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Determination of Oxygen Chemical Diffusion Coefficients in Single Crystal SrTiO₃ by Capacitance Manometry

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ABSTRACT

The oxidation kinetics of a single crystal of SrTiO₃ were measured with a tensivolometric system over the temperature range 700°-975° at 0.03 atm oxygen pressure. The oxidation was found to be oxygen diffusion limited with an activation energy of 14.9 ± 1.3 kcal/mole. Combining the kinetic data with relative defect concentration data yielded an activation energy for oxygen self-diffusion of 57 ± 16 kcal/mole. The enthalpy of formation of doubly ionized oxygen vacancies was calculated to be 126 ± 13 kcal/mol.

Recently, BaTiO₃ was investigated in the temperature range of 300°-1000°C and at oxygen partial pressures as low as 10^{-6} atm with a capacitance manometer (1, 2). Calibration shows the sensitivity of this instrument to be 10-100 times greater than that of a microbalance. As has been reported, changes in oxygen stoichiometry as small as 10^{-8} moles were easily detected on approximately 10g BaTiO₃ samples.

The limit of sensitivity of this particular system was about 3×10^{-9} moles oxygen gas or a 10^{-7} g change in total sample weight. On a smaller volume system, Turcotte *et al.* (3, 4) report an even higher sensitivity of 2×10^{-9} g.

In another study, Greskovich and Schmalzried (5) investigated nonstoichiometry in Co₂SiO₄ and in CoAl₂O₄-MgAl₂O₄ crystalline solutions and determined changes in cobalt vacancy concentrations as low as 10^{-2} atom per cent (a/o).

In addition to being useful in determining changes in stoichiometry, the initial work on BaTiO₃ and that of Greskovich and Schmalzried indicates that the kinetics of oxygen exchange are easily measurable so chemical diffusion coefficients can be calculated by solving Fick's second law for the appropriate boundary conditions of the system (6).

The tensivolometric technique of measuring the gaseous exchange with a solid is both very rapid and sensitive, so an evaluation of this technique for the determination of chemical diffusion coefficients is of practical value. Since both the oxygen diffusion coefficients and the limit of oxygen nonstoichiometry of SrTiO₃ have been measured (7-10), this oxide was chosen to make this evaluation.

In previous experiments with 0.1 μm crystallite-size BaTiO₃ and SrTiO₃ (1), attempts to use the exchange kinetics to calculate chemical diffusion coefficients were not successful. Evidently, the exchange was not entirely diffusion limited. As a result of the small particle size, the exchange can be expected to be dependent upon the surface exchange reaction as well as upon diffusion (11). Thus, to limit control by the surface exchange reaction in this study, oxygen exchange with large single crystal SrTiO₃ was measured.

Experimental

The apparatus used is similar to that described by Conger (1) and Meurer (12). It consists of two symmetrical chambers, separate and vacuum-tight, but with provision for interconnection. The oxide sample is sealed into one side with the other being left empty as a reference. An atmosphere of known oxygen pressure is admitted to both sides and allowed to equilibrate.

After rapidly changing both the sample and reference sides to a new value of oxygen pressure, the two sides are separated. The attainment of a new equilibrium with the sample is followed with a sensor head by monitoring the pressure change (caused by an oxygen loss or uptake) in the sample side of the system relative to the reference side.

The sensor head is an open loop, taut metal membrane capacitance manometer² with a range of 1.3×10^{-8} to 1.3×10^{-3} atm.

The sample and reference tubes were heated in a wire-wound furnace whose maximum temperature was 1000°C. At temperatures up to 1000°C, the furnace temperature was controlled to approximately $\pm 3^\circ\text{C}$ with both linear and radial gradients of less than 2°C in the region where the sample was contained.

If the temperature of the entire apparatus is maintained at constant temperature, the measured pressure change, Δp due to evolution or uptake of gas is related to the change in the number of moles of gas, Δn by the relation $\Delta p = \Delta n RT/V$ where V is the volume of the sample side, R is the gas constant, and T is the temperature.

In actual practice, the expression for the observed pressure change is not so simple since the temperature of the system is not uniform (that is, the gauge and the sample chamber are at different temperatures). The expression will, instead, involve a correction factor arising from temperature gradient effects.

The measured pressure change is thus described as $\Delta p = K(T) \Delta n$ where Δp is the sample-induced pressure change and $K(T)$ is a temperature dependent correction factor containing the gas constant R , the sample side volume V , and some function of gauge and furnace temperatures.

