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## Compensation Modes in Counterdoped Rutile

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Thermogravimetric measurements were conducted on undoped, Nb<sup>5+</sup> or Ta<sup>5+</sup> donor-doped, and Al<sup>3+</sup> acceptor doped rutile at 1000°C and 10<sup>5</sup>–10<sup>-7</sup> Pa oxygen activity. Nb<sup>5+</sup> or Ta<sup>5+</sup> doped rutile was counterdoped by Al<sup>3+</sup> in order to identify the role of Al<sup>3+</sup> acceptor and its effect on donor doped rutile. Our results show that both dopants enter the lattice substitutionally for Ti<sup>4+</sup>, that Al<sup>3+</sup> is as effective an acceptor as Nb<sup>5+</sup> or that Ta<sup>5+</sup> is effective as a donor, and the compensation occurs on a one-to-one basis. Earlier reports indicate that Al<sup>3+</sup> is at best 50–70% efficient as an acceptor. © 1991 Academic Press, Inc.

### Introduction

The degree of nonstoichiometry in nominally pure TiO<sub>2</sub> varies depending on the oxygen activity and the temperature under which it is equilibrated. In general, TiO<sub>2</sub> is known to be oxygen deficient with anion vacancy and interstitial cation defects (1–8). Intrinsic defects of the Schottky type 2[V<sub>O</sub><sup>•</sup>] + [V<sub>Ti</sub><sup>'''</sup>] have been suggested (9). For small deviations from stoichiometry, doubly ionized oxygen vacancies, appear to be the dominant defects, whereas titanium interstitials and singly ionized oxygen vacancies dominate for large deviations from stoichiometry (10). Furthermore, extended defects have also been observed in oxygen-deficient rutile. Bursill and Hyde (11) re-

ported the existence of crystallographic shear planes (CSP) in TiO<sub>1.9985</sub>; later, Blanchin *et al.* (12) showed that upon rapid cooling from reducing temperature CSP were not resolved. It is therefore suggested that the rates of cooling play an important role in revealing extended defects. However, Blanchin and Bursill (13) reported that compositions in the range TiO<sub>1.9994</sub>–TiO<sub>1.9950</sub> did not show CSP, even when rapidly cooled from 1323°K, and instead clustering of small defects was suggested. Crystallographic shear planes were also observed in fine grained rutile when cooled from 700°C in air in the presence of a small electric field (14).

It is accordingly clear that although extensive studies have been made on rutile, its defect structure still remains uncertain. The interest in rutile is due to its semiconducting characteristics when equilibrated in an atmosphere of low oxygen activity. This

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is probably due to the electronic disorder that compensates for the induced ionic defects whose exact nature is not fully understood.

Earlier work on Nb and Ta-doped rutile (14) indicate that the donor (Nb or Ta) substitutes  $Ti^{4+}$  on normal lattice sites. Marucco *et al.* (9) observed both oxygen deficient and metal deficient domains depending on the oxygen activity. Dirstine and Rosa (15) report that for 1–3%  $Nb_2O_5$ -doped rutile, oxygen interstitials or metal deficit are the predominant defects at  $10^5$  Pa, upon reduction at  $10^{-7}$  Pa stoichiometric compositions were observed, and that  $Ti^{4+}$  interstitials become important upon further reduction to  $10^{-13}$  Pa. It is generally accepted that the disorder created by donor doping in rutile is compensated by either electronic transitions, similar to those observed in oxygen deficient rutile, or by a self-compensation mechanism (16) whereby charged point defects are formed. In either case the defect structure of donor doped rutile, similar to undoped rutile, is strongly  $PO_2$ -dependent.

Studies on acceptor doped rutile indicate that the dopant is compensated by oxygen vacancies or small defect clusters (17), and depending on the concentration, crystallographic shear planes may be developed (18). It is further reported that, depending on temperature and oxygen activity, association between the cation acceptor and its compensating oxygen vacancy may occur (19). The authors also suggest that inadvertent acceptor impurities affect the defect structure and behavior of nominally pure  $TiO_2$  and are the cause for the  $-\frac{1}{4}$  power dependence on oxygen activity in the region of  $PO_2 > 10^{-10}$  Pa.

Our earlier postulated model on the defect structure of doped rutile (20) does not fully explain the experimental data obtained from thermogravimetric and electrical conductivity measurements throughout the entire oxygen activity range. This ap-

pears to be the case in most of the cited literature, and more quantitative work is needed to fully understand the behavior of doped rutile. However, at the present time, the compensation modes in counter-doped rutile appear to be well defined and should be reported. This has been accomplished by means of double doping experiments, to determine the relative difference in efficiencies between donors and acceptors in the presence of both.

### Experimental

Samples of undoped and donor-doped (Nb or Ta) rutile as well as that counter-doped with Al, i.e.,  $(Nb + Al)_x Ti_{1-x}O_2$ , were prepared using the liquid mix technique (21). The amount of donor added did not exceed 8 At% to avoid the exsolution of a second phase (22). In the counterdoped samples,  $Al^{3+}$  was added at the expense of the donor. Thermogravimetric measurements were conducted in a system designed to detect weight changes on a 50- to 80-g sample to an accuracy of  $\pm 1$  mg ( $\sim 10^{-5}$  moles) at temperatures up to  $1400^\circ C$  and an oxygen activity range from  $10^5$ – $10^{-11}$  Pa. Buffered gas mixtures were used to obtain the required range of oxygen activity; the latter was monitored by a calibrated  $ZrO_2$  sensor.

