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Chikung J. Yu

Don M. Sparlin
Missouri University of Science and Technology, sparlin@mst.edu

Harlan U. Anderson
Missouri University of Science and Technology, harlanua@mst.edu

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Oxidation Kinetics of Polycrystalline LaCrO₃

CHIKUNG J. YU*

Department of Materials Science and Engineering, Northwestern University, Evanston,
Illinois 60201

DON M. SPARLIN* AND HARLAN U. ANDERSON*,†

Department of Physics and Department of Ceramic Engineering, University of Missouri,
Rolla, Missouri 65401-0249

The oxidation kinetics of polycrystalline LaCrO₃ were determined by measuring the time and temperature dependence of the weight and conductivity change of reduced samples. A region of fast diffusion followed by a smaller, slower diffusion "tail" was observed in the thermogravimetric measurements. This observation can be interpreted as the rapid diffusion along the grain boundaries and subsequent diffusion into the body of the grain. The absence of the "tail" in the conductivity measurements is due to the high hole mobility along the boundaries.

THE PEROVSKITE and pseudoperovskite classes of ternary oxides have received considerable interest because of their remarkable range of properties. This study focuses on the kinetic behavior of LaCrO₃. Lanthanum chromite is technologically important as an interconnector and an electrode in fuel cells. A fast diffusion rate of oxygen ions in the electrode material means reversibility of ionic transport, but, in connection with fuel-cell operation, it means the loss of fuel. Therefore, it is important to understand the oxygen transfer rate involved in this material. Since oxygen transport and electrical conductivity are related to the defect concentration, it is important to understand the defect structure of these materials as a function of dopant content, temperature, and oxygen activity. The purpose of the present work is to make a detailed thermogravimetric and electrical conductivity study of the kinetic behavior of undoped and acceptor-doped specimens over the temperature range 1000° to 1300°C.

Previous studies of LaCrO₃ have shown it to be an orthorhombic derivative of the perovskite structure with intrinsic *p*-type conductivity resulting from the formation of cation vacancies.[1] The work of Anderson *et al.*[2] also shows that isovalent Al³⁺ ions on the Cr sites decrease conductivity, whereas Mg²⁺ doping increases it. Under oxidizing conditions, Mg-doped LaCrO₃ has the high conductivity expected of an acceptor-doped *p*-type material.

Several measuring techniques can determine the oxygen diffusivity of a material. Paladino[3] determined the chemical diffusion coefficient of oxygen for single-crystal SrTiO₃ by measuring the time and temperature dependence of the weight gain of reduced crystals. Quite generally, the restoration of equilibrium is brought about by the diffusion of a charged defect, and a diffusion flux will occur in the solid. The net flux of atoms of one species can be expressed by the phenomenological relation called Fick's law:

$$J = -\tilde{D} \; \text{grad} \; C \qquad (1)$$

where *J* is the number of atoms crossing a unit area in unit time, *C* is the concentration of the mobile species, and the constant $\tilde{D}$ is the chemical diffusion coefficient. The minus sign means that diffusion occurs away from regions of high concentration. The chemical diffusion constant is found to vary with temperature as

$$\tilde{D} = D_0 \; \exp(-E/RT) \qquad (2)$$

where *E* is the activation energy of diffusion.

This equation is mathematically analogous to the absorption of heat by a plate that is initially at a uniform temperature and then exposed to a high surface temperature.[4] The rate at which the diffusing substance enters or leaves the plate, as measured by fractional weight changes, is given by

$$W_t/W_\infty = 1 - \sum_{n=0}^{\infty} \{8/[(2n+1)^2\pi^2]\}$$
$$\times \exp\{-\tilde{D}[(2n+1)^2\pi^2t/4L^2]\} \qquad (3)$$

where $\tilde{D}$ is the chemical diffusion coefficient, *t* the time, and *L* the half-thickness of the specimen. By comparison of the experimentally observed weight change with a theoretical plot of W_t/W_∞ vs $(\tilde{D}t/L^2)^{0.5}$, the chemical diffusion coefficient can be calculated. For compounds exhibiting small deviations from stoichiometry, measurement of the change in electric conductivity is often more convenient[5] to use than the weight change. The procedure is essentially the same as for the thermogravimetric measurement except that the ratio of the electrical conductivity at any time, σ_t, to

