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# The preparation and electrical properties of $\text{TiO}_{2-x}\text{F}_x$

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The substitution of fluorine for oxygen in  $\text{TiO}_2$  was investigated by the reaction of  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{TiF}_3$  under conditions of 4–6.5 GPa and 700–1400 °C. The single phase of  $\text{TiO}_{2-x}\text{F}_x$  solid solution was obtained in the region of  $0 \leq x \leq 0.7$ . According to the x-ray diffraction data, the *a* and *c* axes of the rutile-type structure linearly increased with increasing fluorine content. The electrical resistivities of  $\text{TiO}_{2-x}\text{F}_x$  were in the range from 10 Ω cm for  $x = 0.3$  to 850 Ω cm for  $x = 0.7$  at 300 K and the relationship between  $\ln \rho$  and  $1000/T$  was linear. The activation energies were estimated to be from 0.17 eV at  $x = 0.3$  to 0.28 eV at  $x = 0.7$ . Also, the thermoelectric powers at room temperature changed from  $-250 \mu\text{V/K}$  to  $+50 \mu\text{V/K}$ . The mechanism of electric conduction was discussed on the basis of the extended band model of rutile.

## I. INTRODUCTION

Stoichiometric rutile,  $\text{TiO}_2$  is an insulator. However, when oxygen deficiencies are introduced, the rutile, so-called the reduced rutile, becomes a semiconductor due to the formation of  $\text{Ti}^{3+}$  ions. In order to control the  $\text{Ti}^{3+}$  ion content in the rutile, many studies on the substitution of foreign cations<sup>1</sup> have been carried out and developed widely in applications such as gas and humidity sensors, photocatalyzers, and so on.

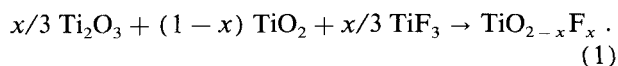
Anion substitution for oxygen in  $\text{TiO}_2$  can also contribute to the formation of  $\text{Ti}^{3+}$  ion in  $\text{Ti}^{4+}$  sites of the rutile structure. The substitution of fluorine can be expected to form  $\text{Ti}^{3+}$  ions without any loss of structural stability, since  $\text{O}^{2-}$  and  $\text{F}^-$  ions have similar ionic radii. In 1967, Chamberland and Sleight<sup>2</sup> reported that the transition metal oxyfluorides of  $\text{TiOF}$ ,  $\text{VOF}$ , and  $\text{FeOF}$  with the rutile-type structure were synthesized at high pressures of 6–6.5 GPa. Studies on various kinds of oxyfluorides were recently summarized in Ref. 3. Chamberland *et al.*<sup>4</sup> have studied the preparation and electrical properties of solid solutions between the transition metal dioxides and oxyfluorides. However, there are some difficulties in understanding the fact that the chemical compositions of solid solution continuously affect the structural and electrical properties.

In the present study, we have reinvestigated the solid solution  $\text{TiO}_{2-x}\text{F}_x$  prepared under high-pressure conditions by means of a belt-type apparatus. Structural and electrical behavior was examined as a function of F content in solid solution. Results on structural characteristics and the electrical conduction mechanism deduced from the band structure of rutile will be discussed.

## II. EXPERIMENTAL

### A. Synthesis

Analytical grade  $\text{Ti}_2\text{O}_3$ ,  $\text{TiO}_2$  (rutile), and  $\text{TiF}_3$  powders were used as the starting materials. The  $\text{TiO}_2$  (rutile) was obtained from the thermal transformation of  $\text{TiO}_2$  (anatase) at 1050 °C for 24 h in air. Mixtures were prepared in desired proportions by the following equation:



Raw materials were weighed and then formed into a paste by mixing with acetone for 10–15 min in an agate mortar (within a  $\text{N}_2$ -filled dry box).