An empirical calibration was necessary in order to relate measured pressure changes to oxygen concentration changes in a sample. This was accomplished by measuring the pressure changes occurring for known changes in gas concentration at a series of furnace temperatures (20°-950°C). The correction factor was found to be independent of oxygen pressure and to be only a function of furnace and gauge temperature. With the system thermostated at $38^\circ \pm 0.01^\circ\text{C}$ and the head temperature constant, the calibration constant varied from 31.0 ± 0.20 atm/mole to 33.8 ± 0.28 atm/mole with the furnace at 20° and 950°C, respectively.

For the minimum detectable pressure change of 1.3×10^{-8} atm, the maximum sensitivity attainable is $\Delta n = 4 \times 10^{-10}$ moles which corresponds to a weight change of 1.3×10^{-8} g of oxygen. Interaction between the gas and the system was found to place a practical limit on detectability of 4×10^{-9} moles oxygen.

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Key words: oxidation, oxygen vacancy concentration, oxygen self-diffusion.

² MKS Instruments, Incorporated, Burlington, Massachusetts 01803.

Due to the limited range of nonstoichiometry of SrTiO₃, it was found that the apparatus could not detect the exchange kinetics by stepping the oxygen pressure in the range 10⁻⁶-1 atm at temperatures below 1000°C. To achieve a detectable pressure change within the temperature and pressure range of the apparatus it was necessary to reduce the sample in either forming gas (8% H₂ in N₂) or CO. The oxidation kinetics were then measured when the reducing gas was replaced by O₂.

The crystal was cut from 99.9 weight per cent (w/o) pure SrTiO₃ boule.³ Prior to use, the crystal was polished and annealed to remove surface roughness and internal strain. The final dimensions of the rectangularly shaped crystal were 1.24 cm × 1.33 cm × 2.04 cm ± 0.02 cm. The weight of the crystal was determined to be 16.9903 ± 0.0002g, with a density of 5.121 ± 0.001 g/cm³. No attempt was made to orient the crystal so any effects of crystallographic directions could not be observed.

Mathematical Analysis

Diffusion coefficient.—When a sample re-equilibrates from an initially homogeneous nonstoichiometric condition, diffusion occurs under the influence of a chemical potential or concentration gradient. This type of diffusion is commonly referred to as chemical diffusion and the diffusion coefficient resulting from it is

termed as the chemical diffusion coefficient, \tilde{D} . The relationship between the chemical diffusion coefficient and self-diffusion coefficient have been extensively treated elsewhere, so will not be discussed here (11, 13, 14).

For a brick-shaped geometry, the solution to Fick's second law which applied to the change in stoichiometry resulting from the oxide crystal re-establishing thermodynamic equilibrium due to changes in oxygen activity was originally derived by Newman (15). Later it was used by Price and Wagner (16) in determining chemical diffusion coefficients for single crystals of NiO and CoO by electrical conductivity techniques. The format presented here is similar to that of Price and Wagner, with the exception of incorporating the measurable parameters of the tensivolometric technique.

For long times the relative defect concentration, $(1 - Q)$, is given by

$$1 - Q = 1 - \frac{\Delta w_t}{\Delta w_\infty} \simeq \frac{512}{\pi^6} \exp \left[-\frac{\pi^2 \tilde{D} t}{4} \left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right) \right] \quad [1]$$

where Δw_t is the weight change at time t , Δw_∞ is the total weight change measured between the initial and

final equilibrium states, \tilde{D} is the chemical diffusion coefficient and $2a$, $2b$, and $2c$ are the sample dimensions. This solution assumes as boundary conditions that the crystal is initially in equilibrium with a certain partial pressure of oxygen, and at time $t = 0$, the surface of the crystal is in immediate equilibrium with another oxygen partial pressure. The re-equilibration is assumed to be limited by diffusion rather than surface reaction and the observed weight change is then just an integrated measure of the adjustment of the defect concentration to the new equilibrium state.

The changes in defect concentration may be expressed either as weight changes in the sample or as changes in the pressure in the tensivolometric apparatus. Therefore, from Eq. [1], weight changes may be equated to the induced pressure changes as follows

$$1 - Q = 1 - \frac{\Delta w_t}{\Delta w_\infty} = \frac{\Delta w_\infty - \Delta w_t}{\Delta w_\infty} = \frac{\Delta P_\infty' - \Delta P_t'}{\Delta P_\infty'} \quad [2]$$

where the total induced pressure change, $\Delta P_\infty'$ equals $\Delta P_x + \Delta P_t$ and the total induced pressure change at time t , $\Delta P_t'$ equals $\Delta P_t + \Delta P_t$. The terms ΔP_t and ΔP_x represent, respectively, the measured differential oxygen pressure as a function of time, and the final measured differential oxygen pressure. The quantity ΔP_t is a correction factor that would be zero if the measurement of ΔP_t began at the instant that the system pressure was changed (that is at $t = 0$, exchange = 0). Since this cannot be the case, ΔP_t will always be greater than zero.

