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Oxygen Activity Dependence Of The Electrical Conductivity Of Li-Doped Cr₂O₃

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the ideal shapes shown in Figs. 3(c) and 3(d) of Ref. 13. It appears that the principal discrepancy between actual and desired index profiles is the failure to achieve a low index at the outer interface.

Achieving low indices at the outer interface requires a very special combination of microstructure and dissolution kinetics. If the interconnected microstructures possess small-diameter regions, or necks, the film will become mechanically unstable when the dissolution distances in the more-resistant phase approach the neck radius. This instability can occur while there is still appreciable solid phase remaining at the surface. Thus, many iterations of heat treatments and acid treatments are anticipated during the optimization of optical properties.

This research has demonstrated proof-of-concept and has set the basis for process optimization. As was the case with the borosilicate glass,³ these results show that the exact nature of these GIAR films is difficult to characterize by simple microstructural models.

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References

- ¹M. J. Minot, "Single Layer, Gradient Refractive Index Antireflection Films Effective from 0.35 to 2.5 μ ," *J. Opt. Soc. Am.*, **66** [6] 515-19 (1976).
- ²A. Iqbal, "Determination of Surface Chemistry of Graded-Index Antireflection Films on Glass"; M. S. Thesis, Massachusetts Institute of Technology, 1981.
- ³A. Iqbal, S. C. Danforth, and J. S. Haggerty, "Development of Porous Anti-Reflective Films on Borosilicate Glasses," *J. Am. Ceram. Soc.*, **66** [4] 302-307 (1983).
- ⁴V. Tengzelius, "Development of Selectively Etched Films on Phase-Separated Na₂O/CaO/SiO₂ Glass"; M. S. Thesis, Massachusetts Institute of Technology, 1982.
- ⁵D. R. Uhlmann and A. G. Kolbeck, "Phase Separation and the Revolution in Concepts of Glass Structure," *Phys. Chem. Glasses*, **17** [5] 146-58 (1976).
- ⁶P. F. James, "Review Liquid-Phase Separation in Glass-Forming Systems," *J. Mater. Sci.*, **10** [10] 1802-25 (1975).
- ⁷D. G. Burnett and R. W. Douglas, "Liquid-Liquid Phase Separation in the Soda-Lime-Silica System," *Phys. Chem. Glasses*, **11** [5] 125-35 (1970).
- ⁸J. E. Hilliard, "Quantitative Analysis of Scanning Electron Micrographs," *J. Microsc.*, **95** [2] 45-58 (1972).
- ⁹E. E. Underwood, "The Stereology of Projected Images," *J. Microsc.*, **95** [2] 25-44 (1972).
- ¹⁰O. S. Narayanswamy, "A One-Dimensional Model of Stretching Float Glass," *J. Am. Ceram. Soc.*, **60** [1-2] 1-5 (1977).
- ¹¹K. C. Lyon, "Prediction of the Viscosities of Soda-Lime-Silica Glasses," *J. Res. Natl. Bur. Stand. A*, **78A**, 497 (1974).
- ¹²S. C. Danforth and J. S. Haggerty, "Microstructural Characterization of Graded-Index Anti-Reflective Films," *J. Am. Ceram. Soc.*, **66** [1] C-6-C-8 (1983).
- ¹³B. Sheldon, J. S. Haggerty, and A. G. Emslie, "Exact Computation of the Reflectance of a Surface Layer of Arbitrary Refractive Index Profile and an Approximate Solution of the Inverse Problem," *J. Opt. Soc. Am.*, **72**, 1049-55 (1982).
- ¹⁴G. W. Morey, *Properties of Glass*. American Chemical Society, Washington, DC, 1954.

Oxygen Activity Dependence of the Electrical Conductivity of Li-Doped Cr₂O₃

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The electrical conductivity of Li-doped Cr₂O₃ was investigated as a function of P_{O_2} , temperature, and dopant content. Results show that the electrical conductivity remains almost unchanged with decreasing P_{O_2} in the high- P_{O_2} region but decreases rapidly at low P_{O_2} . A second phase was found in samples which contained more than 0.85 mol% Li. The results are explained by a model in which the concentration of charge carriers is dependent on the acceptor dopant and oxygen vacancy concentration.

