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Self-compensation in tantalum-doped TiO_2

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The reversible change of oxygen content observed by gravimetric measurements on tantalum-doped rutile (TiO_2) between specified states of oxidation and reduction is proportional to the dopant concentration. These measurements indicate that donor-dopants are ionically 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 non-stoichiometry of the undoped TiO_2. Self-compensation has been measured in TiO_2 with up to 10 at% Ta^{+5} and a single-phase region from $Ta^{+5}_{0.1}Ti^{+3}_{0.1}Ti^{+4}_{0.8}O_2$ to $Ta^{+5}_{0.1}Ti^{+4}_{0.9}O_{2.05}$ has been confirmed. The gravimetric measurements can be explained by either the creation of metal-deficit point defects (self-compensation) or a model involving a shear structure.

1. Introduction

Rutile is an n-type semiconductor at room temperature when equilibrated in an atmosphere of low oxygen activity. There is no general agreement in the literature concerning the defect structure of the non-stoichiometric rutile form of TiO_2. A salient question is whether oxygen vacancies or titanium interstitials are the dominant defects [1–11]. The electrical conductivity in TiO_2 is due to electrons resulting from the electronic disorder introduced by the oxygen non-stoichiometry, This electronic disorder gives rise to an electron spin resonance that is attributed to Ti^{+3} ions in semiconducting TiO_2 [12, 13].

The random point defect model is no longer appropriate for describing the non-stoichiometric disorder in rutile when the deviation from stoichiometry is large ($n < 10$ for Ti_nO_{2n-1}). Magneli and co-workers [14] have estabilshed a series of "shear-type" structures or "Magneli phases" and at least seven stable titanium oxides with $4 \leqslant n \leqslant 10$ for Ti_nO_{2n-1} have been determined from X-ray diffraction data. Additional phases with $n > 10$ have been established [15, 16] through electron microscopy/diffraction studies and shear-type structures for $n \sim 1000$ ($TiO_{1.999}$) have been reported [17, 18]. The anion deficiency in the case of rutile doped with greater than 5 mol% Cr is accommodated by point defects or small defect clusters [19]. These rutile solid solutions are similar to undoped TiO_2 in that they are easily reduced with the introduction of (132) shear planes. If, however, the acceptor-dopants Fe^{+3} and Ga^{+3} are added to TiO_2 the anion deficiency is accommodated by a new type of ⟨210⟩ rutile planar boundary [20].

There are disagreements as to the extent of non-stoichiometry in rutile. From isopiestic and e.m.f. measurements Blumenthal and Whitmore [21] concluded that the homogeneity range of TiO_{2-x} at 900 to 1000° C extends to a value of $x \sim 0.01$. However, Anderson and Khan [22] reported a value of 0.008 for x at 1000° C, based on the unpublished results of Steele and Zador [23]. Recently, Eror [24] reported self-compensation behaviour in TiO_2 doped with up to 8 at% Nb.

The disorder created by Ta^{-5} as a donor-dopant in TiO_2 should lend itself to description by the controlled valency model of Verwey [25]. By this method there would be compensation for the Ta^{+5} on Ti^{+4} sites by the creation of equal numbers of Ti^{+3} ions. The Ti^{+3} ions are then responsible for the increase in electrical conductivity. In this case the donor-dopant dominates the positive side of the electroneutrality equation and, as a consequence, the negative defect concentration would be independent of equilibrium oxygen activity. This compensation mechanism has also been referred to as controlled electronic imper-

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fection [26]. Similarly, the donor-dopant may be compensated for 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 [26], self-compensation [27–30], and stoichiometric compensation [31].

Waring and Roth [32] reported the phase diagram for the system TiO_2–Ta_2O_5. From their diagram, the room-temperature solid solubility limit for Ta_2O_5 in TiO_2 is less than 2.0 mol%. According to the phase diagram of Waring and Roth [32], the second phase formed for Ta_2O_5 concentrations greater than approximately 2.0 mol% in TiO_2 is $TiTa_2O_7$.

Rutile, then, seems like a promising material in which to look for a transition from a random point defect model of non-stoichiometry to an ordered extended-defect model (shear-type structure) with increasing concentrations of disorder that would be introduced by additional oxygen in compensating donor-dopant impurities [31]. It is not absolutely necessary to invoke the creation of shear-type structures to explain the uptake of additional oxygen in the case of donor addition to TiO_2, however, since metal deficit disorder could be accommodated in the open rutile-type structure.

In the present work, gravimetric measurements have been carried out on "pure" and tantalum-doped titanium dioxide and a single-phase region is found under both reducing and oxidizing conditions for tantalum concentrations up to 10 at%.