that after returning to equilibrium, σ_∞, is substituted for the weight-change ratio in Eq. (3). To make this substitution, there must be a known correspondence between the change in weight and the change in electrical conductivity. Two electrons are localized for each oxygen released from the compound and these charged vacancies subsequently serve as donor sites. Therefore, a change in weight is equivalent to a change in the concentration of donor sites. The electrical conductivity ratio can be substituted for percent weight change if the mobility of the charge carrier does not change over the range of oxygen partial pressure studied and the donors are fully ionized.

Diffusion in polycrystalline solids is known to occur along grain boundaries more rapidly than through the interior of the crystals. Many of the kinetic curves found in this study show an extended region of slow exchange that was not expected for a homogeneous system. Therefore, a system consisting of grains and grain boundaries was proposed.[6] The simplest geometry that can be considered is that of parallel grain boundaries embedded in a single-crystal grain. Fisher[7] considered such a geometry when he determined the concentration distribution of diffusing material in a semi-infinite solid having a thin layer or slab of high permeability embedded in it. Since the thickness of the grain boundary is much smaller than that of the grain, any set of parallel slab grain boundaries and their adjacent grains will be similar to Fisher's model. The solution of a parallel slab model can be represented in a matrix representation as

$$C_{j+1} = (A+I)C_j + B \qquad (4)$$

where *I* is the identity matrix, *B* a column vector of constants, *C* the concentration vector that contains all the discrete concentrations, C_j, in the specimen, and *A* is a matrix operator. Once the concentration distribution of diffusing material within any grain and grain boundary is calculated, the concentration distribution for the whole specimen will be known. Moreover, the total amount of diffusing material penetrating into the specimen within a particular time interval can be calculated by summing the variation of concentrations.

EXPERIMENTAL PROCEDURES

The liquid mix technique first proposed by Pechini[8] was used to prepare the powders for these experiments. The compositions used were acceptor-doped (5 mol% Mg) and undoped polycrystalline LaCrO₃. The large-cation-to-small-cation ratio was maintained equal to 1 within experimental error. Magnesium-doped LaCrO₃ was prepared by dissolving lanthanum and magnesium carbonates and chromium nitrate into ethylene glycol, citric acid, and water solutions. These solutions were then slowly evaporated to an amorphous solid, without the formation of any precipitate. They were then calcined at

800°C to remove the organics and to form the oxides. X-ray diffraction (XRD) analysis showed that no second phase formed, implying that, within the limits of XRD analysis, complete solution of the dopants occurred.

Specimens for the measurements were prepared from the powders by first uniaxially hot-pressing solid cylinders in a graphite die. Densities >95% of theoretical were obtained. Platelike specimens (30 by 5 by 1 mm) for thermogravimetric and electrical conductivity measurements were then cut from the resulting cylinders with a diamond wafering saw. Scanning electron microscopy (SEM) was used to produce photomicrographs of the fracture surfaces of the specimens. The microstructure of $LaCrO_3$ was found to exhibit a grain size ranging from 0.5 to 1 μm.

The thermogravimetric apparatus consisted of a digital balance from which 20 to 30 g of platelike specimens could be suspended in a vertical Mo wire wound tube furnace that was sealed from the atmosphere. The composition of the furnace atmosphere could be controlled by flowing gas mixtures composed of forming gas (90% N_2 and 10% H_2), CO_2, N_2, and O_2 through the furnace. When a desired temperature was achieved and full reduction of

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‡Aim 65, Dynatem, Irvine, CA.
§Model 3497A, Hewlett-Packard, Loveland, CO.

the specimen had occurred, the experiment was initiated by taring the balance and then measuring the relative weight change that occurred when the atmosphere was changed from that of reducing gas to oxygen. The weight changes were monitored with a microcomputer‡ that collected data every 2 s. When no further response was observed, the system was assumed to be at equilibrium. The procedure was then repeated to ensure reproducibility. The furnace was then set to a new temperature. Weight changes within 0.1 mg were detectable with the balance, but an inaccuracy of ≈0.3 mg existed because of the fluctuations of temperature and buoyancy of the gas. The temperature was controlled to within 2°C.