I. Introduction

RECENT developments in new energy-related systems have resulted in initiation of many investigations of the electrical properties of refractory oxides. Among these oxides, transition metal oxides with their controllable valency states and high melting

points are particularly applicable for high-temperature electrical conduction; however, one of the limitations of utilizing these transition metal oxides is their unstable electrical conductivity that results from changing oxygen activity and temperature. The same material can change from a conductor to an insulator as the oxygen activity varies from one extreme to another. Therefore, to utilize these materials under stable conditions, it is necessary to understand the electrical conductivity dependence on such variables as oxygen activity, temperature, and the type and amount of impurity.

Chromium oxide, with its high melting point ($2266^\circ \pm 25^\circ\text{C}$) and good high-temperature electrical conductivity, is one of the refractory oxides with potential for high-temperature conduction applications. During the past 30 years the conduction behavior of Cr₂O₃ has been studied by a number of investigators. The results of many of these studies have been summarized by Kofstad.¹ The conduction mechanism of Cr₂O₃ can be divided into two types. In the high-temperature region ($\geq 1300^\circ\text{C}$), the conduction mechanism is believed to originate from intrinsic stoichiometric-type behavior with the conductivity showing no oxygen partial pressure dependence. In the lower-temperature region ($\leq 1300^\circ\text{C}$), the conduction is defect-controlled. The defects originate from either native nonstoichiometry or impurities, and oxygen partial pressure dependence is to be expected.

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It is well known that small impurity contents will substantially alter conductivity²; however, little is known about how impurities influence the stability of conductivity as the oxygen activity and temperature are changed. Even though Kröger-Vink diagrams predict that the conductivity does have a strong activity dependence, this predicted P_{O_2} dependence still needs to be confirmed by experiments. These are the problems that this study is addressing.

Most previous investigations used dense, "pure" Cr₂O₃ samples, which in fact contained varying amounts of impurities and were difficult to equilibrate with the ambient oxygen.¹ To help circumvent these problems, the samples used in the present study were prepared with controlled but large amounts of Li to suppress other impurity effects and the specimens were made porous to improve their equilibration with the ambient P_{O_2} .

In this investigation a defect reaction for Cr₂O₃ was developed and the conductivity dependence on oxygen activity, temperature, and amount of Li dopant was investigated. From this, a theoretical model was proposed to account for the observed behavior.

II. Experimental Procedure

Specimens of varying Li content up to 10 mol% were prepared by dissolving chromium nitrate and lithium carbonate in a weak organic acid-ethylene glycol solution using a procedure explained elsewhere.³ Rectangular bars (25 by 6 by 5 mm) were formed by dry-pressing and sintering in air for 6 h at 1400°C. The samples contained approximately 55% of open porosity after sintering. To ensure electrical contact, Pt wires were embedded in the bars during pressing. The Pt electrodes were fused to four Pt leads, which in turn were connected to a four-terminal dc multimeter to measure the dc resistance. The measurements were made in a controlled atmosphere tube furnace using CO₂/H₂ and O₂/N₂ gas mixtures which were monitored by a zirconia oxygen sensor.

The resistance of the sample was measured at a fixed temperature with the oxygen partial pressure being varied from 10⁻¹ to 10⁻²⁴ MPa over the temperature range of 700° to 1000°C. To ensure that the reaction between the sample and ambient atmosphere had reached equilibrium for each datum point, a sufficient time (30 min to 1 h) was allowed for the resistance to reach a stable value.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies as well as chemical analysis were used to establish the presence of second phase and final Li content.

III. Results and Discussion

(1) Solubility Limit of Li in Cr₂O₃

The Li content is determined by wet chemical analysis[†] and the results are shown in Fig. 1. As can be seen, a large proportion, about 80%, of the Li dopant was lost during sample preparation. The same phenomenon, to a lesser degree of severity, was also observed for Li-doped NiO.⁴ Since some water is associated with the powder fabrication process, the severe Li loss is probably due to the formation of LiOH,⁵ which is volatile under the conditions used.

