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The Electrical Conductivity of Doped and Undoped Uranium Oxide

Z. A. Munir[1]

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The conductivity of undoped and doped uranium dioxide was investigated over the temperature range of approximately 300–1600 K. Activation energies calculated for the undoped samples and those doped with Cr_2O_3 and Gd_2O_3 are in agreement with previously published values. The values calculated for TiO_2- and La_2O_3-doped samples were nearly twice that for the undoped UO_2. The addition of Nb_2O_5 resulted in the extension of the intrinsic region of conductivity to lower temperatures than had been previously reported. The dependence of the extrinsic conductivity of Gd_2O_3- and Cr_2O_3-doped samples on the dopant level supports an impurity compensation model of conduction.

KEY WORDS: Uranium dioxide; electrical conductivity; dopant effect.

1. INTRODUCTION

The energy difference between valence states of cations in many transition and rare earth metal oxides is sufficiently low to give rise to a valence multiplicity with the concomitant deviation from stoichiometry. For such oxides the existence of ionic defects of one type (cation or anion) requires only electronic compensation by a change of the valence state of the other type. Earlier studies had concluded that the conductivity of such materials was that of classical band semiconductors. Somewhat more recently, however, an alternate model was proposed to explain the abnormally low mobilities observed in these oxides. This model, termed the hopping polaron mechanism, attributes the thermal activation of conduction to the mobility, μ, rather than to the number of charge carrier, i.e., [1],

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[1] Division of Materials Science and Engineering, College of Engineering, University of California, Davis, California 95616, USA.

$$\mu = [(1 - f)e\delta_0 a^2/\tau_0 kT] \exp(-E_m/kT), \tag{1}$$

where f is the fraction of sites at which electrons are localized, δ_0 is the fraction of jumps in a certain direction, e is the charge of the electron, $1/\tau_0$ is the phonon frequency, a is the lattice spacing, and E_m is the activation energy for hopping. In contrast, the activation energy for the conductivity of a classical band semiconductor is associated with the intrinsic concentration of charge carriers n, i.e.,

$$n = n_0 \exp(-E_g/2kT), \tag{2}$$

where E_g is the difference in energy between the top of the valence band and the bottom of the conduction band and

$$n_0 = 2(2\pi\, m^*\, kT)^{3/2}\, h^{-3}. \tag{3}$$

Here m^* is the effective mass of the carrier and h is Planck's constant. The conductivity can, therefore, be expressed as

$$\sigma = n_0 \cdot e \cdot \mu \exp(-E_g/2kT), \tag{4}$$

where e is the charge of the carrier. As pointed out above, the experimental support of the polaron mechanism came from the observed mobilities. Recent careful investigations [2], however, have shown that the mobilities are not as low as previously believed and that the conductivity of such oxides may be described by the band conduction model.

In uranium dioxide the valence multiplicity of the cation (U^{+4} and U^{+5}) is compensated by excess oxygen incorporated interstitially and giving rise to a composition of UO_{2+x} with $0 \leq x \leq 0.25$. As with other transition and rare earth metal oxides, the electrical conductivity of uranium oxide has been variously interpreted. Aronson et al. [3] suggested a polaron motion as the mechanism for charge transfer. In the more recent work of Lee [4, 5], the conductivity of UO_{2+x} was investigated as a function of temperature and oxygen pressure, P_{O_2}, and is described in terms of band conduction. At any given temperature (between 900 and 1200°C) the conductivity was found to be independent of the oxygen pressure when $P_{O_2} < 10^{-13}$ atm. These conditions represent an oxide composition closest to stoichiometry ($x \sim 0$).

Considerable interest in the doping of uranium oxide has been generated, in part, from the reported influence of certain additives on sintering and grain size development. Large grain size in UO_2 has been associated with a decreased release of fission gas from irradiated nuclear fuel [6]. The explicit role of the additives on the grain growth in uranium dioxide and their implicit role in the defect nature of this ceramic are of practical as well as theoretical interest. In this paper we report the results of an investigation of the influence of various additives on the electrical conductivity of UO_2. The conductivity of undoped and doped (with TiO_2, Nb_2O_5, La_2O_3, Gd_2O_3, and Cr_2O_3) samples was investigated over the temperature range from 300 to 1600 K under a hydrogen atmosphere. The influence of additive concentration on the conductivity of UO_2 was also investigated for the Cr_2O_3 and Gd_2O_3 cases.

2. EXPERIMENTAL MATERIALS AND METHODS

Doped and undoped sintered uranium dioxide samples[2] with densities of 97%+ of the theoretical value were used in this study. The additives and their levels were 0.5 mol% for Nb_2O_5, La_2O_3, and TiO_2; 0.4 and 0.8 mol% for Cr_2O_3; and 1, 2, and 3 mol% for Gd_2O_3. The electrical conductivities of these samples were measured by a four-probe technique [7] using tungsten wire contacts. Measurements were made from room temperature to 1400–1600 K in a flowing pure-hydrogen atmosphere in both increasing and decreasing heating modes at 10-min intervals. The average rate of temperature rise and fall was approximately $2\ \mathrm{K} \cdot \mathrm{min}^{-1}$.