In order to prevent oxidation of the sample during the high-pressure experiments, the mixtures were initially molded under the pressure of 200 MPa at room temperature and then sealed in a cylindrical platinum capsule. The capsule was arranged in the high-pressure cell assembly as shown in Fig. 1, which consisted of a NaCl sleeve as the pressure medium and a carbon tube as the heater.

Reaction conditions within the high-pressure apparatus were 4–6.5 GPa, pressure and temperature, 700 to 1400 °C for 0.5–4 h. Detailed information on the belt-type apparatus and its cell assembly are described elsewhere.<sup>5</sup> The sample was quenched within a few minutes to room temperature prior to the release of applied pressure.

Temperatures were measured by a Pt/Pt-13%Rh thermocouple; the thermocouple emf was not corrected for pressure. The cell pressure was calibrated through monitoring the electrical changes due to phase transformations of Bi (2.55 and 2.7 GPa) and Ba (5.5 GPa) at room temperature.

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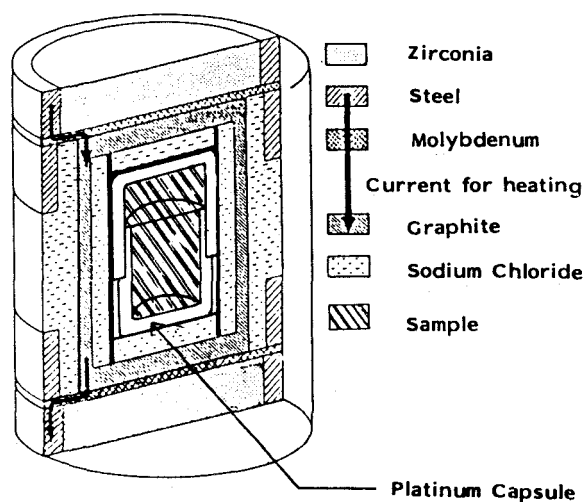


FIG. 1. Schematic drawing of the high-pressure cell assembly.

## B. Characterization

Samples were identified with a Rigaku x-ray powder diffractometer system (Ni-filtered  $\text{CuK}\alpha$  radiation). The integrated intensity and the position of reflections were measured at a scanning rate of  $0.25^\circ/\text{min}$ . Silicon powders were used as an internal standard. Accurate unit cell parameters of the  $\text{TiO}_{2-x}\text{F}_x$  solid solution were determined using a least-squares method.

The chemical compositions of solid solutions were precisely determined by the following procedure. After dissolving the sample into molten  $\text{Na}_2\text{CO}_3$  at  $1000^\circ\text{C}$ , mixtures were dissociated by concentrated  $\text{HNO}_3$  solution. A colorimetric analysis using diantipyrylmethane was used to determine Ti content in order to avoid errors due to the effect of F ion.<sup>6</sup> Fluorine ion contents were quantitatively measured by colorimetric analysis using a 2.5% alufuson reagent (Doujin Chemical Co.),<sup>7</sup> after removing Ti ions as titanium hydroxides through precipitation at  $\text{pH} = 10$ . (Results were Ti 45.41% and F 54.59%. Calculated values for  $\text{TiF}_3$  were Ti 45.66% and F 54.34%.)

Thermogravimetric analysis–differential thermal analysis (TGA–DTA) measurements were performed using a Rigaku TG8110/TAS100 thermal analyzer. The sample was heated in air or argon from room temperature to  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$ ; the temperature was monitored using a Pt/Pt-13%Rh thermocouple. Here  $\alpha\text{-Al}_2\text{O}_3$  was used as reference material. In addition, the bulk samples were also heated in vacuum at a temperature range of  $500\text{--}1000^\circ\text{C}$  for 2–4 h.

Density measurements were performed on bulk samples of  $\text{TiO}_{2-x}\text{F}_x$  using Archimedes' principle. Scanning electron microscopy (SEM) photographs were taken using a JEOL TSM-20 scanning microscope.