X-ray diffraction analysis of a series of compositions showed a second-phase LiCrO₂ appearing in the samples with Li content higher than 0.8 mol%; however, the sensitivity is such that no lattice parameter shifts were observed with increasing Li content. Scanning electron microscopy examination of oxidized samples containing more than 1 mol% Li clearly showed that a second phase was formed on the surface of Cr₂O₃ grains. These results are in agreement with Hagel's measurements,⁶ provided that the volatilization effect of Li is taken into account. Under reducing conditions, second phase was observed for Li content greater than 2 mol%, indicating that the solubility limit increases as P_{O_2} decreases.

The fact that the lattice parameters do not change with Li content

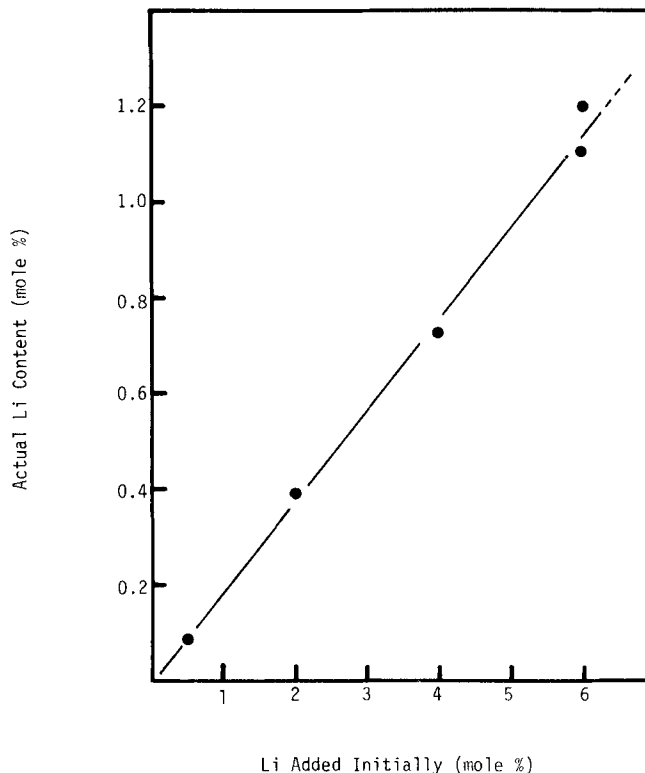
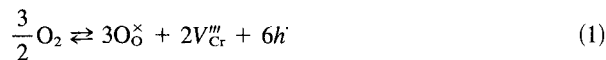


Fig. 1. Chemical analysis of Li-doped Cr₂O₃ plotted as actual Li content vs initial Li content.

makes it difficult to assign Li solubility limits. Judging from the XRD and SEM observations, the solubility limit of Li in Cr₂O₃ is about 0.85 mol% in high oxygen activity but increases to about 2% under reducing conditions since a second phase is found in samples with higher Li content. This suggestion is supported both by the conductivity measurement which will be discussed in this paper and by the thermogravimetric analysis data which is the subject of another report.

(2) Conductivity Measurements

Several studies have shown that Cr₂O₃ is a *p*-type material.⁷⁻⁹ The nonstoichiometry results from the incorporation of excess oxygen through the reaction



where full ionization of the cation vacancy is assumed and Kröger-Vink notation¹ is used.

The equilibrium constant of this reaction then is

$$K_1 = [V_{\text{Cr}}^{\prime\prime}]^2 p^6 P_{O_2}^{-3/2} \quad (2)$$

in which the brackets indicate the activities or concentrations of the enclosed species and p is the electron hole concentration.

If the stoichiometric defect in Cr₂O₃ is assumed to be of the Schottky type, the defect may be described by



The equilibrium constant for such a reaction is

$$K_3 = [V_{\text{Cr}}^{\prime\prime}]^2 [V_{\text{O}}^{\bullet}]^3 \quad (4)$$

Under oxidizing conditions, if an acceptor dopant, such as Li, is added to Cr₂O₃, for every Li ion added, two Cr⁴⁺ ions must be formed to maintain electrical neutrality. However, under reducing conditions, the loss of oxygen from the lattice can also compensate the acceptor by contributing two electrons from every oxygen

[†]Performed by Technical Services Laboratories, Mississauga, Ontario, Canada.

