO_2, and Ti in a 1:2:1 molar ratio was pelletized, covered with Ni foil (0.05 mm thickness), and sealed in an evacuated quartz tube. The quartz ampule was heated in a resistance furnace at 1473 K for several hours under an air atmosphere, and the reaction was then quenched in water.

The ramsdellite form of TiO_2 was then prepared by a combined lithium-ion extraction−oxidation process. The parent $Li_{0.5}TiO_2$ powder samples were stirred in a 1 M HCl solution for several days at room temperature until the powder changed from black to blue-gray to white.[7] The obtained TiO_2(R) powder was washed carefully with ethanol and subjected to chemical and structural experiments.

Characterization. Chemical analysis of the products was carried out by SEM-EDX (JEOL JSM-5400). The chemical formula of the samples was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer, Inc., Optima 3000).

The phase purity and crystal structure of the obtained samples were characterized by X-ray powder diffraction (XRD) profiles, which were measured using a Rigaku RINT2550V diffractometer (operating conditions: 40 kV, 200 mA) with Cu Kα radiation equipped with a curved graphite monochromator. The XRD data were collected for 3 s at each 0.03° step over a 2θ range from 5 to 120° for Rietveld analysis. The computer program JANA2000 was used for the Rietveld analysis.[19]

The electron-density analysis of TiO_2(R) was performed by the maximum entropy method (MEM) using the reported single-crystal data[6] with the computer program PRIMA.[20] The obtained three-dimensional electron-density distributions were visualized with VENUS, which was developed by Dilanian and Izumi.[21] Details of the experimental procedures of the single-crystal MEM analysis have been reported in another paper.[22]

The structural phase transition was confirmed using differential scanning calorimetry (DSC) measurements (SEIKO DSC6200) with 16.54 mg of the TiO_2(R) powder sample. Data were collected between 295 and 723 K, with heating and cooling rates of 5 K/min.

Optical absorption spectra (UV−vis) were measured using a Jasco V-550 spectrophotometer over the range 300−600 nm at 293 K. From the intersection values of the baseline and absorption band edge in the obtained spectra, we estimated the band gap energy of the samples.

The electronic structures of TiO_2(R) and rutile-type TiO_2 were calculated using the full-potential linearized augmented-plane-wave (FLAPW) method with the WIEN2k computer program package.[23] The generalized gradient approximation (GGA) in the formulation of Perdew, Burke, and Ernzherof was used for the exchange and correlation terms.[24] The atomic muffin-tin sphere radii used were 1.9 a.u. for the Ti atom and 1.7 a.u. for the O atom. The plane-wave cutoff was $R_{MT} \times K_{max} = 7.0$, where R_{MT} is the smallest atomic sphere radius in the unit cell and K_{max} is the magnitude of

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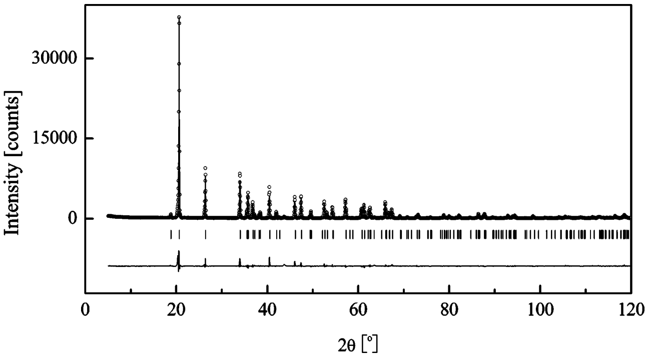

Figure 2. Observed (○) and calculated (solid line) XRD patterns of the TiO_2(R) sample.

the largest **k** vector. The self-consistency was carried out on a 400 *k*-points mesh in the full Brillouin zone. The energy criterion for self-consistency was set to less than 0.001 eV per formula unit. Structural parameters for TiO_2(R) and rutile were used in the calculations.[6,25] We also calculated the electronic structure of the hypothetical intergrowth structure having the ramsdellite and rutile (1:1) domains by using the structural data of $Li_{0.74}Ti_3O_6$ (Figure 1c).[26]

