JOURNAL OF SOLID STATE CHEMISTRY 38, 281–287 (1981)

Self-Compensation in Niobium-Doped TiO_2

N. G. EROR

Oregon Graduate Center, Beaverton, Oregon 97005

Received February 26, 1979; in revised form May 26, 1980

Gravimetric measurements on pure and niobium-doped TiO_2 have shown that the reversible change of oxygen content, between specified states of oxidation and reduction, is proportional to the dopant concentration. These measurements indicate that the donor-dopants are electronically compensated by additional oxygen uptake in the oxidized state. The range of this reversible change in oxygen stoichiometry is up to more than an order of magnitude larger than the oxygen nonstoichiometry of the undoped oxides. Self-compensation has been measured in TiO_2 with donor-dopant concentrations of up to 8 at% Nb^{+5} over the oxygen partial pressure range 10^0–10^{-15} atm. For the case of Nb^{+5}-doped TiO_2 the monoclinic phase "$TiNb_2O_7$" was found to exsolve under oxidizing conditions for Nb^{+5} concentrations >8 at%. The exsolved phase transformed into niobium-doped rutile under reducing conditions. The gravimetric measurements for Nb^{+5} concentrations <8 at% can be explained by the creation of metal-deficit point defects (self-compensation) or a model involving a shear structure.

Introduction

Rutile is an oxygen-deficit, semiconducting transition metal oxide at room temperature when equilibrated in an atmosphere of low oxygen activity and is nonconducting at room temperature when equilibrated in an atmosphere of high oxygen activity. There still seems to be some question as to what point defect model is appropriate for the description of nonstoichiometric disorder in the rutile form of TiO_2—oxygen vacancies or titanium interstitials (*1–4*). Independent of the nature of the atomic disorder, the electrical conductivity is due to electrons resulting from the electronic disorder introduced by the oxygen nonstoichiometry. These electrons are of the odd order type of defect which give rise to an electron spin resonance that is attributed to Ti^{+3} ions in semiconducting TiO_2 (*5, 6*).

For larger deviations from stoichiometry ($n < 10$ for Ti_nO_{2n-1}) the random point defect model is no longer appropriate for describing nonstoichiometric disorder in rutile. Magneli and co-workers (*7*) have established a series of "shear-type" structures or Magneli phases and at least seven stable titanium oxides with $4 \leq n \leq 10$ for Ti_nO_{2n-1} have been determined from X-ray diffraction data. The structures are made up of layers of rutile structure with a width of n TiO_6 octahedra. The successive layers are offset such that the first Ti in the new layer is in an interstitial position relative to the last Ti of the preceding layer. The TiO_6 octahedra share faces across this discontinuity or crystallographic shear plane and thereby reduce the O : Ti ratio as required by the oxygen deficiency. All normally occupied lattice sites are occupied in the basic rutile structural unit and the lattice defect is the crystallographic shear plane that is only one atomic plane wide and also free of point

0022-4596/81/090281-07$02.00/0

defects. Additional phases with $n > 10$ have been established (*8, 9*) through electron microscopy/diffraction measurements and shear-type structures for $n \sim 1000$ ($TiO_{1.999}$) have been reported (*10, 11*).

It is reported (*12*) that for the acceptor-dopant, Cr^{+3}, the isomorphous chromium-substituted series, $(Ti_{n-2}Cr_2)O_{2n-1}$, shows a continuous transition between ordered $Ti_7Cr_2O_{17}$ ($BO_{1.89}$) and $Ti_{18}Cr_2O_{34}$ ($BO_{1.95}$) which is disordered and approaches the rutile-type structure. For chromium concentrations <5 mole%, $Ti_{38}Cr_2O_{79}$ ($BO_{1.975}$) rutile structure defect solid solutions without shear planes are reported (*13*). In this case, the anion deficiency is accommodated by point defects or small defect clusters. These rutile solid solutions are similar to undoped TiO_2 in that they are easily reduced with the introduction of (132) shear planes. Others (*14*) report similar results for <8 mole% Cr additions ($BO_{1.960}$) for samples annealed at 1300°C but find evidence for (132) crystallographic shear planes when the samples were annealed for 40 days at 1000°C. If, however, the acceptor-dopants Fe^{+3} and Ga^{+3} are added to TiO_2 the anion deficiency ($MO_{1.99}$) is accommodated by a new type of $\langle 210 \rangle$ rutile planar boundary (*15*).