Therefore for use with the tensivolometric system, Eq. [1] is rearranged to read

$$1 - Q = (\Delta P_\infty' - \Delta P_t') / (\Delta P_\infty' + \Delta P_t') \simeq 512 / \pi^6 \exp \left[-\pi^2 \tilde{D} t / 4 (1/a^2 + 1/b^2 + 1/c^2) \right] \quad [3]$$

or

$$\log (\Delta P_\infty' - \Delta P_t') \simeq \log (\Delta P_\infty' + \Delta P_t') + \log (512 / \pi^6) - (\tilde{D} t \pi^2 / 9.21) \times (1/a^2 + 1/b^2 + 1/c^2) \quad [4]$$

Defect concentration.—As previously described, the calibration factor $K(T)$ relates the defect-associated change in the number of moles of oxygen in the sample, to the change in pressure in the system. From this relationship and the total induced pressure change, $\Delta P_\infty'$, changes in stoichiometry can be investigated.

The oxidation (or reduction) kinetics for this type of experiment will be determined by the most rapid diffusing cation-hole or anion-electron complex. If the material is predominantly an electronic conductor, then the diffusivity of the ionic defects will control the kinetics. For a binary compound, the most rapid diffusing ionic defect is the majority defect. Due to the additional component in a ternary compound, this is not necessarily true. However, for the case of nonstoichiometric SrTiO_{3-δ}, the majority defect and the fast diffusing ionic defect are the same and have been shown to be oxygen vacancies (7-10). Thus, for SrTiO_{3-δ}, this experiment can determine both the concentration of oxygen vacancies, δ , and the chemical diffusion

coefficient, \tilde{D} . Changes in the parameter δ , ($\Delta\delta$) can be related to changes in the gas concentration, Δn by

$$\Delta\delta = 2\Delta n M / m = 2\Delta P_\infty' M / K(T) m \quad [5]$$

where M is the molecular weight of stoichiometric SrTiO₃, m is the mass of the sample.

The defect concentration can be related to the parameter δ by

$$[\text{defect}] = \delta \rho / M \quad [6]$$

where $[\text{defect}]$ represents the mole concentration (moles/cm³) of some atomic defect and ρ is the density of SrTiO₃. Changes in defect concentration can be represented as

$$\Delta[\text{defect}] = \Delta\delta \rho / M \quad [7]$$

or

$$\Delta[\text{defect}] = [2\rho/m][\Delta P_\infty' / K(T)] \quad [8]$$

Results and Discussion

An illustration of a typical oxidation curve is shown in Fig. 1. If a plot of $\log \Delta P_t$ vs. $\log t$ of the initial part of these data is made, a slope of $1/2$ is obtained which indicates bulk diffusion controls the process (11). Such a plot is not included since it is essentially redundant.

From the oxidation data, ΔP_t vs. time, and Eq. [4], a plot of $-\log (\Delta P_\infty' - \Delta P_t')$ vs. time can be generated. Figure 2 is an example of this relationship. From the intercept of these curves ΔP_t can be obtained which allows the relative defect concentration $(1 - Q)$ to be calculated. If the assumptions leading to Eq. [4] are correct, then a plot of $-\log (1 - Q)$ vs. time will be linear. Figure 3 is an example of such a plot for five different isothermal exchanges from 700° to 975°C. The excellent adaptability of the experimental data to Eq.

³ NL Industries, South Amboy, New Jersey 08879.

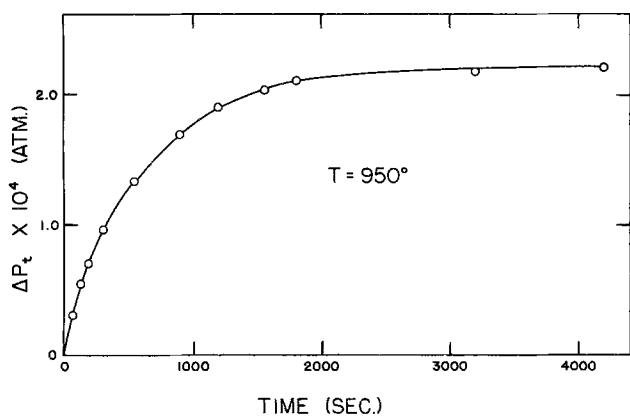


Fig. 1. Typical curve obtained for a sample initially reduced in CO and then oxidized in 0.03 atm O₂. T = 950°C.

