

Oxidation-reduction behaviour of La-doped SrTiO₃

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Thermogravimetric measurements as a function of oxygen activity were performed in the temperature range of 1200 to 1400°C on a series of lanthanum SrTiO₃ compounds. A model which assumes the absorption of excess oxygen in the structure which compensates the donors by formation of cationic defects is postulated. Comparison of this model with the experimental results show reasonable agreement.

1. Introduction

Recently, the perovskite-class oxide SrTiO₃ has received considerable attention due to its possible uses as a dielectric or as a photocatalysis electrode, but unfortunately, the work published to date does not clearly define the defect chemistry of pure and doped SrTiO₃.

The early work of Walters and Grace [1] and Yamada and Miller [2] on single crystal SrTiO₂ gave strong evidence that reduced SrTiO₃ is n-type with oxygen vacancies ($V_{\text{O}}^{\bullet\bullet}$) as the predominant defects, this has been further supported by electron paramagnetic resonance measurements [3]. Chan *et al.* [4] and Balachandron and Eror [5] have performed experiments to study changes in conductivity with partial pressure of oxygen (P_{O_2}) using high purity polycrystalline SrTiO₃ samples and showed that it is a close analogue to BaTiO₃, with a p-n transition resulting from the acceptor impurities present.

Donor doped SrTiO₃ is found to have very low electrical conductivity under oxidizing conditions, which then increases sharply under reduction. It seems apparent that some form of ionic compensation is occurring, and indeed, recent work on lanthanum-doped SrTiO₃ by Eror and Balachandron [6] shows that when reduced, it displays a reversible weight loss which is directly proportional to the donor concentration. However, X-ray diffraction studies, also performed by Eror and Balachandron [7], have shown that the lattice parameters vary linearly with lanthanum content to as high as 40 mol%, and appear to be

the same in both the oxidized and reduced states. Therefore, it is possible to conclude that:

(i) The lattice parameter changes indicate that lanthanum substitutes for strontium in both the reduced and oxidized state without the formation of additional phases;

(ii) The absence of change in lattice parameters between the oxidized and the reduced states eliminates interstitial mechanisms;

(iii) The direct variation with lanthanum content and the magnitude of the weight losses eliminates a grain boundary effect.

It is possible that titanium vacancies, $V_{\text{Ti}}^{\prime\prime\prime}$, or site switching could occur, although they seem energetically unlikely in a perovskite lattice. Titanium vacancies in particular have been suggested as a possible compensation mechanism [8].

Eror and Smyth concluded that the best way to reconcile these apparently contradictory results was to postulate the presence of an as yet undetected crystallographic accommodation of the absorbed oxygen, possibly in a way similar to one of the Ruddlesdon-Popper phases [9]. This is supported by the work of Odekirk *et al.* [10] who found evidence for $V_{\text{Sr}}^{\prime\prime}$ in lanthanum-doped SrTiO₃ using low temperature conductivity measurements, and by Tilley [11] who observed by electron microscopy that excess SrO was accommodated in SrTiO₃ by the formation of lamellar structures.

It was, therefore, the intent of this study to investigate more fully the change in thermo-

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TABLE 1 Typical chemical analysis (mole fraction). Trace element concentration of undoped SrTiO₃ was determined by neutron activation analysis.

Mg	0.00713
Ca	0.00114
Cl	0.00086
Na	0.00026
Fe	0.00010
Ni	0.00010
Al	0.00008
Ba	0.00007
Cu	0.00006
K	0.00005
Cr	0.00002

gravimetric behaviour with P_{O_2} of donor-doped SrTiO₃, and to compare these experimental results with the behaviour predicted by a model based upon a crystallographic defect mechanism.

2. Experimental procedure

Strontium titanate powders were prepared with varying at % lanthanum contents using the liquid mix method first proposed by Pechini [12]. Typical trace element analysis of the prepared powders is presented in Table 1.

