

01 Jan 1989

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Recommended Citation

C. J. Yu et al., "High-temperature Defect Structure Of Nb-doped LaCrO₃," *Journal of Solid State Chemistry*, vol. 78, no. 2, pp. 242 - 249, Elsevier, Jan 1989.

The definitive version is available at [https://doi.org/10.1016/0022-4596\(89\)90104-7](https://doi.org/10.1016/0022-4596(89)90104-7)

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High-Temperature Defect Structure of Nb-Doped LaCrO₃

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Received February 23, 1988; in revised form October 24, 1988

Electrical conductivity and Seebeck measurements on LaCr_{0.98}Nb_{0.02}CrO₃ show that the defect structure of the material is mainly controlled by the extrinsic electrons formed by the Nb donors through the electronic compensation process. The experimental results also indicate that this material conducts electricity via a small polaron mechanism with an electron mobility around 0.004–0.01 cm²/V sec between 1100 and 1300°C. © 1989 Academic Press, Inc.

I. Introduction

The perovskite and pseudoperovskite classes of ternary oxides have received considerable interest due to the remarkable range of properties which they display. Lanthanum chromite has technological importance as an interconnector and as an electrode material in fuel cells. Previous studies (1) on LaCrO₃ have shown it to be an orthorhombic derivative of the perovskite structure with intrinsic *p*-type conductivity due to the formation of cation vacancies. The work of Anderson *et al.* (2) shows that under oxidizing conditions Mg-doped LaCrO₃ has the enhanced conductivity expected of an acceptor-doped *p*-type material. Little work has been reported on donor-doped LaCrO₃. We have measured some of the electrical properties of donor-doped LaCrO₃ so that the defect structure might be better understood.

II. Experimental Procedures

The liquid mix technique first proposed by Pechini (3) was used to prepare the powder for this experiment. The specimen used was Nb-doped polycrystalline LaCrO₃. The sample composition was LaCr_{0.98}Nb_{0.02}O₃. Quantitative amounts of a solution containing Nb⁵⁺, La carbonate and Cr nitrate were dissolved into ethylene glycol, citric acid, and water to prepare Nb-doped LaCrO₃. This solution was then slowly evaporated to an amorphous solid, without the formation of any precipitate, and calcined at 800°C to remove the organics and to form the oxides. X-ray diffraction analysis showed that no second phase formed. This implies that within the limits of XRD analysis complete solution of the dopants occurred.

Specimens for the measurements were prepared from the powder by uniaxially hot pressing solid cylinders in a graphite die. After hot pressing at approximately 1400°C, densities of greater than 95% of theoretical

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were obtained. The resulting cylinders were then cut with a diamond wafering saw into specimens with dimensions of $30 \times 5 \times 1$ mm for thermogravimetric and electrical conductivity measurements and $4 \times 4 \times 12$ mm for the determination of thermoelectric power (Seebeck effect).

The thermogravimetric apparatus consisted of a digital balance from which slabs could be suspended and sealed from the ambient atmosphere in a vertical Mo wire-wound tube furnace. The composition of the furnace atmosphere could be controlled by flowing gas mixtures composed of forming gas (90% N₂ and 10% H₂), CO₂, N₂, and O₂ through the furnace. The weight changes were monitored with a microcomputer (Rockwell Aim 65) that collected data every 2 sec. When no further weight change was observed the system was assumed to be at equilibrium. The procedure was then repeated to ensure reproducibility. The furnace was then raised to a new temperature. Weight changes of 0.1 mg were detectable with the balance. The temperature was controlled within 2°C.

Electrical conductivity measurements were made by attaching Pt wire probes to rectangular shaped specimens. The specimens were notched to assist in the Pt wire attachment. The Pt to sample contacts were further enhanced by the application of Pt paste between the wires and specimens. A four-probe measuring system was used to measure the electrical conductivity of the specimens. An ac current with a frequency of 400 cycles/sec was passed through a reference resistor and the specimen in series. The potential drops across the specimen (V_s) and the reference resistor (V_r) were recorded by means of a microcomputer data acquisition system (Hewlett-Packard Model 3497A). The conductivity of the specimen was found from the ratio V_s/V_r , the resistance of the reference resistor, and the dimensions of the specimen. Temperature control was maintained to within 2°C.