The disorder created by Nb^{+5} as a donor-dopant in TiO_2 should lend itself to description by Verwey's controlled valency model (*16*). By this model there would be compensation of the Nb^{+5} on Ti^{+4} sites by the creation of equal numbers of Ti^{+3} ions. The latter would then give rise to an increased electrical conductivity as has been observed for oxygen-deficient, undoped rutile. In this case, however, the donor-dopant would dominate the positive side of the electroneutrality equation and consequently the negative electronic defect concentration would be independent of equilibrium oxygen activity. This compensation mechanism has also been referred to as controlled electronic imperfection (*17*).

Similarly, the donor-dopant may be compensated by the formation of charged point defects that would also be independent of equilibrium oxygen activity. This compensation mechanism has been referred to as controlled atomic imperfection (*17*), self-compensation (*18–21*), and stoichiometric compensation (*22*).

Roth and Coughanour (*23*) reported a room temperature solid solubility limit of approximately 18 at% niobium in TiO_2. It should be noted that their Nb additions are based on Nb_2O_5 rather than $NbO_{2.5}$ as reported here. Itakura *et al.* (*24*) report a two-phase mixture for >4 mole% Nb_2O_5 in TiO_2 but do not give any details as to what the second phase might be. If the phase diagram of Roth and Coughanour is correct then the second phase should be $TiNb_2O_7$.

Rutile, then, seems like a promising choice in which to look for a transition from a random point defect model of nonstoichiometry to an ordered extended-defect model with increasing concentrations of disorder that would be introduced by additional oxygen in compensating donor-dopant impurities (*22*). For the case of donor-dopants and oxygen excess in rutile the accommodation of extra oxygen could be such that some oxygens are doubly shared instead of triply shared as in the case of normal rutile. This could be accomplished by an increase of corner sharing compared with edge sharing of the TiO_6 octahedra relative to that of the normal rutile structure. The structure of the shear planes is based on the PdF_3 structure with corner sharing of the octahedra (*25*). It has been reported that WO_3 is incorporated into the Nb_2O_5 structure in this manner (*26*). It is not absolutely necessary to invoke the creation of shear-type structures to explain the uptake of additional oxygen, however, since metal deficit disorder could be accommodated in the open rutile-type structure.

Experimental

The Nb^{+5}-donor-doped TiO_2 was prepared by adding the dopant in solution form to a tetraisopropyl-titanium citrate complex solution. There was no evidence of any precipitation in the solutions as they were evaporated to a rigid transparent polymeric glass. The samples were then calcined at 700–900°C and pressed into disks at 50,000 psi and sintered in air at 1450–1550°C. For the gravimetric measurements the samples were equilibrated for sufficient times to establish a constant weight in oxygen or CO/CO_2 mixtures at 1060°C for the oxidized and reduced states, respectively, and cooled to room temperature in less than 5 min in the ambient gas. The CO/CO_2 mixture was adjusted to provide oxygen partial pressures of 10^{-15} atm at the equilibration temperature. This oxygen partial pressure is nearly four orders of magnitude higher in partial pressure than the Ti_3O_5/TiO_2 phase boundary (*27*) and over an order of magnitude higher than that for which Magneli-type phases have been reported (*28*). The samples do see a lower oxygen partial pressure than 10^{-15} atm since they are cooled in the specific ambient CO/CO_2 ratio. As can be seen from Fig. 1 the relative oxygen partial pressures that result from a given CO/CO_2 ratio increase with respect to the Ti_3O_5/TiO_2 boundary as the temperature decreases. All gravimetric measurements were made at room temperature on at least duplicate samples using a Cahn RG microbalance.