The diffusion rates were determined by reducing the specimens in the forming gas followed by oxidizing in oxygen. The onset of oxidation was difficult to determine because of a sudden shift in the rest point of the balance when the gas was switched. This imbalance, which was caused by differences in the flow rates and buoyancies, was corrected by making trial runs using alumina slabs. The actual kinetic data were corrected by adding the weight change of buoyancy to the measured values.

A four-probe measuring system was used to measure the ac electric conductivity of the specimens. An ac current with frequency of 400 Hz was passed through a series reference resistor and the specimen;

the potential drops across the specimen (V_s) and reference resistor (V_r) were recorded with a microcomputer.[§] The conductivity of the specimen was found from the ratio V_r/V_s, the resistance of the reference resistor, and the dimensions of the specimen. A lock-in amplifier was used to measure the component of V_s in phase with V_r. Temperature control was maintained to within 2°C by a time proportioning controller. Accuracy of the resistance measurements was within 0.01 Ω.

RESULTS AND DISCUSSION

The polycrystalline body in the present diffusion model is assumed to consist of identical slab-shaped grains with thin grain boundaries embedded between them. Grain-boundary diffusion is assumed to occur rapidly relative to lattice diffusion, so that the grain boundary is almost completely oxidized first, followed by oxygen diffusion into the grains from the oxygen-enriched grain boundaries.

The grain boundaries can act as sources of, and sinks for, lattice defects and impurities. As a result, a substantial amount of oxygen may be captured by these layers during the oxidation process. This behavior can also be described as a grain-boundary enrichment process for the formation of oxygen-enriched layers at or near the grain boundaries.

Typical results of weight change versus time are displayed in Fig. 1. Figure 1(A) shows the data points plotted as
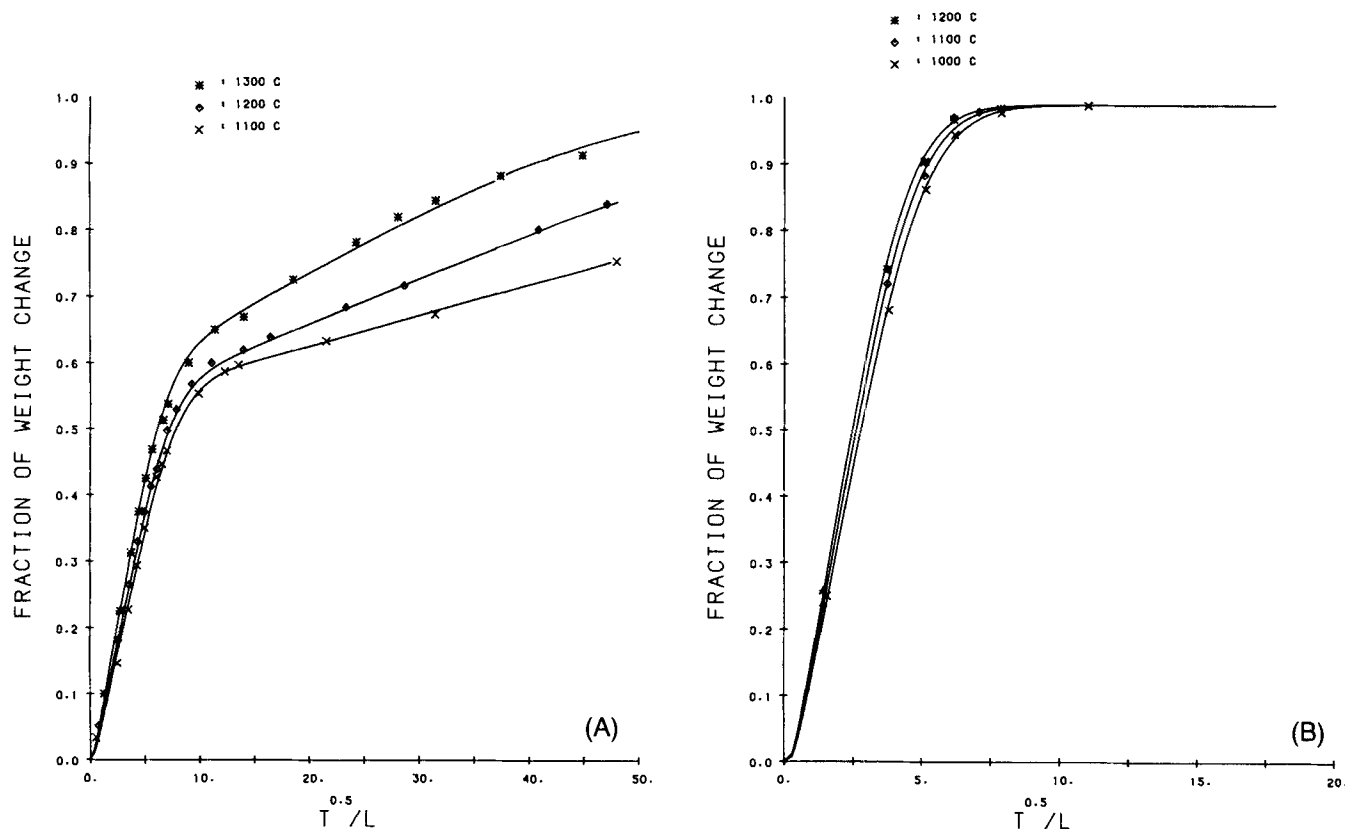