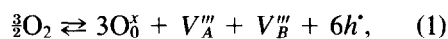
Accuracy of the resistance measurements was to within 0.01 ohm.

The Seebeck coefficient measurements were performed using a rectangular sample bar, $4 \times 4 \times 12$ mm, which was placed between independently heated Pt blocks. Two Pt-Pt/Rh thermocouples were placed in thermal and electrical contact with the Pt blocks. The whole system was placed in a MoSi₂ furnace and heated to a constant temperature. After constant temperature was achieved, one Pt block was heated to establish a thermal gradient across the specimen.

A fixed oxygen activity was maintained during the measurement procedure. The electric potential and temperature differences between the two thermocouples enabled graphs of the dependence of ΔV on ΔT to be plotted. The Seebeck coefficient was obtained from the slope of ΔV versus ΔT .

III. Model Development

The defect structure of donor-doped (Nb) polycrystalline LaCrO₃ was investigated by measuring the equilibrium electrical conductivity, Seebeck voltage, and weight change as functions of oxygen activity and temperature. To facilitate the discussion of the defect model for a ternary oxide of the type ABO_3 , it is helpful to consider a Kroger-Vink diagram. Figure 1 illustrates the variation of defect concentration as a function of oxygen activity for the case of electronic compensation of a donor dopant. For the undoped compound with fully ionized atomic defects, the oxidation reaction is given by the reaction



Where V_A''' and V_B''' are triply ionized vacancies, and h^{\cdot} is the electron hole. The electron concentration is fixed by the Nb concentration as the donor is added to the

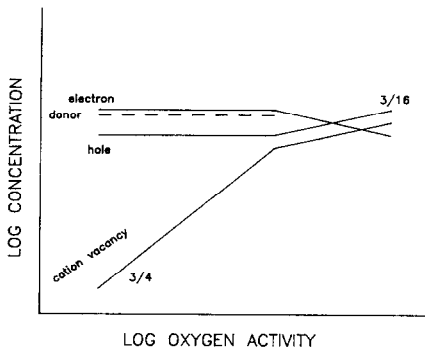


FIG. 1. Defect concentration vs oxygen activity for a donor-doped ternary oxide in which charge neutrality is maintained by formation of an electronic defect.

ternary oxide. The condition of charge neutrality is

$$2[D''] = C_n = \text{constant}, \quad (2)$$

where D'' represents $\text{Nb}_{\text{Cr}}^{\bullet}$, which is a fully ionized substitutional Nb on the Cr site, and C_n is the extrinsic electron concentration. By combining the corresponding mass action expression of the oxidation reaction and the neutrality condition, it is found at low oxygen activity that the concentration of cation vacancies increases as the $\frac{3}{4}$ power of oxygen activity. As the oxygen activity increases, the hole concentration eventually becomes greater than the electron con-

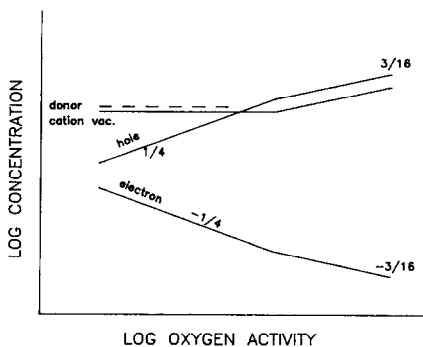


FIG. 2. Defect concentration vs oxygen activity for a donor-doped ternary oxide in which charge neutrality is maintained by formation of a cation vacancy.

centration and the material becomes a p -type conductor with a $\frac{3}{16}$ power dependence on oxygen activity.

In Fig. 2, donors create cation vacancies through an ionic compensation process. The neutrality condition is

$$2[D''] = 3[V_A'''] + 3[V_B'''] \quad (3)$$

and the concentration of cation vacancies is fixed by the Nb concentration. The combination of the mass action expression of the oxidation reaction and the neutrality condition shows that the electron concentration varies as the $-\frac{1}{4}$ power of the oxygen activity and the hole concentration as the $\frac{1}{4}$ power of the oxygen activity. As the oxygen activity increases it may be possible for the conductivity to be controlled by the intrinsic nonstoichiometric defects of the oxide, thereby masking the effect of the donor additions. In that case, p -type conduction with a $\frac{3}{16}$ power dependence on oxygen activity is observed.