Results and Discussion

Synthesis. Figure 2 presents the XRD pattern of the present TiO_2(R) sample measured at 298 K. All of the observed peaks were indexed to the ramsdellite-type structure (Figure 1a), orthorhombic crystal system and space group *Pbnm*, with the exception of a very weak peak at $2\theta = 44°$, which may be assigned to the rocksalt-type TiO or $Li_xTi_{1-x}O$ phase. In fact, a small amount of black powder can be seen in the samples. However, the content of the rocksalt phase found here is very low (0.5 wt %, from a two-phase structural refinement), and its influence on the following structural and optical results is probably negligible. The lattice parameters ($a = 4.8441(4)$ Å, $b = 9.4353(8)$ Å, $c = 2.9634(2)$ Å) and the refined structural parameters of the present TiO_2(R) sample by the Rietveld analysis were consistent with those from the previous report.[7] The chemical composition, analyzed by ICP-AES, was determined to be $Li_{0.004(2)}TiO_2$. It should be noted that the residual Li content in the present samples was considerably smaller than the previous report.[6]

Structural Change upon Heating. The structural change of TiO_2(R) upon heating was investigated by powder X-ray diffraction and DSC measurements. Figure 3 shows the XRD patterns of powders obtained after firing the TiO_2(R) sample at different temperatures for 1 h with a heating rate of 5 K/min followed by rapid cooling. The ramsdellite structure was stable below 423 K, and the peak position of the 110 reflection could not be shifted on heating. However, the diffraction line width increased with increasing temperatures. When the sample was heat treated at 473 K and above, the XRD patterns drastically changed, and the peaks of the original ramsdellite structure had completely disappeared. The pattern at 473 K resembled that of the rutile type, but the peak positions were different. In addition, a broad diffuse scattering in the 2θ range of 25−30° was observed in the patterns between 473 and 623 K (Figure 3). When heated at temperatures above 873 K, the structure was changed to the simple rutile type. The detailed change in peak positions is shown in Figure 4. With increasing temperatures, two peaks at 54.6 and 56.1° at 473 K were gradually shifted to the 121 and 220 reflections of rutile structure (Figure 1b). These facts suggest that the structural change from the ramsdellite to rutile structure is continuous and accompanied by lattice disordering. The structures obtained between 473 and 623 K can be explained as an intergrowth of the ramsdellite and rutile domains, as schematically shown in Figure 1c. A

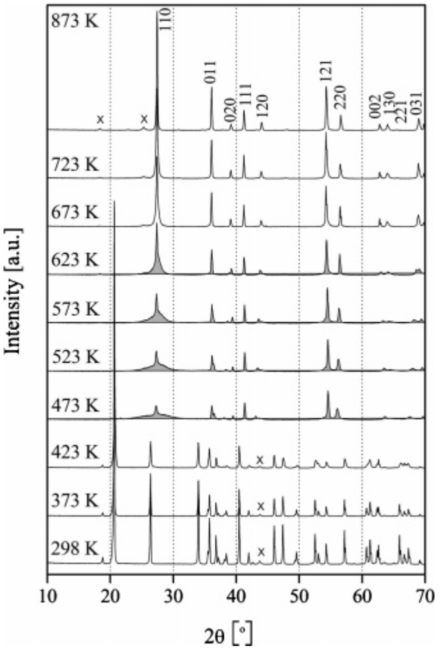

Figure 3. XRD patterns of the TiO_2(R) after calcination in air for 1 h at different temperatures. Patterns were measured at room temperature for samples that were heated and rapidly cooled. The indices for the rutile structure are shown in the pattern at 873 K. Unknown peaks are marked by ×.