Electrical resistance was determined using the standard four-probe technique in the temperature range of  $200\text{--}370\text{ K}$ . Thermoelectromotive forces were measured using two d.c. digital multimeters or a multilogging meter (A&D AD-5311) by applying a temperature gradient along the length of a sample ranging from  $0.3$  to  $5^\circ\text{C}$ . Copper metal was used as an electrode. The values of thermoelectric power were obtained from the slopes of temperature difference versus thermoelectromotive force.

## III. RESULTS AND DISCUSSION

### A. The synthesis and characterization of the solid solution $\text{TiO}_{2-x}\text{F}_x$

Chamberland *et al.*<sup>4</sup> have reported that four solid solutions between  $\text{TiO}_2$  and  $\text{TiOF}$  exist under high  $P$ – $T$  conditions. In the present experiments, we confirmed this by preparing a solid solution of  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ , and  $\text{TiF}_3$  under the conditions of 4 GPa,  $1200^\circ\text{C}$  for 30 min. Samples were opaque and black in color. The powder x-ray diffraction data showed that single-phase samples were only obtained for compositions with  $x \leq 0.7$ . Also, it was confirmed by the chemical analysis that the upper limit of  $x$  in compositions of  $\text{TiO}_{2-x}\text{F}_x$  was near 0.7.

Assuming that no anion vacancies exist and  $\text{F}^-$  and  $\text{Ti}^{+3}$  concentrations are equal for keeping to the electroneutrality, the general formula of solid solutions may be written as  $\text{Ti}_1^{4+}\text{Ti}_x^{3+}\text{O}_{2-x}\text{F}_x^-$ .

According to the powder x-ray diffraction data, all samples of the present solid solutions were identified as the rutile-type structure, but with significant shifts in the position of peaks to higher  $d$  spacings. The ionic radii of  $\text{O}^{2-}$  and  $\text{F}^-$  ions reported by Ahrens *et al.*<sup>8</sup> are 0.140 and 0.133 nm, respectively. Owing to such a similarity of ionic radii, the substitution of  $\text{F}^-$  ions for  $\text{O}^{2-}$  ions in rutile could be well realized without any loss of the structural stability. Lattice parameter results are shown in Fig. 2 as a function of the fluorine content  $x$ .

The  $a$  and  $c$  lattice parameters vary linearly within experimental error and increase with increasing fluorine content. Such changes in lattice parameters are probably brought by both effects of the nature of  $\text{F}^-$  in terms of bonding and a slight difference of ionic radius between  $\text{Ti}^{4+}$  (0.068 nm) and  $\text{Ti}^{3+}$  (0.076 nm). The linearity supports the proposed solid solution relationship.

The  $c/a$  ratio increased with increasing fluorine content. This implied that the length of the  $c$  axis, which corresponded to the stacking of edge-sharing  $\text{TiO}_6$  octahedra, was elongated by the substitution of fluorine for oxygen. In rutile the  $\text{TiO}_6$  octahedron is slightly deformed; the Ti–O distances are 0.1944 nm and 0.1988 nm in the square plane and out of the square plane, respectively.<sup>9</sup> Since the square plane of the octahedron is

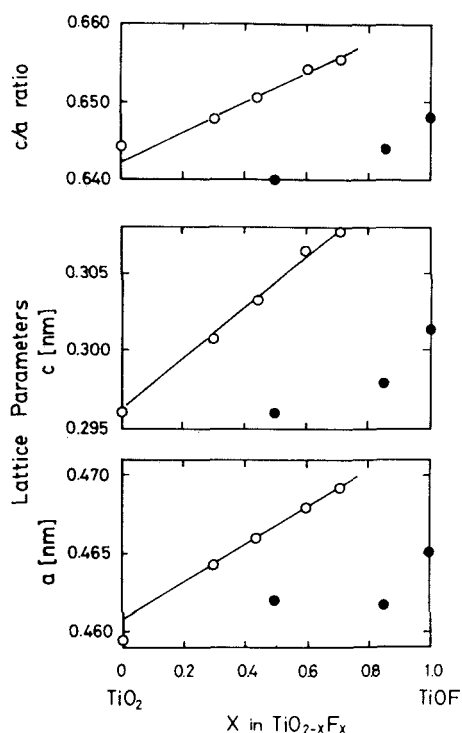


FIG. 2. The lattice parameters and  $c/a$  ratio of  $\text{TiO}_{2-x}\text{F}_x$ :  $x = 0-0.7$  (● is data by Chamberland *et al.*<sup>4</sup>).