Fig. 1. Plots of weight change vs time for (A) undoped $LaCrO_3$ and (B) Mg-doped (5 mol%) $LaCrO_3$; curves displayed are plots of Eq. (4).

weight change versus time for undoped LaCrO₃, whereas Fig. 1(*B*) shows the same for acceptor-doped (5 mol% Mg) LaCrO₃. The solid lines in Fig. 1(*A*) represent the best-fit solution of each set of data to the mathematical expression for a parallel slab model, Eq. (4). Undoped LaCrO₃ is nearly point-defect-free under reducing conditions. As the oxygen activity increases, oxygen is absorbed and the concentration of cation vacancies increases. The transition point between grain-boundary and lattice diffusion indicates that ≈60% of the oxygen gained is captured by either the grain boundaries or those layers adjacent to the grain boundaries. This result suggests that the grain boundaries are acting as sinks for vacancies and become enriched by oxygen.

The addition of acceptors to LaCrO₃ tends to suppress cation vacancies. Under reducing conditions, the oxide contains large concentrations of oxygen vacancies because of the doping of acceptors. As the oxygen activity increases, oxygen is absorbed and the acceptor becomes compensated by the formation of holes. Figure 1(*B*) shows that, for acceptor-doped (5 mol% Mg) LaCrO₃, no significant lattice diffusion was observed. The insignificant lattice diffusion is believed to be due to a combination of the accumulation of oxygen vacancies at the grain boundaries and the small grain size, 1 μm.

Typical results for electrical conductivity change versus time are displayed in Fig. 2. The diffusion coefficients are consistent with the grain-boundary diffusion coefficients calculated from the corre-

sponding thermogravimetric analysis (TGA) measurements listed in Table 1. Lattice diffusion was not observed in any of the specimens investigated, implying that the motion of carriers may be negligible in the bulk and that the electrical conductivity changes are dominated by grain-boundary conduction.

For electronic-conducting materials such as LaCrO₃, the electrical conduction mechanism is dependent on the mobility and concentration of electronic species such as holes. The small ion mobilities cal-

culated from the lattice diffusion coefficients by the application of the Einstein equation cannot explain the apparently insignificant contribution of charge carriers in the lattice to the electrical conductivity. Since there are still substantial concentrations of electronic species with their associated ionic species formed by nonstoichiometric reaction in the lattice, then either a small bulk mobility or a high boundary mobility make the electric contribution in the lattice too small to be observed. Alternatively, it is also possible for

Table I.   Chemical Diffusion Coefficients for Polycrystalline LaCrO₃ and Magnesium-Doped (5 mol%) LaCrO₃*