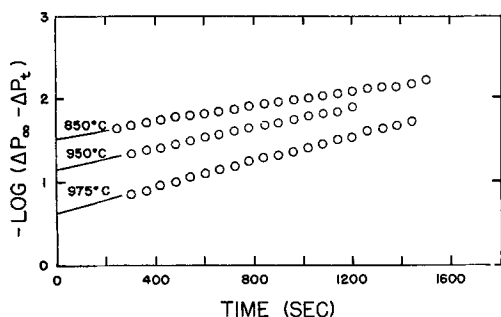


Fig. 2. Plot of Eq. [4] to obtain chemical diffusion coefficients

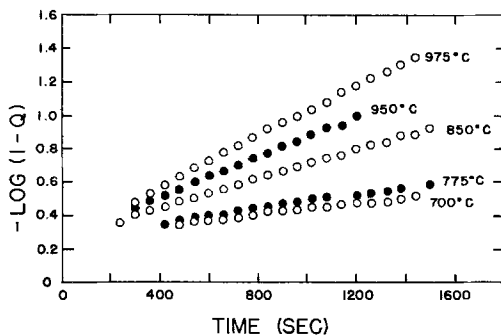


Fig. 3. Plot of log of relative defect concentration vs. time

[4] suggests that the sample oxidation proceeds by a process of homogeneous volume diffusion. The oxygen chemical diffusion coefficient obtained from the slopes of the plots of Eq. [4] can be represented by

$$\tilde{D} = 10^{-1.3 \pm 0.2} \exp\left(-\frac{14,900 \pm 1,300}{RT} \text{ cal/mole}\right) \text{ cm}^2/\text{sec} \quad [9]$$

in the temperature range 700°-975°C at an oxygen pressure of 0.03 atm.

Figure 4 compares the results of this study with previous investigators. The two points at the lower right-hand side of this figure are diffusion coefficients calculated from vacancy mobility data of Blanc and Staebler (17) using the Einstein relation (18).

Paladino (7) measured oxidation kinetics of reduced single crystal SrTiO₃ by a thermogravimetric technique. The calculated oxygen chemical diffusion coefficients in the temperature range 850° and 1460°C, can be represented by

$$\tilde{D} = 0.33 \exp\left(-\frac{22,500 \pm 5,000 \text{ cal/mole}}{RT}\right)$$

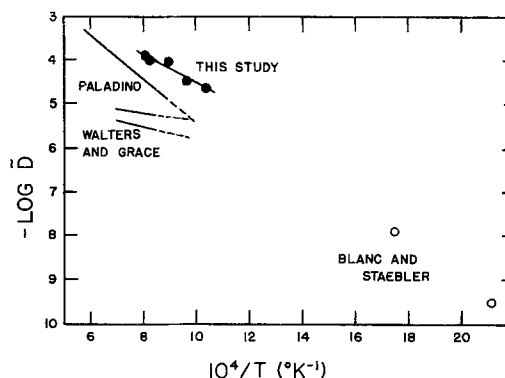


Fig. 4. Compilation of oxygen chemical diffusion data for SrTiO₃.

cm²/sec. The calculated diffusion coefficients of this study are close to those obtained by Paladino. This is an important point since both studies measured oxidation kinetics of reduced single crystal SrTiO₃, so the results of the two techniques should correspond. The enthalpy of motion term also compares reasonably well.

An extrapolation of Blanc and Staebler data into the higher temperature region correlates favorably with both this study and the work of Paladino.

The measurements of Walters and Grace (9) were made by an electrical conductivity technique. They observed an activation energy of only about 6 kcal/mole which is much less than either the results of this study or of Paladino. The reasons for this difference are not understood. However, they did note a difference between samples (as shown by the two lines) which possibly could account for some of the observed differences.

The difference in defect concentrations existing in the crystal in equilibrium with the reducing atmosphere and at 0.03 atm oxygen pressure can be calculated from the values of ΔP_i obtained from Eq. [4]. Table I lists the average change in defect concentrations. The large deviations were due to interactions between the gas and the system. These interactions resulted from the use of reducing gases and are much larger than the detectability limit of the system (4 × 10⁻⁹ moles oxygen).