### Results and Discussion

There appear to be several possible mechanisms by which donors may be compensated in the rutile structure. We observed that at elevated temperatures Nb- or Ta-doped rutile absorbs oxygen in excess of that required by the stoichiometric composition in a manner similar to our earlier observations on donor-doped  $SrTiO_3$  (23) and  $BaTiO_3$  (24). Due to the complexity of the compensation process in rutile, we were not able to fully explain our results in terms of the proposed model. More data are needed

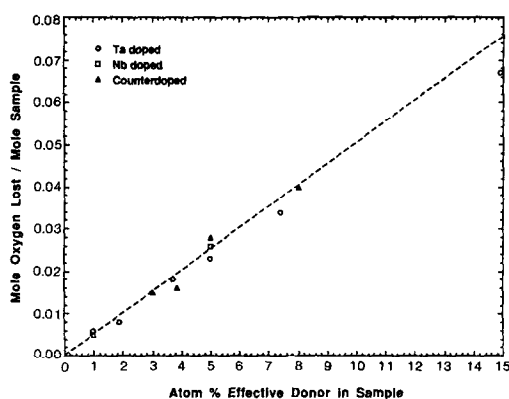


FIG. 1. A comparison between experimental and calculated maximum reversible oxygen exchange as a function of net donor in  $\text{TiO}_2$  at  $1000^\circ\text{C}$ .

to understand the behavior of donor-doped rutile as a function of oxygen activity. However, an interesting trend was observed when the donor dopant was counterbalanced by an acceptor in the host lattice.  $\text{Nb}^{5+}$  was counterbalanced by  $\text{Al}^{3+}$  and the relative difference in efficiencies between the donor and acceptor was found valid throughout the composition range investigated, i.e.,  $\text{Al}^{3+}$  was found to be just as effective as an acceptor as  $\text{Nb}^{5+}$  is as a donor and the resulting compensation is on a one-to-one basis. This is illustrated in Fig. 1 and 2, and is contrary to Chen and Smyth's (25) report on doped *n*-type oxides where they indicate that Al is less than 50% effective in creating acceptor levels. In Fig. 1, the oxygen deficit is determined as a function of donor dopant at  $1000^\circ\text{C}$ . The observed oxygen exchange was equivalent to that theoretically expected up to a donor concentration of 8 At%. At higher concentration, a deviation from the predicted behavior was observed and is probably due to the solubility limit of  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  in  $\text{TiO}_2$ , which is reported (22) to be 8 At% under oxidizing conditions, beyond which exsolution of the monoclinic phase  $\text{TiNb}_2\text{O}_7$  is expected. It is of interest to note that, within the solubility limit, the  $\text{Al}^{3+}$ -counterdoped samples fully

compensate an equivalent amount of donor, rendering it ineffective, and the observed oxygen exchange (Fig. 1) is due to the residual net donor. If indeed background acceptor impurities alter the defect characteristics, in the manner earlier reported (26, 27), a one-to-one compensation would not have been observed. Furthermore, the reported (22) impurity-defect association does not seem to be evident from our results.

These observations were further confirmed from reversible weight change experiments as a function of effective net dopant at  $1000^\circ\text{C}$  and  $10^5$ – $10^{-7}$  Pa, as shown in Fig. 2. Samples containing net residual acceptor dopant  $[\text{Nb}_{\text{Ti}}] - [\text{Al}_{\text{Ti}}] < 0$ , show a reversible weight loss characteristic (dashed line) and was independent of oxygen activity and acceptor content within the range of our experimental conditions. However, as the concentration of donor increased to the point where a net residual donor prevailed,  $[\text{Nb}_{\text{Ti}}] - [\text{Al}_{\text{Ti}}] > 0$ , a gradual increase in the reversible weight loss was observed, and was found to be proportional to the net residual donor concentration. This is illustrated by the experimental data points shown in Fig. 2. A theoretical plot calcu-

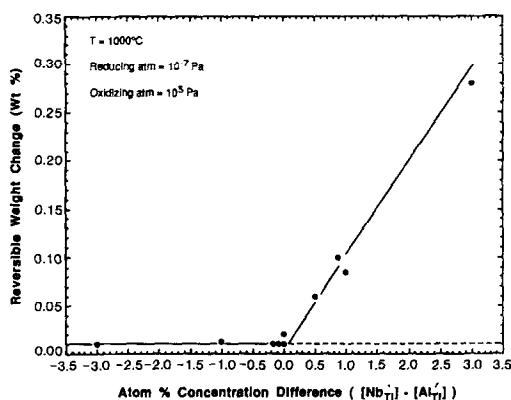


FIG. 2. Reversible weight changes in  $\text{TiO}_2$  cycled from  $10^{-7}$  to  $10^5$  Pa oxygen at  $1000^\circ\text{C}$  as a function of  $\text{Nb}^{5+}$  and  $\text{Al}^{3+}$ .

lated on the basis of the net effective charge is also shown in Fig. 2 (solid line) and found to be in good agreement with the experimental data.

Our results indicate that  $\text{Al}^{3+}$  acceptor and  $\text{Nb}^{5+}$  or  $\text{Ta}^{5+}$  donor enter the rutile structure substitutionally for  $\text{Ti}^{4+}$ . The acceptors appear to play a significant role in the behavior of donor-doped rutile and that inadvertent impurities did not alter the defect characteristics of this system.

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