parallel to the  $c$  axis, it can be estimated that the six  $\text{Ti}-X$  ( $X = \text{O}$  and  $\text{F}$ ) distances become gradually equal as the fluorine content is increased.

When the data reported by Chamberland *et al.*<sup>4</sup> is plotted in Fig. 2, it is found that there is no linear relationship between lattice parameters and fluorine content. Lattice parameters of  $\text{TiOF}$ ,  $a = 0.4651$  nm and

$c = 0.3013$  nm, are quite different from the values expected from the extrapolation of the present data.

Figure 3 shows the SEM photograph of the fracture surface of the  $\text{TiO}_{2-x}\text{F}_x$  ( $x = 0.45$ ) sample. The grain size was in the range of  $1-10 \mu\text{m}$ , and distributed at random. In addition, intergranular porosity was observed. The relative density was 70%–80% of theoretical as calculated from the lattice parameters. As seen in Fig. 3, the morphology of the small grains differed from the large grains.

Judging from the shape of the large grains, the encircled crystal in Fig. 3 shows a typical rutile morphology; the upper face of the pentagon is the (010) face and the lateral faces correspond to the (110) faces. It is considered that such crystals may grow locally as repeating either the evaporation–condensation process of the gas phase or the dissolution–precipitation process of the liquid phase under high-pressure conditions.

Figure 4 shows the TGA-DTA curves measured in air and in a flow of argon gas. The sample of  $\text{TiO}_{2-x}\text{F}_x$  ( $x = 0.7$ ) exothermically decomposed at  $680^\circ\text{C}$  in air or  $770-780^\circ\text{C}$  in a flow of argon gas. The weight loss was due to reoxidation and consequent dissociation of fluorine. Upon heating at  $500-600^\circ\text{C}$  in a vacuum, the solid solution of  $\text{TiO}_{2-x}\text{F}_x$  decomposed into  $\text{Ti}_2\text{O}_3$  and  $\text{TiO}_2$ .

## B. The electrical properties of $\text{TiO}_{2-x}\text{F}_x$

Figure 5 shows an Arrhenius plot of logarithm resistivity versus reciprocal temperature for  $\text{TiO}_{2-x}\text{F}_x$ . The resistivity at 300 K was in the range of  $10-850 \Omega \text{ cm}$  and increased fairly with increasing fluorine content.