To ensure that the composition of the UO_2 is as close to stoichiometry as possible, all samples were annealed in a pure hydrogen atmosphere prior to their use in the conductivity measurements. The purity of the flowing hydrogen atmosphere was monitored continuously during conductivity measurements by determining the oxygen activity by means of a calcia-stabilized zirconia emf cell which was attached to the flow system downstream from the conductivity measurement cell. Under these conditions it was established that a $P_{O_2} < 10^{-20}$ atm was maintained during each experiment. Temperatures were measured by means of a W/W-26% Re thermocouple which was placed in contact with the samples.

3. RESULTS

The electrical conductivities, σ, of undoped UO_2 and UO_2 doped with 0.5 mol% TiO_2, 0.5 mol% La_2O_3, and 0.5 mol% Nb_2O_5 are shown in Fig. 1 as a function of the temperature. The effect of the dopant concentration on the conductivity of UO_2 is shown in Fig. 2 for the Gd_2O_3-doped samples (at 1, 2, and 3 mol%) and for the Cr_2O_3-doped samples (at 0.4 and 0.8 mol%). Also shown in Fig. 2 are lines representing the intrinsic conductivity and the conductivity of a 0.5 mol% Cr_2O_3-doped UO_2 reported earlier [8].

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[2] Provided by the Berkeley Nuclear Research Laboratories, Gloucestershire, England.

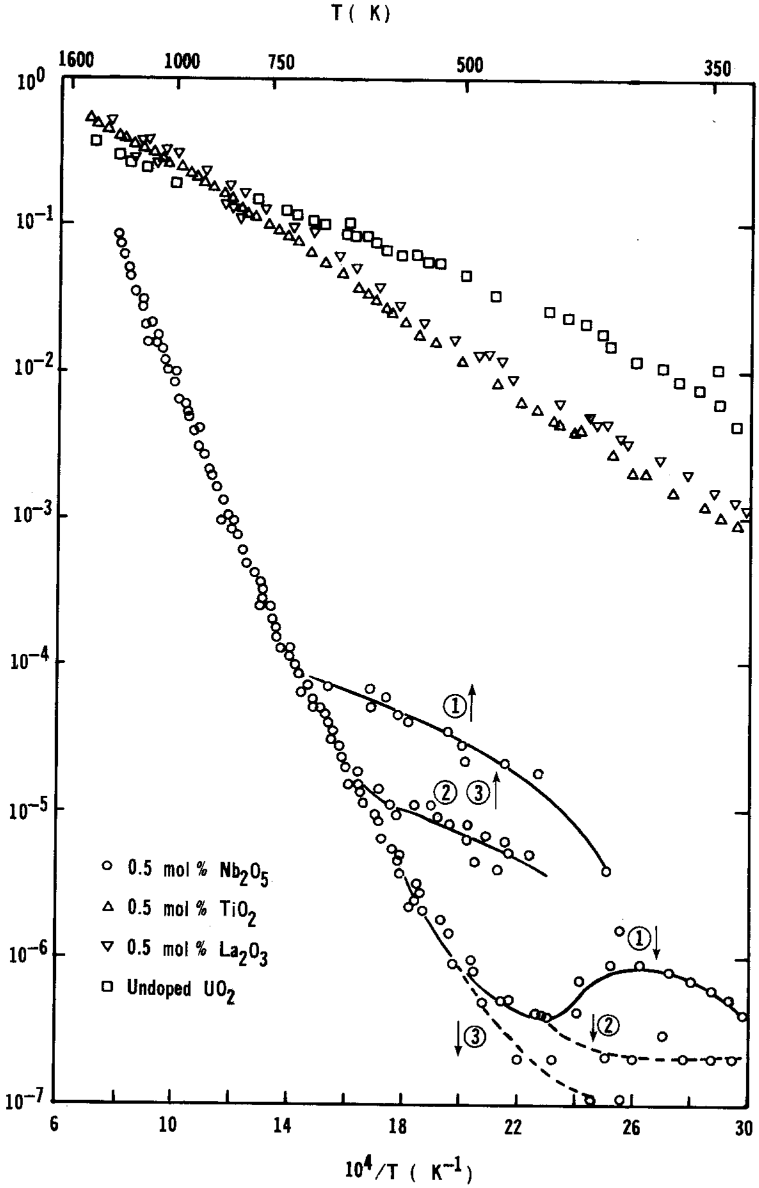

Fig. 1. The electrical conductivity of undoped and doped samples of uranium dioxide.