Results and Discussion

As can be seen in Fig. 2 there is an excellent agreement between the calculated amount of oxygen necessary to compensate the Nb^{+5} dopant and the measured *reversible* oxygen weight change between the oxidized state at 1 atm oxygen and the reduced state established in CO/CO_2 mixtures. These data represent the results for Nb^{+5} additions from 0.5 to 16 at%. Except for the 0.5 at% Nb^{+5}-doped sample, which is near the crossover point between the maximum oxygen nonstoichiometry of undoped TiO_2 and that necessary to compen-

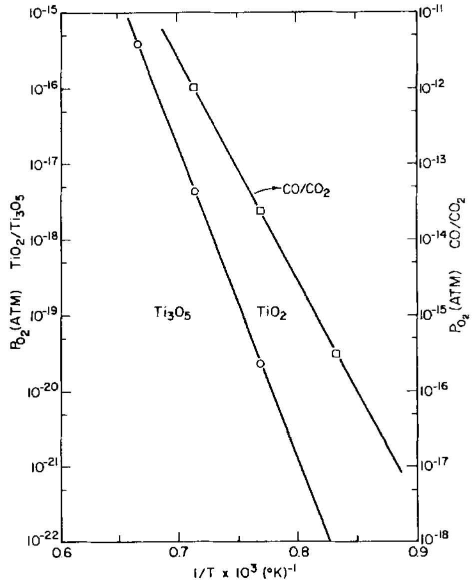

FIG. 1. Equilibrium oxygen partial pressures for the Ti_3O_5/TiO_2 phase boundary and for an equimolar ratio of CO/CO_2 as a function of temperature.

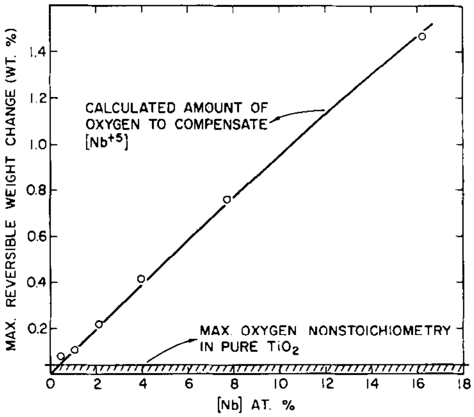

FIG. 2. Maximum *reversible* weight change observed for TiO_2, between 10^{-15} and 10^0 atm oxygen partial pressure, as a function of Nb^{+5} dopant concentration.

sate the added dopant, there is a correlation of 95% or better between the measured amounts of reversible oxygen weight change and that calculated based on the assumption that each added oxygen ion will neutralize two Nb^{+5} dopant ions.

Undoped TiO_2 samples were used as standards during the gravimetric measurements to be sure that all oxidizing and reducing conditions were in the single-phase field of TiO_2 as described above. In the oxidized state the undoped TiO_2 was white in color and insulating while all of the doped samples were gray and somewhat conducting—approximately 10^{-5} (ohm-cm)$^{-1}$. This observation could be due to the presence of a small amount of controlled valency compensation in all of the doped samples since only a very small (<0.1 at%) concentration of Ti^{+3} is necessary for substantial semiconduction at room temperature.

X-Ray diffraction measurements indicated the presence of a very small amount of second phase for the 8 at% Nb^{+5}-doped TiO_2 that had been equilibrated in oxygen at 1060°C. This observation is in agreement with that reported by Itakura *et al.* (*24*). This second phase was not observed in the as fired or reduced samples. We were able to identify the second phase to be monoclinic $TiNb_2O_7$ (*29*), which is in agreement with the phase diagram of Roth and Coughanour (*23*). This monoclinic second phase was not found when the same samples were equilibrated in a reducing atmosphere of 10^{-15} atm oxygen partial pressure. For these reduced samples there were satellite peaks on the low-angle side of the strong TiO_2 tetragonal X-ray diffraction lines. This indicated that the niobium contained in the $TiNb_2O_7$ phase is soluble in the tetragonal rutile structure under the conditions of the reducing atmosphere. This new rutile phase is richer in Nb than the parent Nb-doped rutile phase and has slightly larger lattice parameters which results in the X-ray diffraction peaks being shifted to lower angles than those of the parent phase. For the case of 16 at% Nb^{+5}-doped TiO_2 there is more than twice as much of the second phase than for the 8 at% Nb^{+5} dopant concentration. These observations indicate that there is some solid solution of Nb^{+5} in TiO_2 under oxidizing conditions and that the solid solubility limit of niobium in TiO_2 is strongly dependent upon the equilibrium oxygen partial pressure. For the samples containing 16 at% niobium the $TiNb_2O_7$ second phase was observable in the form of needles. The morphology of the needles was still visible in the samples equilibrated at 10^{-15} atm oxygen partial pressure but there was no longer any evidence of the presence of the monoclinic $TiNb_2O_7$. As with the case of the reduced 8 at% niobium-doped samples, there were satellite peaks on the low-angle side of the X-ray diffraction lines for the tetragonal rutile structures. From the intensity of the $TiNb_2O_7$ diffraction peaks, it is estimated the solid solubility of niobium in TiO_2 to be ~6 at% at 1060°C in oxygen.