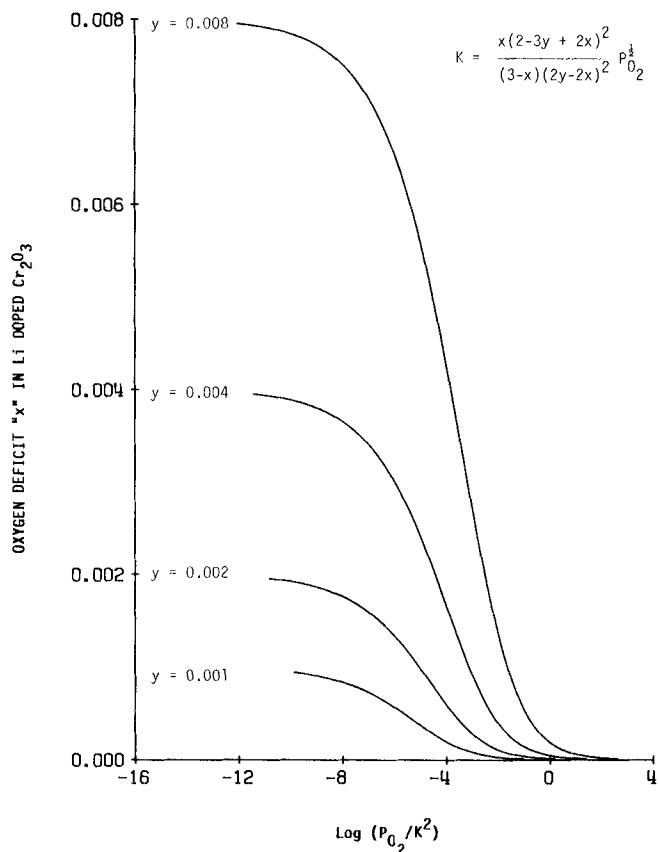


Fig. 2. Theoretical curves of oxygen deficit, x , vs P_{O_2} at doping levels y .

vacancy which will in turn reduce the carrier concentration.

The neutrality condition for the combination of these defects can be expressed as

$$2[V_{O^{\bullet}}] + p = 3[V_{Cr^{\bullet}}] + 2[Li_{Cr}^{\prime\prime}] \quad (5)$$

This assumes that these defects are fully ionized and that Li substitutes for Cr in the structure. For high Li content, Eq. (5) becomes

$$2[V_{O^{\bullet}}] + p \approx 2[Li_{Cr}^{\prime\prime}] \quad (6)$$

or

$$p = 2y - 2x \quad (7)$$

where x and y are the concentrations of oxygen vacancies and Li, respectively.

The combination of Eqs. (2) and (4) yields

$$\frac{K_3}{K_1} = \frac{[V_{O^{\bullet}}]^3}{p^6} P_{O_2}^{3/2} \quad (8)$$

By substituting Eq. (7) into Eq. (8)

$$\left(\frac{K_3}{K_1}\right)^{1/3} = \frac{x}{[2(y-x)]^2} P_{O_2}^{1/2} \quad (9)$$

Equation (9) can be further simplified to

$$x^2 - x\left(2y + \frac{P_{O_2}^{1/2}}{c}\right) + y^2 = 0 \quad (10)$$

in which

$$c = 4\left(\frac{K_3}{K_1}\right)^{1/3} \quad (11)$$

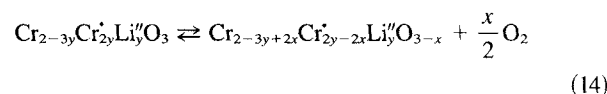
The oxygen deficit, x , can be obtained by solving Eq. (10):

$$x = \frac{\left(2y + \frac{P_{O_2}^{1/2}}{c}\right) - \left[\frac{P_{O_2}^{1/2}}{c}\left(4y + \frac{P_{O_2}^{1/2}}{c}\right)\right]^{1/2}}{2} \quad (12)$$

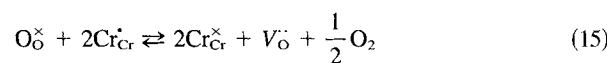
The carrier concentration is given by substituting Eq. (12) into Eq. (7):

$$p = \frac{P_{O_2}^{1/2}}{c} [(4ycP_{O_2}^{-1/2} + 1)^{1/2} - 1] \quad (13)$$

An equivalent way of expressing the variation in neutrality condition with oxygen activity is to write the following oxidation-reduction reaction:



This reaction can be simplified so that it deals only with the reactants and products:



The equilibrium constant for Eq. (15) is then

$$K_{15} = \frac{[Cr_{Cr}^{\times}]^2[V_O^{\bullet}]}{[O_O^{\times}][Cr_{Cr}^{\times}]^2} P_{O_2}^{1/2} \quad (16)$$

which on substituting the molar concentrations into Eq. (16) becomes

$$K_{15} = \frac{x(2-3y+2x)^2 P_{O_2}^{1/2}}{(3-x)(2y-2x)^2} \quad (17)$$

This equilibrium constant is identical to Eq. (9), if the activities of the normal Cr and O sites in the Eq. (16) are unity.