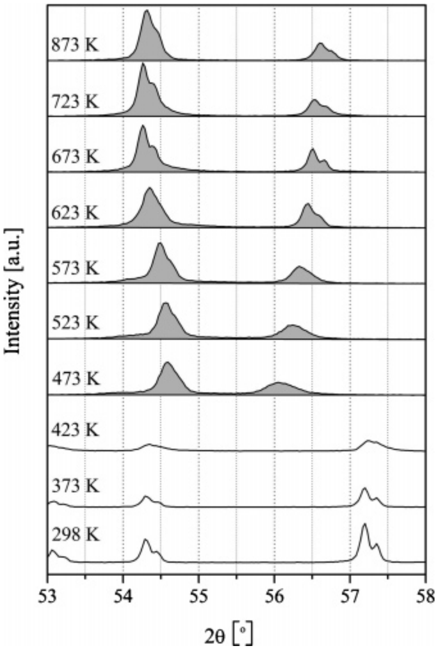

Figure 4. Parts of the XRD patterns of the TiO_2(R) after calcination in air for 1 h at different temperatures.

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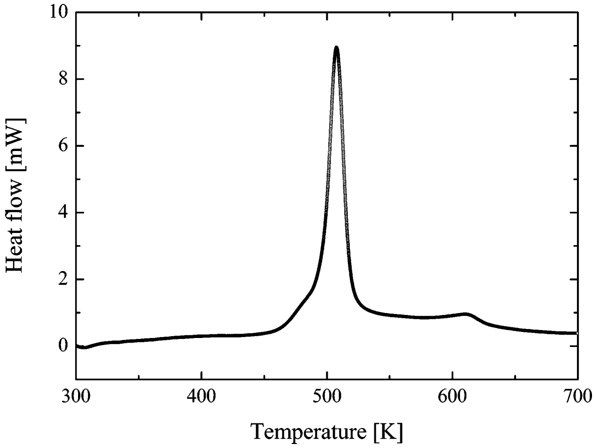

Figure 5. DSC curve of the $TiO_2(R)$ sample with a heating rate of 5 K/min.

similar domain structure is found in the γ-MnO_2, which is one of the well-known manganese dioxide compounds. The disordered model of the γ-MnO_2 structure was first proposed by de Wolff,[27] and the X-ray diffraction pattern was recently evaluated by changing the order parameter p and microtwinning.[28,29] In the present intergrowth structure of TiO_2 between 473 and 873 K, the rutile character increases as the heating temperature is increased, which is thought to be the origin of the peak shifts that occur upon heating (Figure 3).

In the γ-MnO_2 structure, the 110 peak of the ramsdellite structure gradually shifts to higher angles together with an increase in the order parameter p.[29] However, such a peak shift could not be observed in the present XRD patterns, as mentioned above. The intergrowth structure clarified with the order parameter for γ-MnO_2 may be observed between 423 and 473 K in the present TiO_2 sample. We are now trying to determine the precise crystal structure of the intergrowth phase.

Figure 5 shows the DSC curve of the heating process. A sharp exothermic peak can be seen at around 500 K. In addition, a weak and broad maximum at 610 K was also observed. The former exothermic reaction suggests the ramsdellite−intergrowth phase transition, and the latter corresponds to the intergrowth−rutile transition; these can be assigned on the basis of the XRD results. A similar strong exothermic peak was previously reported at 520 K in the DTA trace.[7] It should be noted that the baseline between 450 and 620 K in the present DSC curve drifted to the exothermic side. This may be associated with the above-mentioned continuous structural changes from the ramsdellite to the rutile structure.

The structural transformation to the brookite structure upon heating was previously reported by using single-crystal samples.[6] This transformation may be caused by the residual Li in the single-crystal samples. The lithium content in the present $TiO_2(R)$ polycrystalline samples is considerably smaller than the values reported for the single-crystal samples,[6] as mentioned above. In fact, the lattice parameters (a = 4.9022(14) Å, b = 9.4590(12) Å, c = 2.9585(14) Å) for the single-crystal sample[6] were slightly different from those (a = 4.8441(4) Å, b = 9.4353(8) Å, c = 2.9634(2) Å) of the present polycrystalline sample. Accordingly, in the present study, none of the brookite-type peaks could be observed in the XRD patterns (Figure 3).