The single compound, $TiNb_2O_7$, was prepared and it was found to have the morphology of the observed needles described above. Using the structure data of Wadsley the calculated X-ray diffraction pattern was found to agree with our measured powder pattern data. When the $TiNb_2O_7$ samples were equilibrated with an oxygen partial pressure of 10^{-15} atm the structure tended to the orthorhombic modification proposed by Wadsley (*30*). Accompanying this change in structure is a large change in oxygen stoichiometry. The measured reversible change in oxygen stoichiometry is equivalent to having 58 ± 1% of the niobium in $TiNb_2O_7$ as Nb^{+4} in the reduced state compared with all of the niobium as Nb^{+5} in the fully oxidized state at 1 atm oxygen pressure—there is, of course, probably a mixture of both Ti^{+3} and Nb^{+4} in the reduced state. Since the Ti/Nb ratio was fixed at 0.5, the formula for the single-phase composition prepared under a reducing atmosphere of 10^{-15} atm oxygen partial pressure can be written as $TiNb_2O_{6.42\pm.01}$. Wadsley (*29*) stated that the unit cell contains 12 formula weights so that the composition of the unit cell of the orthorhombic structure would be $Ti_{12}Nb_{24}O_{77.0}$, compared with $Ti_{12}Nb_{24}O_{84}$ for the monoclinic unit cell.

It may be concluded that either the monoclinic structure attributed to $TiNb_2O_7$ is stable over a range of composition deficient in Nb, or there is significant mobility of Ti and/or Nb during the oxidation–reduction equilibrations. This conclusion is based on the observation that the second phase identified as "$TiNb_2O_7$" that is exsolved under oxidizing conditions in Nb^{+5}-doped TiO_2 forms the niobium-doped rutile structure under reducing conditions, whereas samples of pure $TiNb_2O_7$ do not form the tetragonal rutile structure when equilibrated with an atmosphere of the same low oxygen activity.

It should also be noted that $TiNb_2O_7$ is white, insulating, and very friable, whereas the $TiNb_2O_{6.42}$ is black, conducting, and very resistant to fracture. All of these properties are reversible although the time for thermodynamic equilibrium to be established under a reducing atmosphere is an order of magnitude longer than that necessary to achieve the oxidized state.

All of the gravimetric measurements observed for the Nb^{+5}-doped TiO_2 could be explained by exolution of the "$TiNb_2O_7$" phase under oxidizing conditions and the formation of $Ti^{+4}Nb_x^{+4}O_{2(1+x)}$ (or a combination of Nb^{+5} and Ti^{+3}) under reducing conditions. This model requires that there be a negligible amount of solid solution of Nb^{+5} in TiO_2 in the oxidized state. On the other hand, since in the fully oxidized state there is considerably more than twice as much $TiNb_2O_7$ present in the 16 at% Nb^{+5}-doped samples as in those containing 8 at% Nb^{+5}, the solubility limit of Nb^{+5} in TiO_2 should be between 4 and 8 at% at 1060°C for an oxygen pressure of 1 atm. The gravimetric observation for the range of niobium-dopant concentration where there is always solid solution (independent of oxygen partial pressure) would be by the takeup of extra oxygen into the rutile structure. The mechanism by which the accommodation takes place could be by metal deficit point defects (self-compensation) or the creation of a shear-type structure. A second phase, $TiNb_2O_7$, is exsolved before the effect of the extra oxygen concentration is sufficient to be detected as a significant change in lattice parameter for metal deficit disorder, or the extra X-ray lines of a shear-type structure. For the metal deficit rutile structure model the correlation of the reversible weight change measurements with Nb^{+5} dopant concentration is extended to higher Nb^{+5} concentrations by the total dissolution and exolution of the "$TiNb_2O_7$" phase as a function of oxygen partial pressure.