Figure 2 is a plot of Eq. (17), which illustrates that little oxygen deficiency exists in the high- P_{O_2} region, whereas in the low- P_{O_2} region it increases very rapidly. This relation agrees with Kassner *et al.*,¹⁰ who used a different approach to predict the pressure dependence of the vacancy concentration. Because the formation of oxygen vacancies reduces the carrier concentration, the conductivity decreases with decreasing P_{O_2} . Thus the conductivity of Li-doped Cr_2O_3 is expected to have no change in the high- P_{O_2} region, but should decrease rapidly in the low- P_{O_2} region. The details of this influence are discussed below.

(A) *Oxygen Partial Pressure Dependence of Conductivity:*

The electrical conductivity can be expressed as:

$$\sigma = e\mu p \quad (18)$$

in which e is the charge, and μ is the mobility.

By substituting Eq. (13) into Eq. (18)

$$\sigma = e\mu \frac{P_{O_2}^{1/2}}{c} [(4ycP_{O_2}^{-1/2} + 1)^{1/2} - 1] \quad (19)$$

In the high- P_{O_2} region, where

$$4ycP_{O_2}^{-1/2} \ll 1 \quad (20)$$

the expansion of Eq. (19) reduces to

$$\sigma_H = 2e\mu y \quad (21)$$

Thus, the conductivity in the high- P_{O_2} region is dominated by the dopant content y and has no P_{O_2} dependence.

The combination of Eq. (19) and Eq. (21) yields

$$\frac{\sigma}{\sigma_H} = \frac{P_{O_2}^{1/2}}{2yc} [(4ycP_{O_2}^{-1/2} + 1)^{1/2} - 1] \quad (22)$$

The use of this expression allows examination of the temperature and P_{O_2} dependence of conductivity of porous samples, provided the mobility is not concentration-dependent. Since only porous

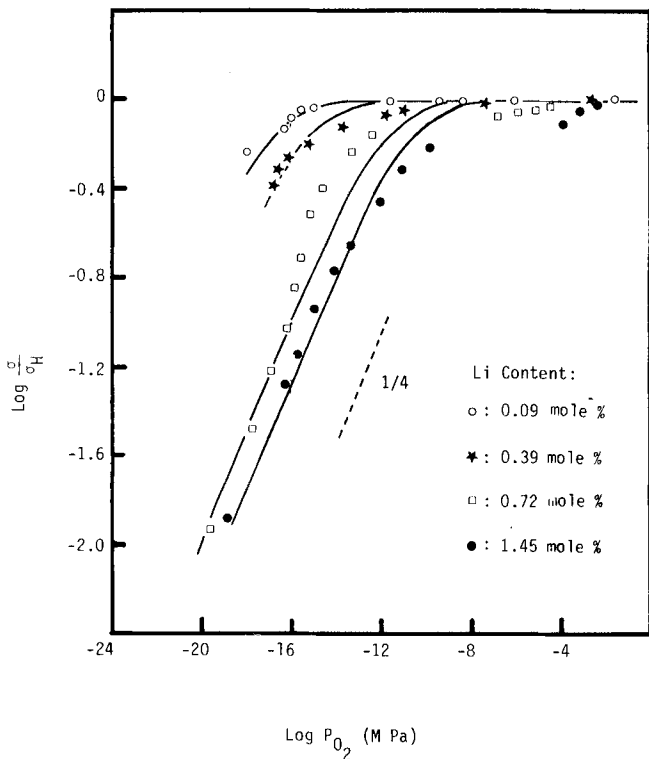


Fig. 3. Conductivity dependence at 1000°C on P_{O₂} for samples with Li contents indicated. Solid curves are theoretical plots of Eq. (22).