The temperature dependence of the resistivity can be generally expressed as

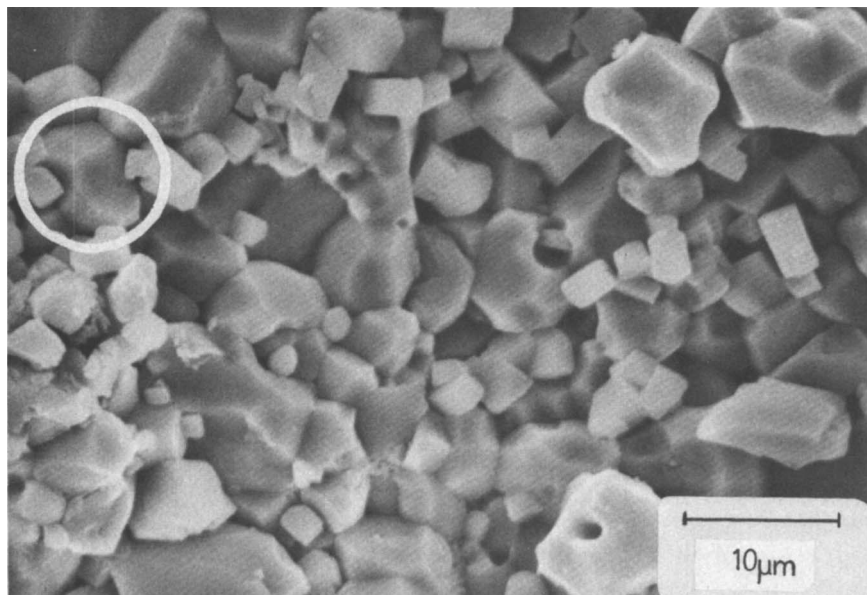


FIG. 3. A SEM photograph of the fracture surface of  $\text{TiO}_{2-x}\text{F}_x$  ( $x = 0.45$ ).

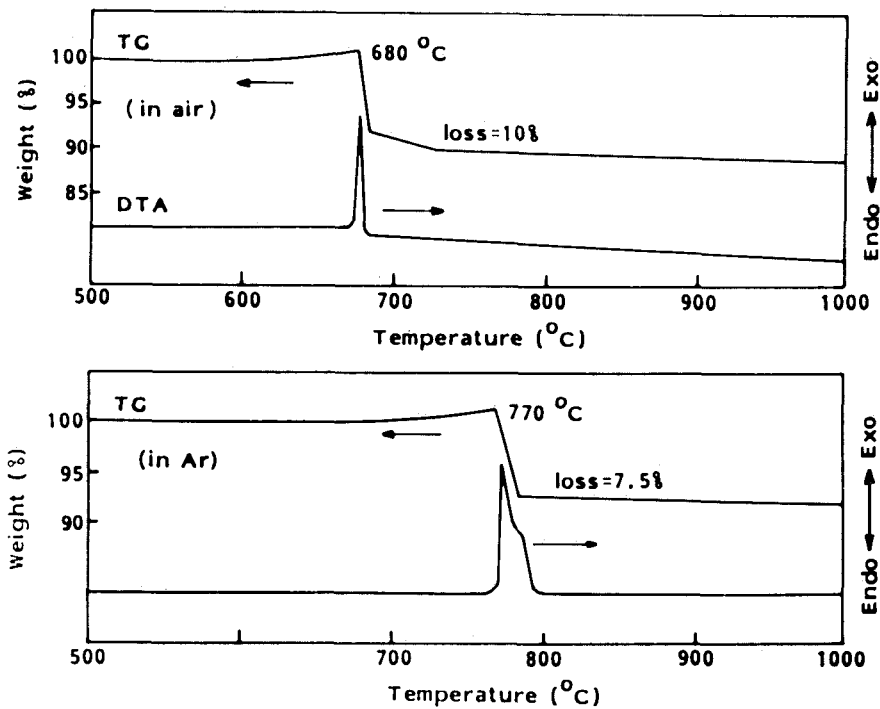


FIG. 4. The TGA-DTA curves of  $\text{TiO}_{2-x}\text{F}_x$  measured in air and in a flow of argon gas.