For the case of the random point defect model for nonstoichiometry the consideration of a Kröger–Vink diagram for the general case of a binary oxide MO with a donor-dopant is helpful. We will for the purpose of illustration consider Schottky–Wagner disorder to describe the nonstoi-

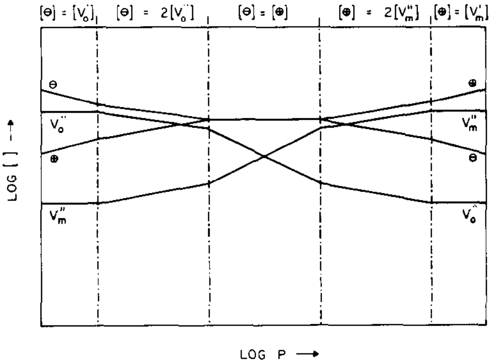

FIG. 3. Log of the defect concentration for the oxide MO with Schottky–Wagner disorder as a function of log Kp_{ox} = log p.

chiometry and limit the Kröger–Vink diagram to the fully ionized atomic defects, V_M'' and $V_O^{\cdot\cdot}$, and the electrons and electron holes, $[\Theta]$ and $\oplus$. Figure 3 illustrates this particular model and if we consider the left side of the figure (n-type region) we recognize the familiar $[\Theta] \propto p_{O_2}{}^{-1/4}$ where $[\Theta] = [V_O^{\cdot}]$, and $[\Theta] \propto p_{O_2}{}^{-1/6}$, where $[\Theta] = 2[V_O^{\cdot\cdot}]$ regions of the electrical neutrality condition. In Fig. 4 we have added a donor-dopant, I_M, that is always fully ionized, $I_M^{\cdot}$, to the binary oxide MO described in Fig. 3. Note that for sufficient departures from stoichiometry it may be possible for the electrical conductivity to be controlled by $[\Theta] = [V_O^{\cdot\cdot}]$ and thereby mask the effect of the donor-dopant. The two major points to be derived from Fig. 4 are that the electronic n to p transition has been shifted to higher oxygen partial pressures while the metal excess to metal deficit transition has been shifted to lower oxygen partial pressures. This means that there may be significant regions of oxygen partial pressure where the dominant atomic disorder is metal deficit, while the electrical conductivity is n type and that with the shift of the transition of metal excess to metal-deficit disorder to lower oxygen partial pressures there may be significantly larger concentrations of atomic disorder than for the undoped oxide ($[V_M''] \propto p_{O_2}{}^{-1/2}$ for the region $[\Theta] = [I_M^{\cdot}]$). The concentration of $V_M^{\cdot\cdot}$ will increase with increasing oxygen partial pressure in this region until $[V_M''] \sim \frac{1}{2}[I_M']$. The possibility of self-compensation is, therefore, built into the random defect model of nonstoichiometry if the oxide is stable over a sufficiently wide range of oxygen partial pressure.

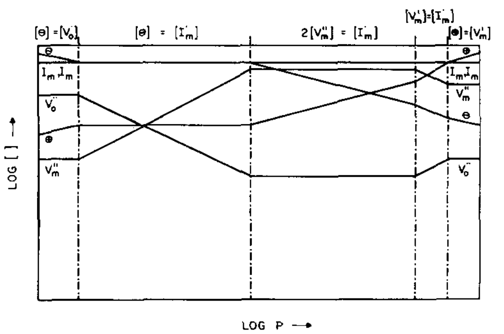

FIG. 4. Log of the defect concentration for the oxide MO with a fully oxidized donor-dopant, I_M, and Schottky–Wagner disorder as a function of $\log Kp_{ox} = \log p$.