IV. Results and Discussion

Plots of the Seebeck coefficient of 2 m% Nb-doped LaCrO_3 vs oxygen activity for three different temperatures are shown in Fig. 3. The oxygen activity at which the values of the Seebeck coefficient change their sign shifts to higher oxygen activity with increasing temperature. This shift indi-

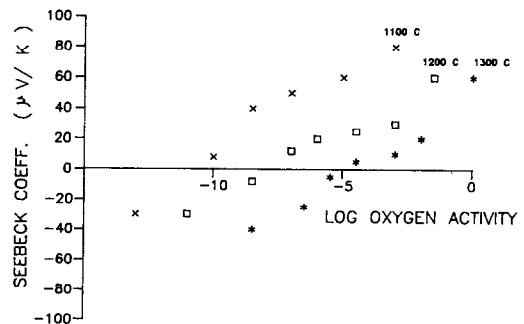


FIG. 3. Measured Seebeck coefficient as a function of oxygen activity and temperature.

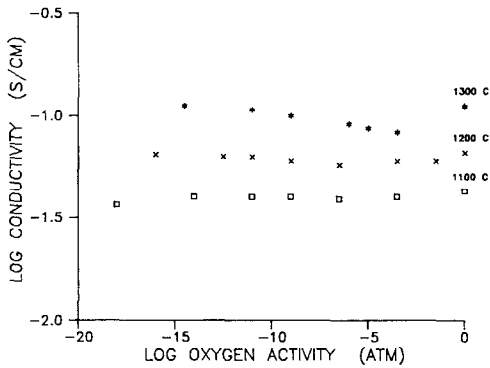


FIG. 4. Measured electrical conductivity as a function of oxygen activity and temperature.

icates that n -type conduction is favored by higher temperature.

Figure 4 shows a plot of log electrical conductivity of 2 m% Nb-doped LaCrO₃ versus log oxygen activity for three different temperatures. For oxygen activity below 10^{-5} atm., the electrical conductivity is not sensitive to the oxygen activity. This indicates that a constant carrier concentration exists at lower oxygen activity. The only carrier whose conductivity predominates in this oxygen activity region with a constant carrier concentration is the extrinsic electron. The extrinsic electrons originate from the ionic compensation of the donors in the system and their concentration is fixed by the donor level. In the region of higher oxygen activity, the electrical conductivity increases slightly with oxygen activity for all the temperatures investigated. Since the creation of intrinsic electrons is strongly suppressed in the high oxygen activity region and the concentration of extrinsic electrons is fixed by the donor content, the only carrier which can contribute to the increment of electrical conductivity is the hole which originates from the native oxygen excess nonstoichiometry of p -type LaCrO₃. Since the increment of electrical conductivity is so small, hole conduction is not expected to predominate in this region.

It has been shown by Mizusaki *et al.* (4, 5) that at a fixed temperature the thermoelectric power can be expressed as a function of carrier concentration by the relations

$$Q_n = -k/e \ln[(1 - x_n)/x_n] \quad (4)$$

and

$$Q_p = k/e \ln[(1 - x_p)/x_p] \quad (5)$$

where Q_n is the Seebeck coefficient for electrons and Q_p is that for holes, k is the Boltzmann constant, and x_n and x_p are the molar fractions of the n -type and p -type carriers, respectively. The Seebeck coefficient, Q , of the material is

$$Q = (\sigma_n Q_n + \sigma_p Q_p) / (\sigma_n + \sigma_p), \quad (6)$$

where σ_n and σ_p are the electrical conductivities resulting from electrons and holes, respectively. The electrical conductivity can then be expressed as

$$\sigma = e\mu_n C_n + e\mu_p C_p, \quad (7)$$

where μ_n and μ_p are the mobilities for electrons and holes, respectively, σ the electrical conductivity, e the unit charge, and C_n and C_p the concentrations of electrons and holes. The concentration of electrons and holes can be related to their mole fraction by

$$C_n = Ax_n/V \quad (8)$$

and

$$C_p = Ax_p/V, \quad (9)$$

where A is Avogadro's constant, and V the molar volume of LaCrO₃

It is assumed that the reference point under reducing atmosphere is LaCr_{0.98}Nb_{0.02}O₃ with the Nb in complete solid solution. The neutrality condition thus becomes

$$2[\text{Nb}^{**}] + C_p = C_n, \quad (10)$$

where $[\text{Nb}^{**}]$ is the concentration of fully ionized Nb. It is possible that Nb either

forms a second phase with oxygen or is just partially ionized; however, the TGA data (which will be shown later) agrees with the assumption that the Nb is fully dissolved in the solid solution.