Measuring technique	Type of diffusion	Temp (°C)	Chemical diffusion coefficient (cm²/s)
	LaCrO₃		
Thermal gravimetry	Lattice	1300	0.8×10^{-11}
		1200	0.4×10^{-11}
		1100	0.2×10^{-11}
Thermal gravimetry	Grain-boundary	1300	1.6×10^{-4}
		1200	1.4×10^{-4}
		1100	1.2×10^{-4}
Electrical conductivity	Grain-boundary	1300	2.2×10^{-4}
		1200	1.9×10^{-4}
		1100	1.6×10^{-4}
	Magnesium-doped (5 mol%) LaCrO₃		
Thermal gravimetry	Grain-boundary	1200	3.8×10^{-4}
		1100	3.4×10^{-4}
		1000	3.0×10^{-4}
Electrical conductivity	Grain-boundary	1200	4.8×10^{-4}
		1100	4.2×10^{-4}
		1000	3.7×10^{-4}

*Grain size: 1 μm.

* ' 1300 C
◇ ' 1200 C
× ' 1100 C

(A)

* ' 1200 C
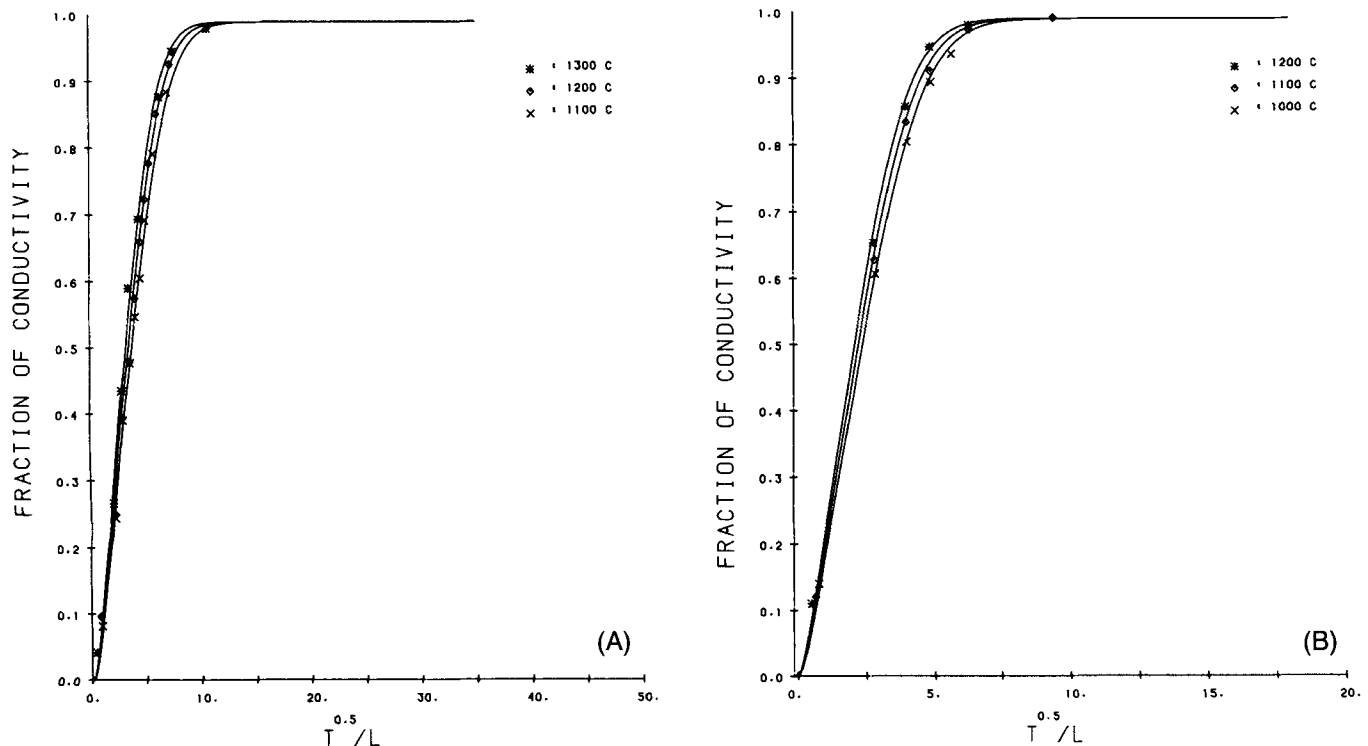◇ ' 1100 C
× ' 1000 C

(B)

Fig. 2.   Plots of electrical conductivity change vs time for (*A*) undoped LaCrO₃ and (*B*) Mg-doped (5 mol%) LaCrO₃; curves displayed are plots of Eq. (3).