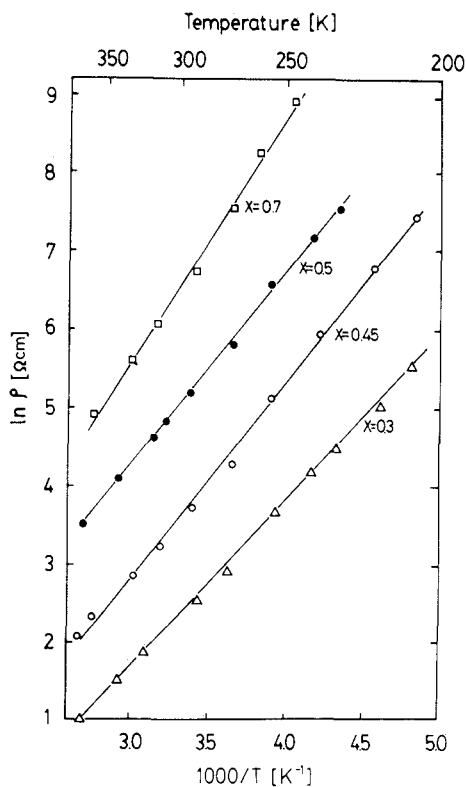


FIG. 5. The relationship between log resistivity,  $\ln \rho$  and the reciprocal temperature,  $1000/T$ , for  $\text{TiO}_{2-x}\text{F}_x$ :  $x = 0.30, 0.45, 0.50,$  and  $0.70$ .

$$\rho = \rho_0 T^b \exp(\Delta E/kT), \quad (2)$$

where  $\rho_0$  and  $b$  are constant,  $\Delta E$  is the apparent activation energy,  $k$  is the Boltzmann constant, and  $T$  is the absolute temperature.

As shown in Fig. 5, linear relationships between  $\ln \rho$  vs  $1000/T$  are experimentally found in all samples of solid solutions. This implies that the value of  $b$  in Eq. (2) corresponds to zero. Although the substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  should result in the formation of  $\text{Ti}^{3+}$  in the  $\text{Ti}^{4+}$  site of rutile, it is difficult to adopt the hopping mechanism proposed by Hurd<sup>10</sup> for elucidating the present results. Consequently, the conduction mechanism may be associated with the thermal excitation of electrons into the conduction band.

Figure 6 shows the activation energies determined from a least-squares fit of Eq. (2) as a function of F content. The activation energy linearly increased from 0.17 to 0.28 eV with fluorine content from 0.2 to 0.7. The present results are different from the data reported by Chamberland *et al.*,<sup>4</sup> who reported that  $\text{TiO}_{2-x}\text{F}_x$  had semiconducting electrical properties with room-temperature resistivities of 3–17  $\Omega$  cm and activation energies below 0.14 eV. When the present linear relationship between  $\Delta E$  and the fluorine contents is interpolated, the value of  $\Delta E$  is  $\approx 0.125$  eV at  $x = 0$ . This value is in good agreement with the value of 0.12–0.14 eV given in the reduced rutile reported by Breckeridge and Manghani.<sup>11</sup>

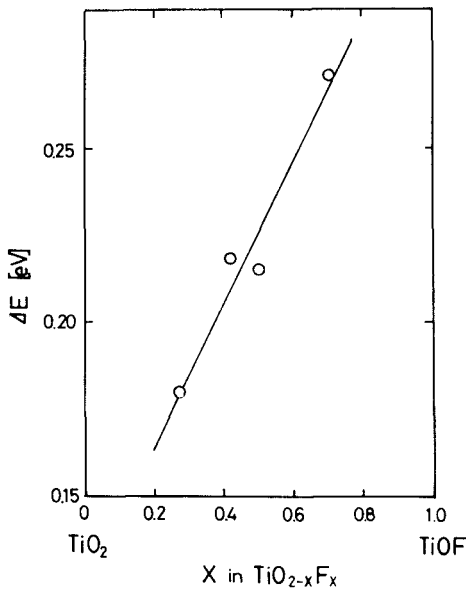


FIG. 6. Activation energy as a function of fluorine content.

The thermoelectric power coefficient measured at room temperature is shown in Fig. 7. The thermoelectric power coefficient decreased with increasing fluorine content and changed sign from negative to positive near  $x = 0.67$ , which corresponds to the substitution of two  $\text{F}^-$  ions for every six  $\text{O}^{2-}$  ions in the  $\text{TiO}_6$  octahedron.