Karim and Aldred (6) have performed extensive electrical conductivity, Seebeck measurements, and magnetic susceptibility measurements on undoped and Sr-doped LaCrO_3 and have presented convincing evidence that the electrical conductivity obeys a small polaron conduction mechanism with a hole mobility equal to approximately $0.25 \text{ cm}^2/\text{V sec}$ at 1200°C . Flandermeyer (7) has made measurements on Mg-doped LaCrO_3 which yield a hole mobility of $0.05 \text{ cm}^2/\text{V sec}$ in the temperature range between 1200 and 1300°C . If the hypothesis is made that the amount of donor added to the oxide is too small to alter the band structure, then hole mobilities measured by the previous studies can be combined with the measurements from this study to determine the electron and hole concentrations as a function of oxygen activity and temperature.

For small values of electron and hole concentrations, Eq. (4) and (5) can be simplified to

$$Q_n = k/e \ln(x_n) \quad (11)$$

and

$$Q_p = -k/e \ln(x_p), \quad (12)$$

which, when combined with Eqs. (6)–(10) and the hole mobility under reducing conditions, yield the expressions for the electron mobility and the product of Seebeck coefficient and electrical conductivity,

$$\mu_n = \{\sigma - eA\mu_p(x_n - 2x_d)/V\}/(eAx_n/V) \quad (13)$$

and

$$Q\sigma = \{Ak\mu_n x_n \ln(x_n)\}/V - \{Ak\mu_p(x_n - 2x_d)\ln(x_n - 2x_d)\}/V, \quad (14)$$

respectively, where x_d is the mole fraction of Nb. Using Seebeck and electrical con-

ductivity data measured under reducing conditions, the values of electron mobility and electron mole fraction in reducing atmospheres can be calculated. As the oxygen activity increases, the neutrality condition of Eq. (10) is no longer valid due to the formation of cation vacancies. The general expression for the neutrality condition needs to be used. This expression is given by

$$2[\text{Nb}'''] + C_p = C_n + 3[V_m'''], \quad (15)$$

where $[V_m''']$ is the concentration of cation vacancies. Since the value of the electron mobility is known from Seebeck and electric conductivity measurements under reducing conditions, the variation of the electron and hole mole fraction as a function of oxygen activity can be calculated from Eq. (16) and (17). They are

$$x_p = \{\sigma - eA\mu_n x_n/V\}/(eA\mu_p/V) \quad (16)$$

and

$$Q\sigma = Ak\mu_n x_n \ln(x_n)/V - Ak\mu_p x_p \ln(x_p)/V. \quad (17)$$

If Nb is forming a second phase or if cation vacancies exist in reducing atmospheres with a reference point equal to $\text{LaCr}_{0.98}\text{Nb}_{0.02}\text{O}_{3+2x}$, Eq. (10) remains valid for the calculation of electron mobility but the mole fraction of donors in the equation must be decreased by the value of $2x$. Once the concentrations of electrons and holes are known, the concentration of cation vacancies can be calculated from their respective neutrality conditions. Figure 5 shows the weight change versus oxygen activity at 1100°C . The solid lines correspond to the weight change due to the formation of cation vacancies calculated from the Seebeck and electrical conductivity measurements for various percentages of the added Nb forming a second phase. These results suggest that the Nb is fully dissolved in the solid solution with no evidence of the for-

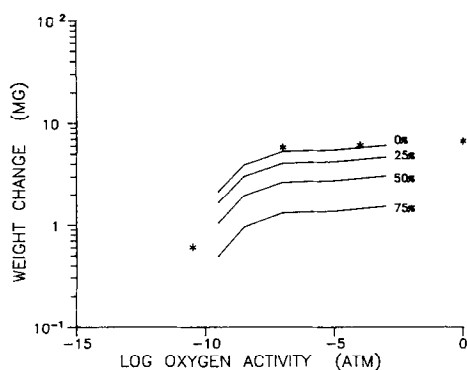


FIG. 5. Measured weight change vs oxygen activity at 1100°C. The curves displayed are the corresponding vacancy concentration change calculated from Seebeck and conductivity measurements for various percentages of the added Nb forming a second-phase rather than solid solution.