The experimental apparatus consisted of a balance, from which a relatively large powder

sample (60 to 80 g) was weighed, to an accuracy of ± 0.1 mg, and suspended in a vertically mounted tube furnace. Flowing gas mixtures of either O₂/N₂ or CO₂/H₂/N₂ were used to establish the oxygen activity which was monitored by a calibrated ZrO₂ oxygen sensor.

The oxygen activity values were verified by using a reduced Fe₂O₃ sample and observing the haematite–magnetite and the magnetite–wustite phase boundaries which were in good agreement with those reported in the literature [13, 14].

To minimize volatiles the powder samples were heated to 1400°C prior to introduction into the thermogravimetric (TGA) system. The specimens were then heated to the desired temperature and the relative weight change was recorded as P_{O_2} was varied in a stepwise fashion. The samples were then returned to their original oxidation state to determine if any irreversible weight losses had occurred. With a gas flow rate of 0.5 cm sec⁻¹, and 60 to 80 g samples, weight changes of 1 mg, or 6×10^{-5} moles oxygen, were detectable with this system. The temperature control was accurate to within 2°C.

3. Results and discussion

Typical results of these experiments are displayed in Fig. 1, where the moles of excess oxygen per

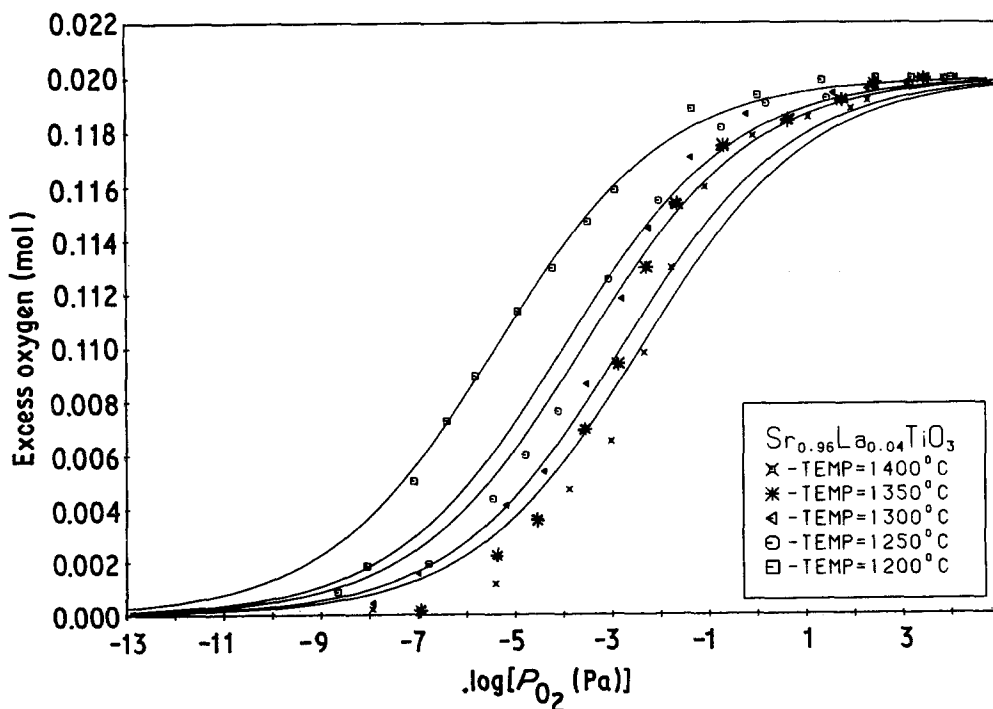
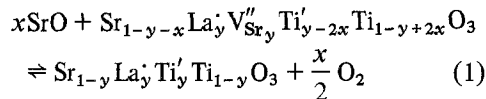


Figure 1 Plot of moles excess oxygen against $\log P_{O_2}$ for 4 at % lanthanum-doped SrTiO₃ at various temperatures.

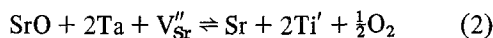
mole of $\text{Sr}_{0.96}\text{La}_{0.04}\text{TiO}_3$ are plotted against $\log P_{\text{O}_2}$ in the temperature range 1200 to 1400° C. The total number of moles of oxygen absorbed is approximately equal to the expected value of half the total number of moles of lanthanum present, which implies that full compensation of the lanthanum is being achieved. Within the sensitivity range of the system no irreversible weight loss was detected for any of the samples. The solid curves shown are the values predicted from the proposed model.