It is believed that either the hydrogenlike donor sites or helium-atom-like donor sites associated with oxygen vacancies contributes to the electric conduction of reduced rutile. As  $\text{F}^-$  is a donor dopant on the oxygen sublattice, it is expected that increasing the  $\text{F}^-$  content would increase the electron concentration and hence

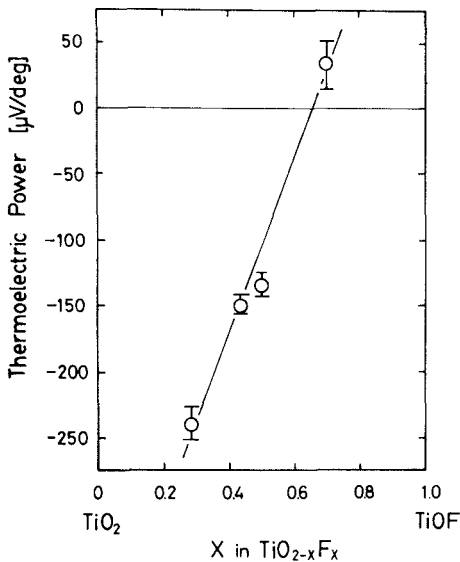


FIG. 7. Thermoelectric power coefficient of  $\text{TiO}_{2-x}\text{F}_x$ :  $x = 0.30, 0.45, 0.50,$  and  $0.70$ .

electrical conductivity. However, it is slightly difficult to introduce this model directly into the present results. Even if the reason that the electrical conductivity decreases with increasing F content could be found, it is still ambiguous whether or not such a model can be applicable at the large concentration of  $\text{F}^-$  content in  $\text{TiO}_2$ .

Goodenough *et al.*<sup>12</sup> proposed the band structure shown in Fig. 8 for reduced rutile. This schematic figure was constructed using the orthogonal axis system in Fig. 9.

Assuming that the conduction may herein be interpreted using this model, the thermal excitation of the  $d$  electrons of  $\text{Ti}^{3+}$  in the nonbonding level  $a_{1g}$  to the  $\pi^*$  band may incidentally be responsible for the conductivities of the solid solution,  $\text{TiO}_{2-x}\text{F}_x$ . Little information on variations of electron mobility and concentration with temperature could be obtained.

Increasing the  $\text{F}^-$  content in rutile increases the extent of ionic bonding, in accordance with the difference in electronegativity between  $\text{Ti-O}$  and  $\text{Ti-F}$ . Since the atomic periodicity is altered, it is expected that the extent of an energy gap between  $\pi^*$  and  $a_{1g}$  would occur. The present experimental data seems to reflect qualitatively on this tendency, in which the conductivity decreased and activation energy increased with increasing  $\text{F}^-$  content.

On the other hand, the substantial reason that the hold conduction dominates at  $x = 0.67$  is not understood yet, but the mechanism appears to have some relation with the tolerance to the substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  in rutile.

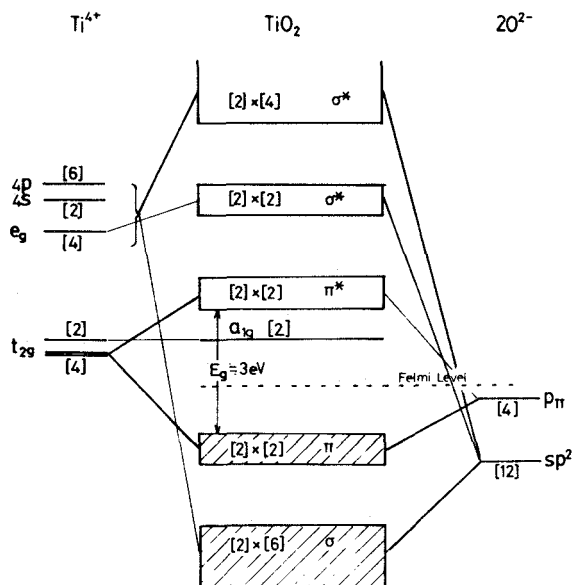


FIG. 8. Schematic energy diagram for rutile,  $\text{TiO}_2$ , proposed by Goodenough.<sup>12</sup>