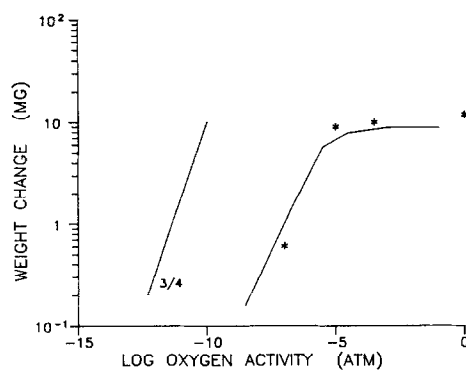


FIG. 7. Measured weight change vs oxygen activity at 1300°C. The solid line is the corresponding weight change due to the vacancy concentration change calculated from Seebeck and conductivity measurements.

mation of a second phase. Figures 6 and 7 show the experimental results for weight change versus oxygen activity at 1200 and 1300°C, respectively. The solid lines are calculated weight changes versus oxygen activity due to the formation of cation vacancies with the assumption that Nb does not form a second phase. The hole mobility used here is $0.05 \text{ cm}^2/\text{V sec}$ as determined by Flandermeyer (7). The variation of cat-

ion vacancy concentration as a function of oxygen activity at the threshold point (sharp weight change) has a slope close to $\frac{3}{4}$ in agreement with the defect model shown in Fig. 1. Figure 8 shows the variation of electron mole fraction as a function of oxygen activity. In reducing atmospheres, all the calculated electron mole fractions have values close to 0.04 which is the maximum

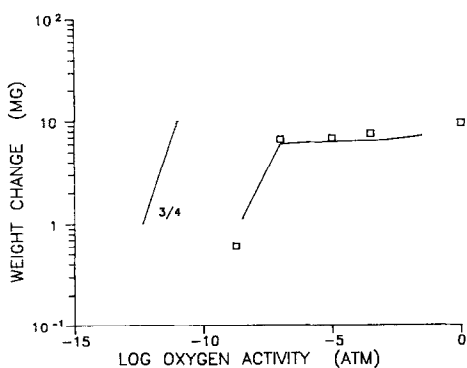


FIG. 6. Measured weight change vs oxygen activity at 1200°C. The solid line is the corresponding weight change due to the vacancy concentration change calculated from Seebeck and conductivity measurements.

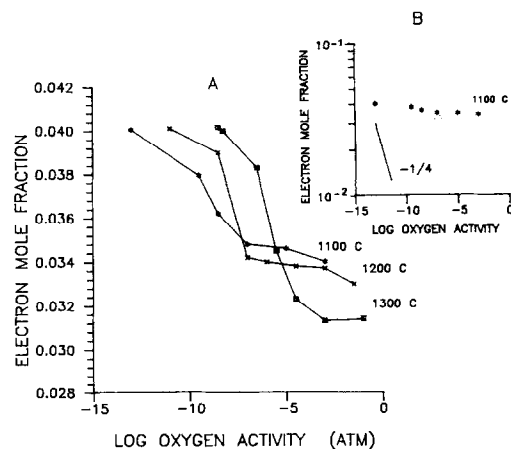


FIG. 8. (A) Calculated electron mole fraction vs log oxygen activity for various temperature. (B) Calculated electron mole fraction in logarithmic scale vs log oxygen activity at 1100°C.

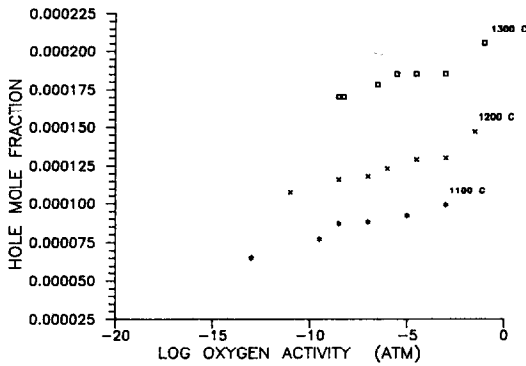


FIG. 9. Calculated hole mole fraction vs log oxygen activity for various temperatures.

electron mole fraction predicted by electronic compensation of the donors.

However, as can be seen in Fig. 8B, the slope of the electron mole fraction versus oxygen activity on a logarithmic scale is more shallow than $-\frac{1}{4}$.