Ruddlesdon and Popper [9] first noted that the Sr–Ti–O system forms a series of $x\text{SrO}\cdot y\text{TiO}_2$ compounds, and specifically identified Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$. These compounds appear as varying numbers of SrO layers interleaved within perovskite layers, leaving the oxygen sublattice intact. The assumption is that the donor dopant induces the absorption of oxygen which reacts to form an SrO layer and leaves strontium vacancies, V_{Sr}'' , in the host lattice to compensate for the donor. This excess oxygen is removed under reduction and the compensation of the donor becomes electronic, sharply increasing the electrical conductivity. Since the SrO and the associated V_{Sr}'' form layers of different composition on specific crystal planes without altering the perovskite lattice, this could be considered to be a crystallographic shear mechanism.

This model therefore assumes that the lanthanum donor is compensated by an equal number of Ti^{3+} ions at low P_{O_2} to give a good electronic conductor, which is virtually free of ionic defects. With increasing P_{O_2} , oxygen is absorbed, which reacts to form the SrO layers characteristic of a Ruddlesdon–Popper-type phase and leaves V_{Sr}'' in the host lattice to compensate for the La^{3+} . Assuming Kroger–Vink notation [15], this reaction can be written as:



where y = moles lanthanum, and $x/2$ = moles oxygen absorbed. This can be simplified to:



The model predicts that a maximum of $y/2$ moles of oxygen will be absorbed from the reduced state by SrTiO_3 donor-doped with y moles of lanthanum which is in agreement with experiment.

The suggested V_{Ti}''' mechanism [8], although energetically unlikely, will yield the same oxygen pressure dependence as the proposed model; with our experimental set-up it is not possible to distinguish between the two mechanisms.

Fig. 2 shows that the amount of excess oxygen

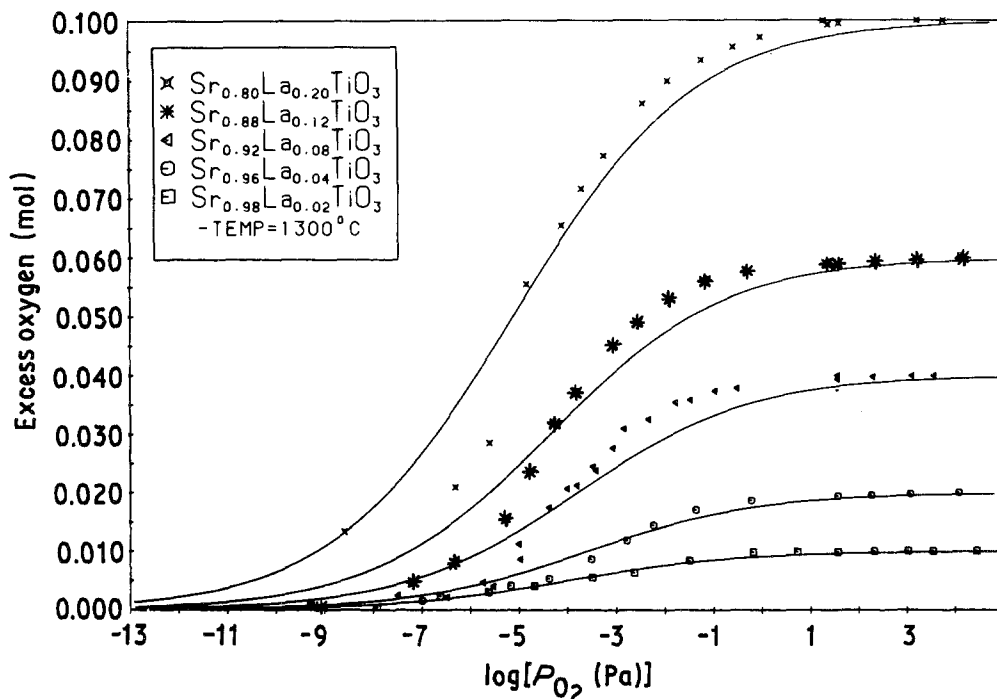


Figure 2 Plot of moles excess oxygen against $\log P_{\text{O}_2}$ at 1300° C for different lanthanum contents in SrTiO_3 .

absorbed is dependent on the dopant content. Furthermore, in the region where full compensation is expected, a linear relationship is observed between the amount of absorbed oxygen and the dopant content.