Table II.   Temperature Dependence of the Chemical Diffusion Coefficients for Polycrystalline LaCrO$_3$ and Magnesium-Doped (5 mol%) LaCrO$_3$

Measuring technique	Type of diffusion	Temperature dependence
	LaCrO$_3$	
Thermal gravimetry	Grain-boundary	$\tilde{D}_{gb}=1.15\times10^{-3}\exp(-6.2\pm0.3\ \mathrm{kcal}/RT)\ \mathrm{cm}^2/\mathrm{s}$
Thermal gravimetry	Lattice	$\tilde{D}_{gb}=2.35\times10^{-6}\exp(-30.0\pm1.5\ \mathrm{kcal}/RT)\ \mathrm{cm}^2/\mathrm{s}$
Electrical conductivity	Grain-boundary	$\tilde{D}_{gb}=1.95\times10^{-3}\exp(-6.8\pm0.3\ \mathrm{kcal}/RT)\ \mathrm{cm}^2/\mathrm{s}$
	Magnesium-doped (5 mol%) LaCrO$_3$	
Thermal gravimetry	Grain-boundary	$\tilde{D}_{gb}=1.71\times10^{-3}\exp(-4.4\pm0.2\ \mathrm{kcal}/RT)\ \mathrm{cm}^2/\mathrm{s}$
Electrical conductivity	Grain-boundary	$\tilde{D}_{gb}=2.3\times10^{-3}\exp(-4.6\pm0.5\ \mathrm{kcal}/RT)\ \mathrm{cm}^2/\mathrm{s}$

grain boundaries to trap electrons to the depletion of the bulk of a small grain. If this is true, then the equilibrium is expected to be dominated by the grain-boundary process alone. Further changes in electrical conductivity resulting from oxygen absorption by the bulk will be small and probably cannot be measured by the techniques used in this study.

In elemental semiconductors where dangling bonds give rise to a high concentration of surface states at grain boundaries, the sheet conductance in the boundary plane is found to be large.[9] If the surface states are saturated by the uptake of oxygen at boundaries, then an enhanced mobility may be found along the grain boundary. The different chemical composition of grain boundary resulting from an increased defect population might also have an enhanced electronic mobility because of a defect band. In NiO[10] for which the lattice mobility is small, enhanced mobility has been found along boundaries. However, the nature of surface states and boundary mobilities in polycrystalline oxides is virtually unknown.

Good agreement was obtained between the results of thermogravimetric and electrical conductivity measurements for

grain-boundary chemical diffusion over the temperature range studied. The temperature dependence of the grain-boundary and lattice chemical diffusion coefficients determined by a least-squares analysis is given in Table II. A large difference in magnitude of the preexponential term and the activation energy between the grain-boundary and lattice diffusion coefficients indicates that the boundary is indeed a short circuit for diffusion.

CONCLUSIONS

In the present study it was observed that grain-boundary diffusion is more rapid than lattice diffusion in LaCrO$_3$. A substantial amount of oxygen is absorbed in those oxygen-enriched layers adjacent to the grain boundaries. Consequently, diffusion occurs along the grain boundaries and subsequently spreads to the volume of the crystals. As long as the rate of grain-boundary diffusion is several orders of magnitude greater than that of lattice diffusion, the diffusion into the grains is initiated after the boundaries are saturated. This change in the diffusion mechanism accounts for the extended slow uptake of oxygen observed in the thermogravimetric measurements.

There were no regions ascribed to the lattice diffusion observed from the electrical conductivity measurements. This result is thought to be due to the different conduction mechanisms between the boundaries and grains for chemical and electrical transport.

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