In the highest oxygen activity range, if cation vacancies rather than electrons compensate the donor, then Fig. 2 predicts that the electron concentration should vary as the $-\frac{1}{4}$ power of the oxygen activity and the hole concentration should start to dominate the neutrality conditions. The electron concentration does decrease at the threshold points; however, due to the high Nb concentration (2 m%), the hole concentrations are suppressed to the point that only a small increase in hole concentration occurs (Fig. 9) and the oxygen dependencies predicted in Fig. 2 do not occur. This suggests that electronic compensation dominates the process even under oxidizing atmospheres. Perhaps if the oxygen activity could be increased to several orders of magnitude higher than 1 atm, the predicted behavior could be observed. Our experimental conditions did not allow this to occur.

The self consistency of the calculation of the electron and hole concentrations can be checked by the np product expression

$$x_n x_p = K_i, \quad (18)$$

where K_i is the equilibrium constant of ionization. The equilibrium constant should be independent of oxygen activity at a fixed temperature. Figure 10 shows the results of K_i versus oxygen activity for various temperatures. Comparison of each of the three temperature curves shows that the variances are small compared with their respective means. The activation energy of ionization, which is also the band gap of the material, was determined to be 17.5 ± 2.0 Kcal/mole.

In proposing the above defect model of Nb-doped LaCrO_3 , it is necessary to show that the electrical conduction of this material is small polaron in nature. Goodenough (8) has shown that small polaron mobility can be expressed as

$$\mu = A(1 - x) \exp(-E/kT)/kT, \quad (19)$$

where x is the fraction of occupied states, A is a structural constant, and E is the hopping energy. The values of electron mobility determined by this study are 0.00042, 0.0063, and 0.0011 $\text{cm}^2/\text{V sec}$ for 1100, 1200, and 1300°C, respectively. The hole mobility used here is 0.05 $\text{cm}^2/\text{V sec}$ as determined by Flandermeyer (7). A plot of $\ln(\mu T)$ versus $1/T$ should give a straight line whose slope is proportional to the hopping energy. The results of this plot yield a hop-

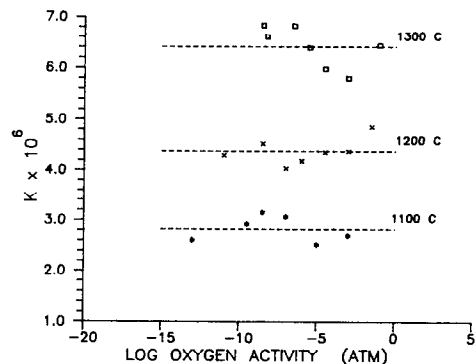


FIG. 10. Equilibrium constant of ionization K vs log oxygen activity for various temperatures. Dashed lines are the average K values.

ping energy equal to 23.4 ± 3.6 Kcal/mole, thus indicating that the hopping model does apply to the motion of electrons in Nb-doped LaCrO₃.

V. Conclusions

The experimental results show that the introduction of donor impurities such as Nb create extrinsic electrons which dominate the defect structure in the low oxygen activity region. As the oxygen activity increases, the electron concentration decreases sharply at threshold values with a corresponding increase of cation vacancies due to the partial transformation from electronic compensation to ionic compensation. As the oxygen activity increases further, a small amount of compensation is provided by intrinsic holes formed from the native oxygen excess nonstoichiometry of the oxide. The concentration of electrons in the material indicates that electrons remain the majority carriers. Therefore, the defect structure is mainly controlled by the extrinsic electrons generated from the Nb donor.

The electron and hole concentration product for each of the three temperatures yields a band gap energy equal to 17.5 Kcal/mole. TGA data agree with the cation vacancy concentrations calculated from Seebeck and electrical conductivity measurements. The corresponding weight change indicates that there is no evidence

of second-phase segregation in the material. The electron mobility data for Nb-doped LaCrO₃ show that this material conducts via a small polaron conduction mechanism with electron mobilities ranging from 0.004 to 0.01 cm²/V sec in the temperature range between 1100 and 1300°C.

Acknowledgments

The authors extend their appreciation for the support received from the Basic Energy Science Division of the Department of Energy. The authors also thank Dr. Jen-Ho Kuo and George Carini for their assistance in the Seebeck and the electrical conductivity measurements.

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