2. Experimental procedure

The tantalum-doped TiO_2 was prepared by the liquid mix technique [31, 33, 34]. Required amounts of tetraisopropyl titanate solution (from Dupont Co., Tyzor) and tantalum oxalate solution (from Kawecki Berylco Industries, Boyertown, Penn.) were mixed and there was no evidence of any precipitation in the solutions as they were evaporated to a rigid, transparent, uniformly coloured polymeric glass. The glassy samples which retain homogeneity on an atomic scale were calcined at 800° C. The various calcined compositions were then pressed into pellets at 335 MPa and sintered in air at 1350° C. For gravimetric measurements the samples were equilibrated in oxygen or in carbon dioxide–carbon monoxide mixtures at 1050° C for the oxidized and reduced states, respectively, and quenched in the ambient gas. The CO–CO_2 mixture was adjusted to provide an oxygen partial pressure of 10^{-15} atm at the equilibrating temperature. This oxygen partial pressure is nearly four orders of magnitude higher in partial pressure than the Ti_3O_5/TiO_2 phase boundary [35] and more than an order of magnitude higher than that for which Magneli-type phases have been reported [36]. All gravimetric measurements were made at room temperature (and repeated at least once on duplicate samples) on a Cahn model 4100 electrobalance.

3. Results and discussion

Gravimetric measurements on "pure" TiO_2 and on samples doped with up to 10 at% Ta^{+5} have shown that the reversible change in oxygen content, between specified states of high and low oxygen activity, is proportional to the dopant concentration. If it is assumed that each added oxygen will neutralize two Ta^{+5} dopant ions, there is a correlation of better than 96% between the measured increase in weight on oxidation of a sample that had been equilibrated in an atmosphere of low oxygen activity and the calculated amount of oxygen required to neutralize the dopant.

The driving force for additional uptake of oxygen is the compensation of the electronic disorder introduced by the donor-dopant. Such charge compensation has been described for the case of doped elemental semiconductors [37] where the solid solubility of impurities is found to be proportional to the concentration of electronic disorder. The increase in energy that is required to introduce an ion into the host lattice is more than compensated by the decrease in electronic disorder. The amount of energy gained by the compensation of the electronic disorder is determined by its ionization energy and may be of the order of an electron volt.

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. In the oxidized state the undoped sample was white in colour and insulating while all of the doped samples were grey and somewhat conducting (approximately 10^{-5} ohm^{-1} 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.

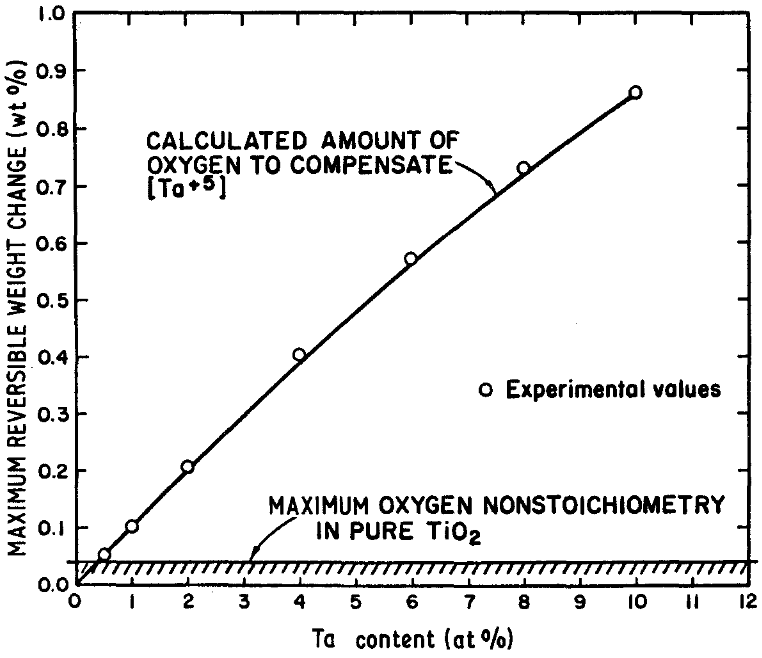

Figure 1 Maximum reversible weight-change observed for TiO_2, between 10^{-15} and 10^0 atm oxygen partial pressure, as a function of Ta^{+5} dopant concentration.