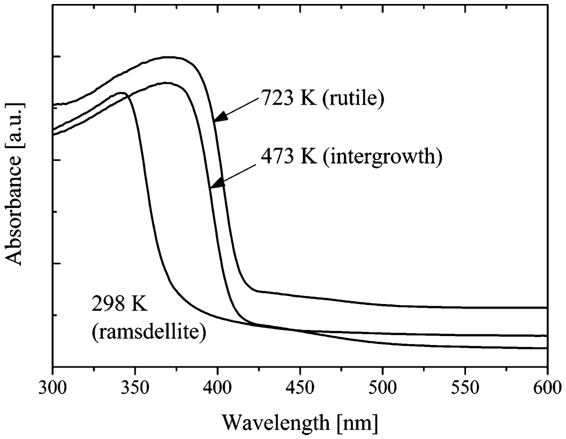

Figure 6. UV−vis absorption spectra for the as-prepared $TiO_2(R)$ at 298 K and after calcinations at 473 and 723 K.

Electronic Structures. The UV−visible absorption spectra for the as-prepared $TiO_2(R)$ at 298 K, after heating at 473 K, and at 723 K in the range from 300 to 600 nm are shown in Figure 6. Because of the small sample weights (15−50 mg) for these samples, accurate absorption spectra, unfortunately, could not be measured in the present experiments. However, the values of the absorption band edges were successfully estimated using these spectra. The derived band gaps are 3.34 eV for $TiO_2(R)$, 3.04 eV for the intergrowth phase, and 3.00 eV for rutile. The value for rutile agrees well with that of 3.02 eV reported in the literature. Interestingly, the band gap energy for $TiO_2(R)$ is the largest among those for the known TiO_2 compounds reported experimentally, e.g., 3.20 eV for anatase. Furthermore, the gap energy changed abruptly from 3.34 to 3.04 eV in the present intergrowth phases of the ramsdellite and rutile domains upon introduction of the rutile character.

The band structures for $TiO_2(R)$, rutile, and their intergrowth phases were calculated by the FLAPW method in the present study. Because the average crystal structure of the intergrowth phase could not be revealed, the calculations were performed using the structural parameters for the related compound $Li_{0.74}Ti_3O_6$,[26] which had a ramsdellite and rutile (1:1) domain structure, as shown in Figure 1c. $Li_{0.74}Ti_3O_6$ crystallizes in monoclinic symmetry and has a completely (1:1) ordered structure consisting of ramsdellite and rutile domains, whereas such an ordered structure and monoclinicity could not be observed in the present XRD patterns. However, we think that the present band-structure calculations of an ideal (1:1) ordered structure could be helpful in understanding the changes in electronic structure together with an increase in the rutile character.

Figure 7 compares the electron-density distributions of $TiO_2(R)$ obtained by the single-crystal MEM analysis and the FLAPW calculations. Both three-dimensional electron-density distributions were visualized with VENUS, the program developed by Dilanian and Izumi.[21] From the MEM analysis in Figure 7a, strong covalent-bonding features between the Ti and O atoms could be observed in $TiO_2(R)$.

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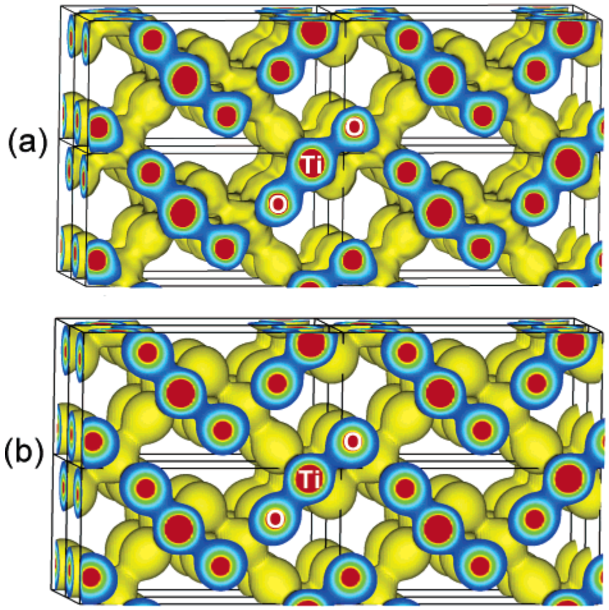

Figure 7. Three-dimensional electron-density distributions of TiO_2(R) obtained by (a) the single-crystal MEM analysis and (b) the FLAPW calculations. These figures were drawn with the VENUS program developed by Dilanian and Izumi. The isosurface density level colored with light yellow is equal to 0.5 Å^{-3}.