S. Andersson (*25*) has worked out the structure that would be compatible with crystallographic shear in rutile with excess oxygen but none has been reported for donor-doped TiO_2.

References

1. P. KOFSTAD, *J. Less-Common Metals* **13,** 635 (1967).
2. L. N. SHEN *et al.*, *Phys. Rev. B* **10,** 1823 (1974).
3. C. PICARD AND P. GERDANIAN, *J. Solid State Chem.* **14,** 66 (1975).
4. P. H. ODIER *et al.*, *J. Solid State Chem.* **12,** 324 (1975).
5. H. P. R. FREDERIKSE, *J. Appl. Phys.* **32,** 2211 (1961).
6. P. F. CHESTER, *J. Appl. Phys.* **32,** 2233 (1961).
7. S. ANDERSSON *et al. Acta Chem. Scand.* **11,** 1641 (1957).
8. B. G. HYDE AND L. A. BURSILL, *in* "The Chemistry of Extended Defects in Non-Metallic Solids" (L. Eyring and M. O'Keefe, Eds.), pp. 347–378, North-Holland, Amsterdam (1970).
9. J. S. ANDERSON AND R. J. D. TILLEY, *J. Solid State Chem.* **2,** 472 (1970).
10. L. A. BURSILL AND B. G. HYDE, *Philos. Mag.* **23,** 3 (1970).
11. J. S. ANDERSON, Nat. Bur. Stand. Publication 364, pp. 295–317, U.S. Govt. Printing Office, Washington, D.C. (1972).
12. S. ANDERSSON, A. SUNDHOLM, AND A. MAGNELI, *Acta Chem. Scand.* **13,** 989 (1959).
13. R. M. GIBB AND J. S. ANDERSON, *J. Solid State Chem.* **4,** 379 (1972).
14. D. K. PHILP AND L. A. BURSILL, *J. Solid State Chem.* **10,** 357 (1974).
15. R. M. GIBB AND J. S. ANDERSON, *J. Solid State Chem.* **5,** 212 (1972).
16. E. J. W. VERWEY *et al.*, *Philips Res. Rept.* **5,** 173 (1950).
17. F. A. KRÖGER AND H. J. VINK, *in* "Solid State Physics" (F. Seitz and D. Turnbull, Eds.), Vol. III, pp. 307–435, Academic Press, New York (1956).

18. R. F. BREBRICK, "Progress in Solid State Chemistry," Vol. III, Pergamon, Oxford/New York (1966).
19. G. MANDEL, *Phys. Rev. A* **134,** 1073 (1964).
20. G. MANDEL, *Phys. Rev. A* **136,** 826 (1964).
21. F. A. KRÖGER, "Physical Chemistry: An Advanced Treatise" (H. Eyring, Ed.), Vol. X, pp. 229–259, Academic Press, New York (1970).
22. N. G. EROR AND D. M. SMYTH, "The Chemistry of Extended Defects in Non-Metallic Solids" (L. Eyring and M. O'Keefe, Eds.), pp. 62–74, North-Holland, Amsterdam (1970).
23. R. S. ROTH AND L. W. COUGHANOUR, *J. Res. Nat. Bur. Stand.* **55,** 209 (1955).
24. M. ITAKURA *et al.*, *Japan J. Appl. Phys.* **6,** 311 (1967).
25. S. ANDERSSON AND J. GALY, *J. Solid State Chem.* **1,** 576 (1970).
26. R. S. ROTH AND A. D. WADSLEY, *Acta Crystallogr.* **19,** 26, 32, 38, 42 (1965).
27. J. P. COUGHLIN, Nat. Bur. Stand Bull. 542, U.S. Govt. Printing Office, Washington, D.C. (1954).
28. V. R. PORTER, Ph.D. Thesis, The Pennsylvania State University (1965).
29. A. D. WADSLEY, *Acta Crystallogr.* **14,** 660 (1961).
30. A. D. WADSLEY, *Acta Crystallogr.* **14,** 664 (1961).