As can be seen in Fig. 1 there is excellent agreement between the calculated amount of oxygen necessary to compensate the Ta^{+5} dopant and the measured reversible oxygen weight-change between the oxidized state at 1 atm oxygen and the reduced state of equilibration in a CO_2–CO mixture. For the 0.5 at% Ta^{+5} doped sample, the measured reversible oxygen weight-change is near the cross-over point between the maximum oxygen non-stoichiometry of undoped TiO_2 and that necessary to compensate the added dopant. For the 10 at% Ta^{+5} concentration, the observed reversible weight-change amounts to a 20-fold increase in oxygen non-stoichiometry compared with that of the undoped TiO_2.

When the tantalum content in TiO_2 exceeded 10 at%, extra lines appeared in the X-ray diffraction pattern of the samples that had been equilibrated in oxygen at 1050° C. These extra lines were present when the same samples were equilibrated in a reducing atmosphere of 10^{-15} atm oxygen partial pressure. These new reflections were all assignable to the phase $TiTa_2O_7$ described by Waring and Roth [32]. The intensity of these new reflections of the $TiTa_2O_7$ phase increased as the tantalum content was increased beyond 10 at%. This solid solubility limit of about 10 at% Ta in TiO_2 is higher than the value reported in the literature [32]. It is to be pointed out here that Eror [24] observed the presence of a very small amount of second-phase $TiNb_2O_7$ for the 8 at% Nb^{+5}-doped TiO_2 that had been equilibrated in oxygen at 1060° C. This second-phase was not found when the same samples were equilibrated in a reducing atmosphere. The observation of Eror [24] indicated that niobium contained in the $TiNb_2O_7$ phase is soluble in the tetragonal rutile structure under the conditions of the reducing atmosphere. No such behaviour is observed in the present investigation.

For a Ta^{+5} concentration of approximately 20 at%, the oxidation kinetics became extremely slow (probably due to the presence of the second-phase) so that good quantitative results were difficult to obtain. It is possible to increase the amount of the disorder created by a given donor-dopant concentration by substituting a + 6 valent dopant for Ti^{+4}. Such a dopant would require twice as much reversible oxygen weight-change for electronic compensation as would an equal atomic concentration of Ta^{+5} on Ti^{+4} sites.

Under the reducing conditions, the compensation for the Ta^{+5} dopant is by the formation of equal amounts of Ti^{+3}, i.e., $Ta_x^{+5}Ti_x^{+3}Ti_{1-2x}^{+4}O_2^{-2}$. For the oxidizing conditions, the extra charge of tantalum dopant is compensated by additional oxygen taken into the rutile structure $(Ta_x^{+5}Ti_{1-x}^{+4}O_{2+(x/2)}^{-2})$. Our gravimetric observation is in excellent agreement with the amount of oxygen exchange predicted by the above compensation mechanism between the reduced and oxidized states. The mechanism by which the accommodation of the

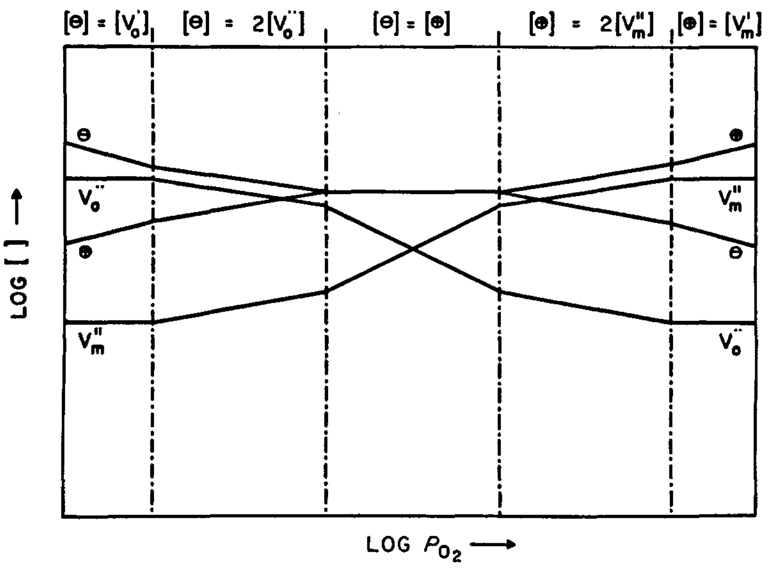

Figure 2 Log of the defect concentration for the oxide MO with Schottky–Wagner disorder as a function of log P_{O_2}.

additional oxygen takes place could be by metal deficit point defects (self-compensation) or by the creation of a shear-type structure. A second-phase, $TiTa_2O_7$, is exsolved before the effect of the extra oxygen concentration is sufficient to be detected as a significant change in lattice parameters for metal deficit disorder, or the extra X-ray lines of a shear-type structure.