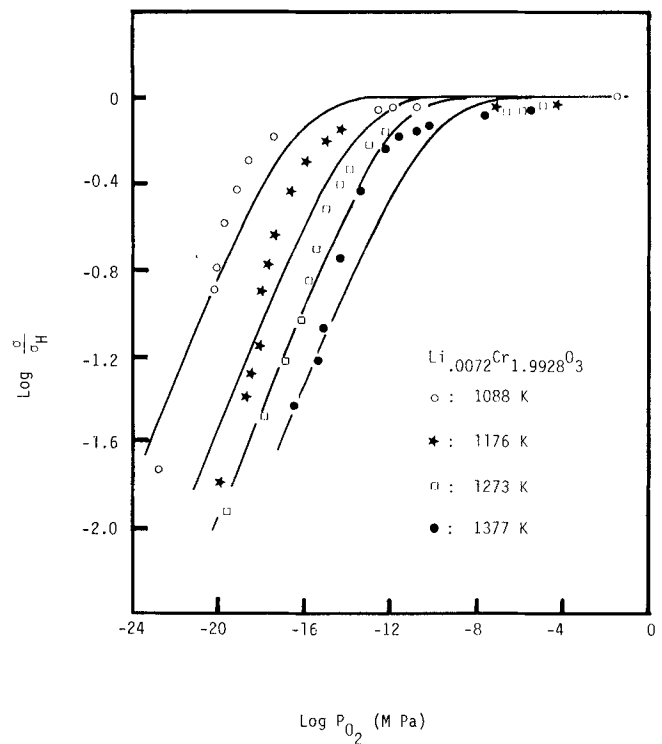


Fig. 4. Conductivity vs P_{O₂} curves for sample doped with 0.72 mol% Li under the influence of temperature. Solid curves are theoretical predictions from Eq. (22).

samples were used in this investigation, only relative values of conductivity are reported and an expression such as Eq. (22) is applied to the results.

In the low-P_{O₂} region where

$$4ycP_{O_2}^{-1/2} \gg 1 \tag{23}$$

Eq. (22) becomes

$$\frac{\sigma}{\sigma_H} = \frac{P_{O_2}^{1/4}}{(yc)^{1/2}} \tag{24}$$

Therefore, the conductivity has a P_{O₂}^{1/4} dependence in the low-P_{O₂} region.

The experimental results of the electrical conductivity dependence on P_{O₂}, measured isothermally for different Li contents, are shown in Fig. 3. The general characteristics of these curves are: (1) The conductivity remains relatively unchanged with little P_{O₂} dependence in the high-P_{O₂} region, (2) the conductivity decreases as about P_{O₂}^{1/4} in the low-P_{O₂} region, and (3) the position of the “transition zone” between the high- and low-P_{O₂} regions is influenced by the Li content and temperature.

(B) *Composition Dependence of Conductivity:* According to Eq. (21), in the high-P_{O₂} region, the conductivity is proportional to the Li content. Thus, the conductivity should increase linearly with Li content within the range of the solid solution of Li in Cr₂O₃ unless a second phase starts to form. This indeed appears to be the case up to the high-P_{O₂} solubility limit of 0.85 mol% Li. However, due to the uncertainties in the effect of porosity, absolute conductivity values obtained by dense samples are needed to confirm this point.

On the other hand, the relative conductivity in the low-P_{O₂} region is inversely dependent on the square root of the Li content, as predicted by Eq. (24). This dependence is observed to the P_{O₂} solubility limit of 2 mol% Li and can be seen qualitatively in Fig. 3.

As mentioned before, the Li content influences the location of

the “transition zone.” By knowing the position of this “transition,” the oxygen activity below which rapid decreases in conductivity are to be expected can be determined. This position can be obtained by determining the location of the inflection point of Eq. (22). This yields the relationship of the form

$$(P_{O_2})_t = (Ay)^2 \tag{25}$$

where A = 10K₁₅ and (P_{O₂})_t is the P_{O₂} where the inflection is located. The precise value of A depends on how the position of the inflection point is defined. Regardless of the value of A, the form of the relation remains the same. The expression indicates that the position of the “transition knee” should shift to higher P_{O₂} as the square of the Li content. This dependence is observed and is qualitatively seen in Fig. 3. Thus, the net result is that the range of stable conductivity decreases as Li content increases.