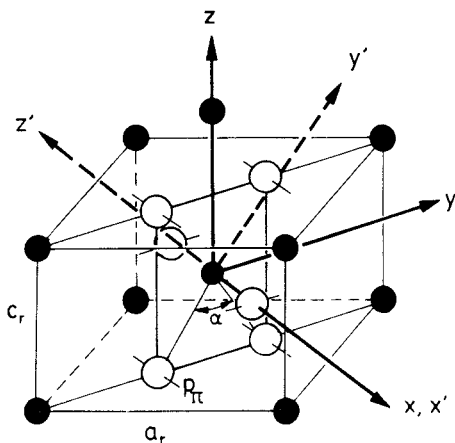


FIG. 9. The atomic arrangement of rutile. Open circles are  $\text{O}^{2-}$  ions shown with the orientation of  $p$  orbitals. Closed circles are  $\text{Ti}^{4+}$  ions.

#### IV. CONCLUSIONS

In summary:

(1) The solid solution  $\text{TiO}_{2-x}\text{O}_x$ , with a rutile structure, was synthesized in the compositional range of  $0 \leq x \leq 0.7$  under the condition of 4 GPa and 1200 °C. From the results of chemical analysis, the chemical formula could be represented as  $\text{Ti}_{1-x}^{4+}\text{Ti}_x^{3+}\text{O}_{2-x}\text{F}_x^-$  by assuming electroneutrality.

(2) The  $a$  and  $c$  lattice parameters and  $c/a$  ratio increased with increasing fluorine content up to  $x = 0.7$ . This was due both to differences of bonding nature between Ti–O and Ti–F and ionic radii between  $\text{Ti}^{3+}$  and  $\text{Ti}^{4+}$ .

(3) The electrical resistivity and thermoelectric power coefficient were systematically measured as a

function of fluorine content. The solid solution showed semiconducting characteristics with  $\rho = 10\text{--}850 \text{ } \Omega \text{ cm}$  at room temperature and a  $\Delta E$  of 0.18–0.27 eV. The conduction mechanism seemed to be understood by modifying the model proposed by Goodenough.

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#### REFERENCES

- <sup>1</sup>G. H. Johnson, *J. Am. Chem. Soc.* **36**, 97 (1953).
- <sup>2</sup>B. L. Chamberland and A. W. Sleight, *Solid State Commun.* **5**, 765 (1967).
- <sup>3</sup>J. H. Holloway and D. Laycock *Advances in Inorganic Chemistry and Radiochemistry*, edited by H. J. Emeleus and A. G. Sharpe (Academic, London, 1984), Vol. 28, p. 73.
- <sup>4</sup>B. L. Chamberland, A. S. Sleight, and W. H. Cloud, *J. Solid State Chem.* **2**, 49 (1970).
- <sup>5</sup>O. Fukunaga, S. Yamaoka, T. Endoh, M. Akaishi, and H. Kanda, *High Pressure Science and Technology*, edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. 1, p. 846.
- <sup>6</sup>H. E. Merwin, *Am. J. Sci.* **28**, 119 (1969).
- <sup>7</sup>H. Hashitani, H. Yoshida, and H. Muto, *Jpn. Analyst* **16**, 44 (1967).
- <sup>8</sup>L. H. Ahrens, *Geochim. Cosmochim. Acta* **2**, 155 (1952).
- <sup>9</sup>F. A. Grant, *Rev. Mod. Phys.* **31**, 646 (1959).
- <sup>10</sup>C. M. Hurd, *Philos. Mag. B* **50**, L29 (1984).
- <sup>11</sup>R. G. Breckeridge and M. H. Manghnani, *Geophys. Res. Lett.* **5**, 491 (1953).
- <sup>12</sup>J. B. Goodenough, *Bull. Soc. Chim. Fr.* **1965**, 1200.