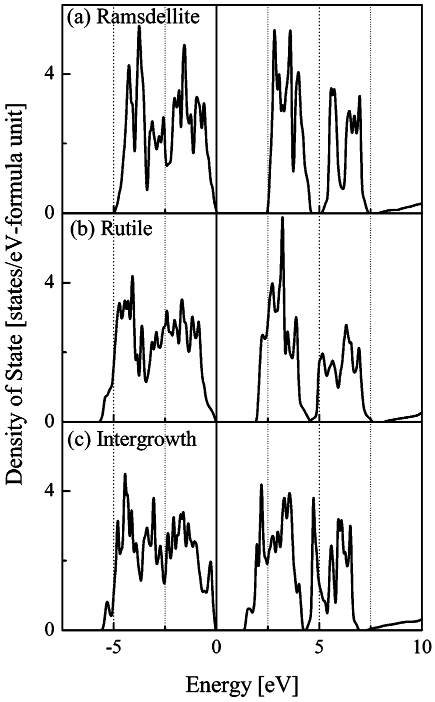

Figure 8. Calculated total densities of states of (a) TiO_2(R), (b) rutile, and (c) the hypothetical intergrowth structure with ramsdellite and rutile (1:1) domains.

Furthermore, the electron-density distributions obtained theoretically were in good agreement with the experimental observations.

Figure 8 shows the total densities of states for these titanium dioxides. The origin of energy is at the Fermi level. The density of states of rutile-type TiO_2 agrees well with those reported previously.[30−32] The valence band of TiO_2(R) in the range from −4.8 to 0.0 eV consists of the O-2p orbital hybridized with the Ti-3d orbital. The energy states ranging from 2.5 to 5.0 eV and 5.0 to 7.5 eV are attributed to the t_{2g} states and the e_g states of the Ti-3d orbital, respectively. A band gap of TiO_2(R) was estimated to be 2.4 eV, whereas the band gaps of the rutile and hypothetical intergrowth phases were calculated to be 1.8 and 1.3 eV, respectively. The value for TiO_2(R) is apparently larger than those of the rutile and intergrowth phases. This tendency of the calculated band gap values was very consistent with that of the above-mentioned experimental values, namely 3.34 eV for TiO_2(R), 3.00 eV for rutile, and 3.04 eV for intergrowth, although the experimental values were larger than the calculated ones. Because the present calculation is based on the density-functional theory in its local approximation, which is strictly valid only for the ground state, it is well-known that this method results in an underestimation of band gaps.[32] In fact, the reported band gaps of rutile, anatase, and brookite as obtained by a similar calculation method are 1.78, 2.04, and 2.20 eV, respectively.[32] From these results, the largest band gap of 3.34 eV for TiO_2(R) among the known TiO_2 compounds has been confirmed by the present calculations.

Conclusion

The present study investigated the crystal and electronic structural changes of TiO_2(R) upon heating. From the results of the UV−vis absorption measurements, it was revealed that the band gap energy (3.34 eV) for TiO_2(R) was the largest among those for the known TiO_2 compounds, and the gap energy changed abruptly to 3.04 eV in the intergrowth phase of the ramsdellite and rutile domains by means of the introduction of the rutile character. These experimental results were very consistent with those of the present FLAPW calculations. Accordingly, the band gap may be controlled from 3.34 to 3.00 eV by various heating treatments using the TiO_2(R) as a starting material.

On the other hand, low-temperature synthetic techniques called “chimie douce” have resulted in major developments in the solid-state chemistry of transition-metal oxides. Some metastable polymorphs of titanium dioxide were produced in previous studies.[3−7] In the present study, a novel intergrowth form of TiO_2 between rutile and ramsdellite-type structures, just like the γ-MnO_2 structure, has been found for the first time.

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