The fit between the predicted and the observed curves is quite good; however, there is a tendency for the slope of the actual data at P_{O₂} below the inflection point to be steeper than predicted. This is probably due to clustering or complex formation which is not taken into account by the simple model which assumes dilute solution behavior. However, it is obvious that the oversimplified model presented does describe the overall behavior quite well and only deviates at the intermediate-P_{O₂} region. Currently, attempts to extend the simple model to include non-Henry’s law behavior are being made with the intent of achieving a better match between theory and experiment.

(C) *Temperature Dependence of Conductivity:* The temperature dependence of the electrical conductivity is illustrated in Fig. 4. In agreement with Eqs. (24) and (25) in the low-P_{O₂} region, the conductivity decreases and the “transition knee” shifts to a higher P_{O₂} as the temperature increases. Because the conductivity is a function of both carrier concentration and mobility, it is necessary to examine the temperature dependence of these two factors under conditions at which they can be separated. Again it must be pointed out that the lack of agreement between theory and

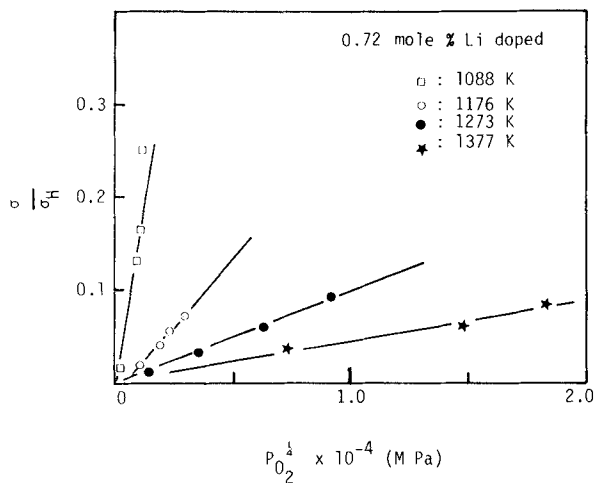


Fig. 5. Plot of relative conductivity in low- P_{O_2} region as a function of $P_{O_2}^{1/4}$ for temperatures indicated.

experiment in the intermediate P_{O_2} region is due to an oversimplified model.

In the high- P_{O_2} region, the carrier concentration is determined by the impurity content and therefore any temperature dependence should be due to the mobility term. In this region a temperature dependence is observed which relates to an activation energy for the mobility of 16.4 ± 3.0 kJ/mol ($\approx 0.17 \pm 0.02$ eV). This value is an average of that obtained for each Li content separately.

In the low- P_{O_2} region, the rapid decrease in carrier concentration is controlled by Eq. (17) and dominates the conductivity. An inspection of Eq. (17) shows that, for a given P_{O_2} , the oxygen vacancy concentration, x , must increase with increasing temperature, because

$$K_{15} = A_0 \exp\left(\frac{-\Delta G}{RT}\right) \quad (26)$$

in which A_0 is a constant, ΔG the Gibbs free energy, R the gas constant, and T the temperature (K). Thus, the overall carrier concentration must decrease with increasing temperature.

The equilibrium constant K_{15} can be obtained from Eq. (24) by plotting σ/σ_H vs $P_{O_2}^{1/4}$ in the low- P_{O_2} region. Such a plot is shown in Fig. 5. The temperature dependence of the equilibrium constant then is found by plotting $\ln K$ vs $1/T$. The plot (Fig. 6) yields a value of 307.7 ± 15 kJ/mol (3.2 ± 0.2 eV) which from Eq. (16) should be the enthalpy of formation of oxygen vacancies in Cr_2O_3 .

Thus, it is evident that both increases in temperature and Li content tend to reduce the P_{O_2} range over which the electrical conductivity can be expected to be invariant.