Assuming that the activities of the various species involved can be approximated by their mole fractions and that the activity of SrO is not unity as a true exsolved phase would be, but also equal to its mole fraction, then the equilibrium constant for Equation 2 can be written in terms of y , the number of moles of lanthanum present, and x , the number of moles of excess oxygen (also equal to the number of moles of SrO present).

$$K = \frac{[1 - y - x][y - 2x]^2 P_{O_2}^{1/2}}{[x]^2 [1 - y + 2x]^2} \quad (3)$$

Thus the equilibrium constant can be evaluated experimentally. The parameter, x , can be expressed in terms of the observed weight loss by this expression:

$$x = \frac{1}{2} - \frac{1}{16}w \quad (4)$$

where w is the observed weight loss per mole sample.

As it is not possible from the nature of such TGA experiments to be certain that full oxidation or reduction has been achieved, the absolute values found were not considered as reliable as the relative changes in weight. Therefore, a differential technique was developed by noting that both x and y are small compared to 1, so that Equation 2 can be approximated by:

$$K^{1/2} = \frac{y - 2x}{x} P_{O_2}^{1/4} \quad (5)$$

This expression can then be differentiated with respect to x and $\log P_{O_2}$ to obtain:

$$\frac{dx}{d(\log P_{O_2})} = \frac{K^{1/2} P_{O_2} x^2}{(0.5758)y} \quad (6)$$

If the approximation is made that $dx/d(\log P_{O_2}) = \Delta x/\Delta \log P_{O_2}$ then a K value can be calculated from any pair of data points. Near the inflection point of the weight loss curve the values of K were quite constant and the six consecutive data points yielding the lowest variance in K were averaged to find a best fit K . These average equilibrium constants were substituted into

Equation 3 to generate the predicted excess oxygen lost, x , against $\log P_{O_2}$ curves seen in Figs. 1 and 2. The fit between the predicted curve and the observed weight loss can be seen to be quite good, although there is a persistent tendency for the slope of the actual data at the inflection point to be sharper than the calculated dependence. From the temperature dependence of the equilibrium constant K , the enthalpy, ΔH , for Reaction 1 is determined using a least-squares fit and found to be $-309 \pm 9 \text{ kJ mol}^{-1}$ throughout the composition range up to 12 at% lanthanum. The calculated ΔH for the 20 at% lanthanum sample was significantly higher. This may be due to the formation of clusters or association of defects [16] which are not taken into account by the simple model. The general expression of the equilibrium constant for the oxidation-reduction Reaction 1 is found to be,

$$K = 1.8 \times 10^6 \exp \frac{(-309 \pm 9 \text{ kJ mol}^{-1})}{RT}$$

Further analysis of this data can be performed by rewriting Equation 5 to obtain:

$$\frac{x}{y} = \frac{1}{(K^{1/2} P_{O_2}^{1/4} + 2)} \quad (7)$$

Since K is always a small number relative to 2, as P_{O_2} approaches 1 atmosphere, x/y approaches $\frac{1}{2}$, but as P_{O_2} decreases, then this expression can be approximated by:

$$\frac{x}{y} = \frac{P_{O_2}^{1/4}}{K^{1/2}} \quad (8)$$

Therefore, a plot of $\log(x/y)$ against $\log P_{O_2}$ should be constant at high P_{O_2} , and then change to a 1/4 slope at low P_{O_2} . This behaviour is shown in Fig. 3 for the 4 at% lanthanum-doped sample at different temperatures; and in Fig. 4 for different dopant contents at 1300°C. The 1/4 power dependence on the oxygen activity, as predicted by Equation 8, followed fairly well. Again, at the lowest P_{O_2} the non-conformity with the model is observed which may be due to clustering of complexes which are not taken into account by this simple model. However, it is obvious that the oversimplified model presented does describe the overall behaviour quite well and only breaks down at the low P_{O_2} limit. Currently, attempts