The results obtained from making exchanges with no sample in the apparatus showed that the pressure change occurring with the system alone amounted to as much as 20% of that occurring with the sample; however, this interaction ceased in less than 15 min which is short compared to the total exchange times of 2-24 hr. Since only the latter part of the exchange data was used to make diffusion coefficient calculations, this interaction did not influence diffusion measurements. However, since the defect concentration calculation is dependent upon the total induced pressure change, it is greatly influenced by any gas-system interaction. In fact at the lowest temperature, 700°C, measurements could not be made. At the higher temperatures the interaction places about a 50% scatter in the data. This interaction is a systematic problem which will have to be corrected before precise defect concentration determinations can be made if reducing gases need to be used.

Table I. Oxygen vacancy concentrations in SrTiO₃ single crystal after reduction in CO

| Temperature (°C) | Vacancy concentration (cm ⁻³) |
|------------------|---|
| 775 | 3.5 ± 2.0 × 10 ¹⁷ |
| 850 | 7.8 ± 1.5 × 10 ¹⁷ |
| 950 | 5.6 ± 4.5 × 10 ¹⁸ |
| 975 | 7.6 ± 3.5 × 10 ¹⁸ |

The determination of the chemical diffusion coefficient \tilde{D} , and the oxygen vacancy concentration $[V_{O^{\cdot\cdot}}]$, makes it possible to calculate the oxygen self-diffusion coefficient from the relation (19)

$$D_{O \rightarrow SrTiO_3} = \frac{[V_{O^{\cdot\cdot}}]D_{V_{O^{\cdot\cdot}}}}{N} \quad [10]$$

where N is the total number of oxygen ions in the lattice per cubic centimeter. The oxygen vacancy diffusion coefficient, $D_{V_{O^{\cdot\cdot}}}$, can be calculated directly from the oxygen chemical diffusion coefficient by the relation (11,14)

$$D = (1 + |z|)D_{V_{O^{\cdot\cdot}}} \quad [11]$$

where z is the charge on the diffusing ion which in this case is two. This relationship is valid only when electronic conductivity predominates which is the case for $SrTiO_3$ (10).

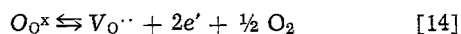
The resulting calculated oxygen self-diffusion coefficient is given by

$$D_{O \rightarrow SrTiO_3} = 60 \exp \left(- \frac{57,000 \pm 16,000}{RT} \text{ cal/mole} \right) \text{ cm}^2/\text{sec} \quad [12]$$

If the assumption is made that the diffusion is via intrinsic defects rather than impurity generated defects, then the activation energy is composed of two separate enthalpy terms according to the relation

$$D_{O \rightarrow SrTiO_3} = D_0 \exp \left(- \frac{\Delta H_m + \Delta H_{V_{O^{\cdot\cdot}}}/3}{RT} \right) \quad [13]$$

where ΔH_m is the enthalpy of motion of a doubly ionized oxygen vacancy plus two electrons, and $\Delta H_{V_{O^{\cdot\cdot}}}$ is the enthalpy of formation of this defect. From the above relation, the energy of formation of doubly ionized oxygen vacancies resulting from the reaction



under the condition

$$[e'] = 2[V_{O^{\cdot\cdot}}] \quad [15]$$

can be calculated to be 126 ± 13 kcal/mole. Within the range of the experimental error, this value is comparable to 133 kcal/mole which was found by Yamada and Miller (10).

The validity of such a calculation is questionable since it requires that the acceptor impurity content be low enough that it does not exceed the native defect concentration. For the specimen used in this study, the total acceptor impurity concentration is reported to be less than 10^{18} atoms/cm³. The measured oxygen vacancy concentrations exceed this level at temperatures above 900°C, however the values obtained at temperatures as low as 775°C did not show any systematic variation which would suggest a shift to extrinsic behavior. Thus, perhaps the actual acceptor impurity might be less than that reported by chemical analysis.

Summary

The correlation between the oxygen vacancy diffusion coefficients obtained in this study and those found in previous determinations adequately demonstrates the applicability of the capacitance manometer system to the measurement of the diffusion coefficient of the rate controlling species. Interactions of the reducing

gas with the system caused a rather large variation in the calculated defect concentration. Even with this difficulty, the calculated enthalpy of formation for the oxygen vacancy was very close to the best value in the literature. This suggests that when this systematic problem has been removed from the system, it should be possible to obtain defect concentration data which are compatible to those obtained by other techniques.

It should also be noted that the apparatus, even when operating in a very insensitive manner as was done here, is capable of determining changes in oxygen content of less than 10^{-5} moles which corresponds to weight changes of less than 10 μ g.

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