IV. Conclusions

A model, which appears to explain the experimental results, shows that the electrical conductivity of Li-doped Cr_2O_3 is controlled by the oxygen activity, temperature, and Li content. Among these factors, oxygen activity produces the most profound influence on conductivity. In the high- P_{O_2} region, the conductivity is controlled by the Li content and increases with Li content up to the solubility limit of 0.85 mol% Li. In this region little P_{O_2} dependence is observed, whereas in the low- P_{O_2} region, the conductivity is controlled by the formation of oxygen vacancies and has about a $P_{O_2}^{1/4}$ dependence in this region. The neutrality condition is given by the difference in Li and oxygen vacancy content, so the

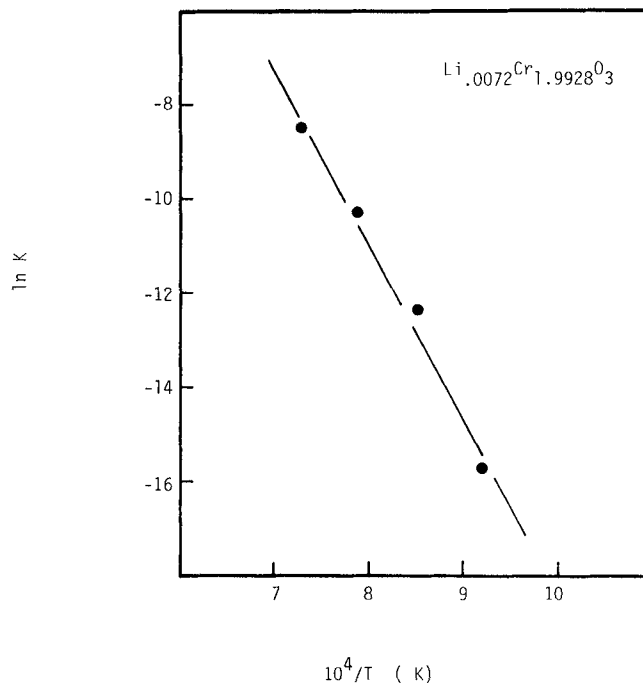


Fig. 6. Plot of equilibrium constant as a function of temperature for sample doped with 0.72 mol% Li.

conductivity decreases with increasing temperature as a result of decreased carrier concentration. The P_{O_2} at which the conductivity starts to decrease increases with increase of either temperature or Li content. As a result the P_{O_2} region over which the electrical conductivity is independent of P_{O_2} decreases with increasing temperature and Li content. The overall agreement between theory and that observed is good except in the intermediate- P_{O_2} region. It is believed that the divergence results from use of a dilute solution model which does not take into account either defect interactions or other reaction mechanisms.

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References

- P. Kofstad; pp. 203–208 in *Nonstoichiometry, Diffusion, and Electrical Conductivity in Binary Metal Oxides*. Wiley-Interscience, New York, 1972.
- R. R. Heikes and W. D. Johnson, "Mechanism of Conduction in Li-Substituted Transition Metal Oxides," *J. Chem. Phys.*, **26** [3] 582–87 (1957).
- M. Pechini, "Method of Preparing Lead and Alkaline Earth Titanates and Niobates and Coatings Using the Same to Form a Capacitor." U.S. Pat. No. 3 330 697, July 1967.
- Y. Iida, "Evaporation of Lithium Oxide from Solid Solution of Lithium Oxide in Nickel Oxide," *J. Am. Ceram. Soc.*, **43** [3] 171–72 (1960).
- A. E. Van Arkel, U. Spitsbergen, and R. D. Heyding, "Note on the Volatility of Lithium Oxide," *Can. J. Chem.*, **38**, 446–47 (1954).
- W. C. Hagel, "Electrical Conductivity of Li-Substituted Cr_2O_3 ," *J. Appl. Phys.*, **36** [8] 2586–87 (1965).
- D. B. Meadowcroft and F. G. Hicks, "Electrical Conduction Processes and Defect Structure of Chomic Oxide," *Proc. Br. Ceram. Soc.*, **23**, 33–41 (1972).
- L. N. Cojocaru, "Electrical Properties of Non-Stoichiometric Cr_2O_3 ," *Z. Phys. Chem., N. F.*, **64**, 255–62 (1968).
- J. A. Crawford and R. W. Vest, "Electrical Conductivity of Single-Crystal Cr_2O_3 ," *J. Appl. Phys.*, **38** [8] 2413–18 (1964).
- T. F. Kassner, L. C. Walters, and R. E. Grace; pp. 357–71 in *Thermodynamics*, Vol. II. International Atomic Energy Agency, Vienna, 1966.