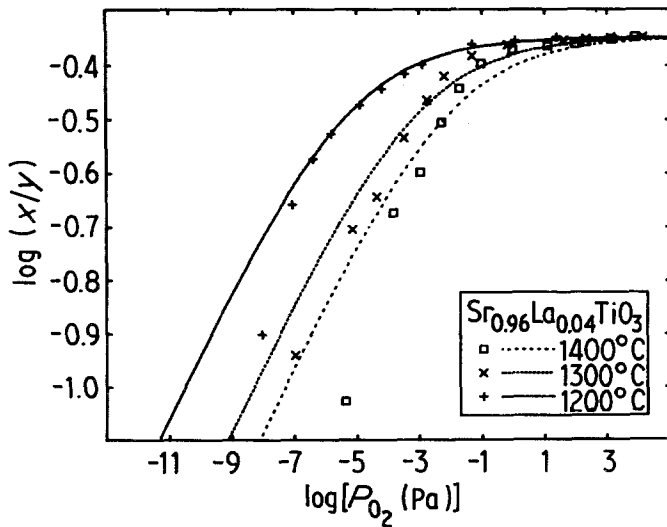


Figure 3 Plot of relative defect concentration against P_{O_2} for 4 at % lanthanum-doped $SrTiO_3$ at various temperatures.

to extend the simple model to include more complex defects are being made with the intent of achieving a better match between theory and experiment.

4. Conclusion

The results of a series of experiments investigating weight change with P_{O_2} for lanthanum-doped $SrTiO_3$ show that a reversible weight change occurs, upon oxidation–reduction, which is related to the amount of lanthanum present. To explain this behaviour a model is proposed which assumes that at low P_{O_2} the donor is electronically compensated, but that at high P_{O_2} ionic compensation occurs by the absorp-

tion of sufficient oxygen to form SrO and V''_{Sr} that are accommodated in the lattice by an extended defect structure, instead of an exsolved second phase. The reasonable correlation between the actual data and the predicted weight changes, the correctly predicted power dependence of the log moles SrO against log P_{O_2} plots, and the ability to calculate equilibrium constants from the data lend considerable credence to this model.

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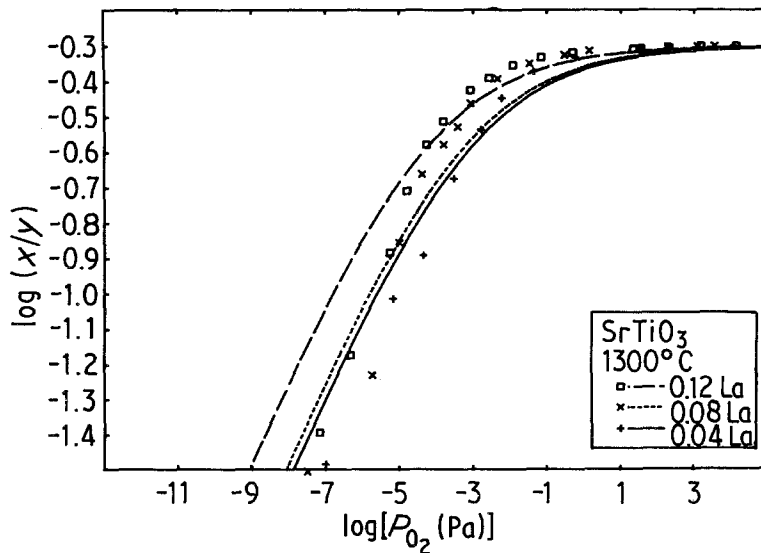


Figure 4 Plot of relative defect concentration against P_{O_2} at $1300^\circ C$ for $SrTiO_3$ doped with various lanthanum contents.

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