A Kroger–Vink diagram [26] is a useful representation to consider when discussing the random point defect model for non-stoichiometry in a binary oxide. We will, for the purpose of illustration, consider Schottky–Wagner disorder to describe the non-stoichiometry for the general case of a binary oxide MO with a donor-dopant. Fig. 2 illustrates the variation of defect concentrations as a function of oxygen partial pressure, P_{O_2}, for the case of fully ionized atomic defects, V_M'' and $V_O^{\cdot\cdot}$, and the electrons and electron holes, ⊖, and ⊕. The familiar $[\ominus] \propto P_{O_2}^{-1/4}$, where $[\ominus] \approx [V_O^{\cdot}]$ and $[\ominus] \propto P_{O_2}^{-1/6}$, where $[\ominus] \approx 2[V_O^{\cdot\cdot}]$ regions of the electrical neutrality condition are illustrated in Fig. 2. Fig. 3 shows the case of a binary oxide MO with a donor-dopant, I_M, that is always fully

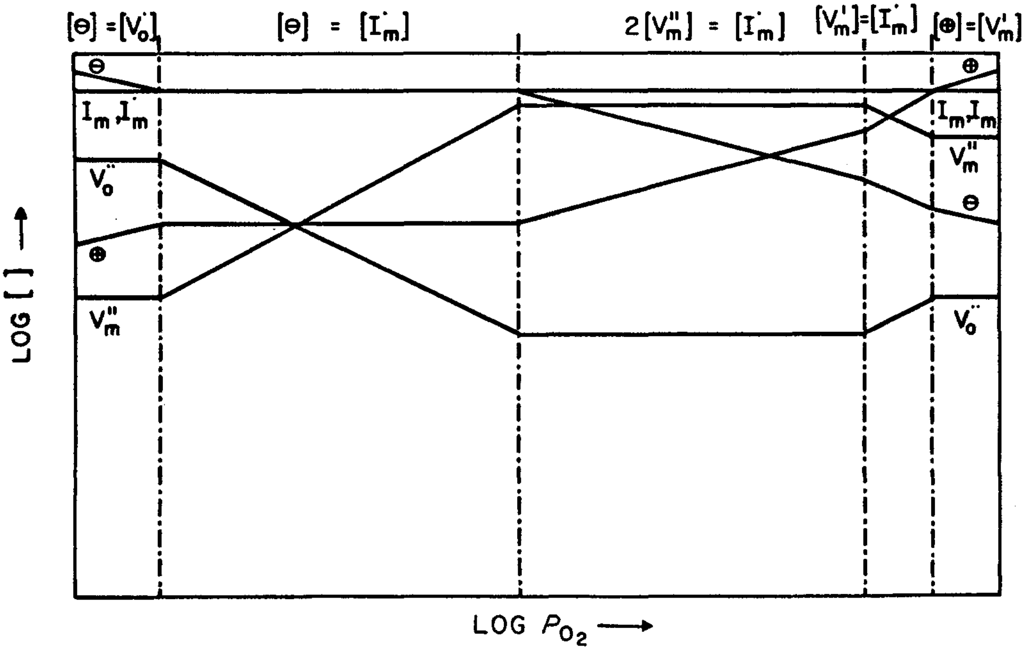

Figure 3 Log of the defect concentration for the oxide MO with a fully ionized donor-dopant, I_M, and Schottky–Wagner disorder as a function of log P_{O_2}.

ionized, $I_{\dot{M}}$. It is seen from Fig. 3 that, for sufficient departures from stoichiometry, the electrical conductivity is controlled by $[\ominus] \approx [V_O^{\cdot}]$ and the effect of the donor-dopant is not seen. The two major points to be derived from Fig. 3 are that the electronic n to p transition has been shifted to higher oxygen partial pressures and the metal excess to metal deficit transition has been shifted to lower oxygen partial pressures. This means that with the shift of the transition of metal excess to metal deficit disorder to lower P_{O_2} values, there may be significantly larger concentrations of atomic disorder than for the undoped oxide. The possibility of self-compensation is built into the random defect model of the non-stoichiometry if the oxide is stable over a sufficiently wide range of oxygen partial pressures.

The present authors [38] have suggested that for lanthanum-doped strontium titanate the compensation may be by the formation of shear-type structure in the oxidized state. Andersson and Galy [39] have 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.

This work suggests a bridge between two separate schools of thought on non-stoichiometry: the case of random, point defects in which aliovalent cations are incorporated into the host lattice without a change in either structure or cation–anion ratio, and the case of extended defect structures in which the dopant ions are compensated by subtle structural changes [40–42].

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