Typically, conductivity results are expressed as

$$\sigma = \sigma_0 \exp(-E_A/kT), \tag{5}$$

where $\sigma_0 = n_0 e\mu$ and E_A is the activation energy which is equal to $E_g/2$ for the intrinsic conductivity. Values for σ_0 and E_A for the samples investigated in

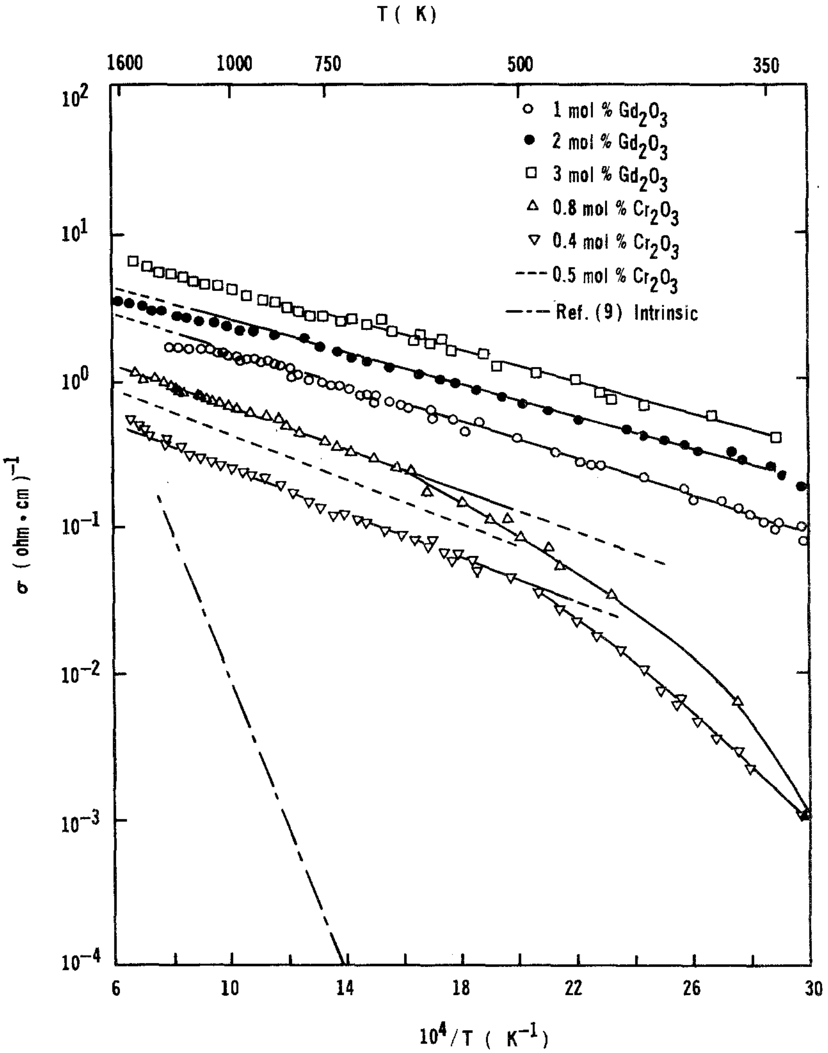

Fig. 2. The effect of the dopant concentration on the conductivity of Gd_2O_3- and Cr_2O_3-doped UO_2.

Table I. Activation Energies and σ_0 for Doped and Undoped UO_2

Dopant (mol%)	σ_0 $(\Omega \cdot \mathrm{cm})^{-1}$	Q (eV)	ΔT (K)	n[a]	r[b] (%)
None	1.010	0.13	435–1248	100	99.1
0.4 Cr_2O_3	1.884	0.17	417–1527	172	99.0
0.8 Cr_2O_3	4.319	0.16	455–1481	126	97.3
1.0 Gd_2O_3	5.509	0.12	37–1110	146	98.8
2.0 Gd_2O_3	7.442	0.10	383–163	106	99.7
3.0 Gd_2O_3	16.134	0.11	363–1512	173	94.2
0.5 TiO_2	4.244	0.25	317–1410	135	98.8
0.5 La_2O_3	4.534	0.24	300–1369	147	99.9
0.5 Nb_2O_5	441.83	0.94	714–1267	197	99.8

[a] The total number of experimental points in this range.
[b] Correlation coefficient for data fit of Eq. (5).

this work are listed in Table I along with the temperature ranges over which the relationship, Eq. (5), holds true. Also given in Table I are the total numbers of experimental determinations and the correlation coefficient for the mathematical fit of the data to Eq. (5). Typically the behavior of the $\ell n\ \sigma$ vs $1/T$ plots showed nonlinearity at low temperatures (<500 K) and in the vicinity of the extrinsic–intrinsic transition temperature. With the exception of the Nb_2O_5-doped samples, all others showed behaviors consistent with the extrinsic behavior of undoped UO_2 up to the highest temperature of investigation. For Nb_2O_5-doped samples, the temperature dependence of the conductivity appears to resemble the intrinsic behavior of UO_2. Activation energy calculations support these conclusions. In the range 714–1267 K, the activation energy for the latter samples is 0.94 eV, a value which is more than a factor of seven greater than the value for the undoped samples. The conductivities of the niobia-doped samples showed considerable scatter and a definite hysteresis at the lowest temperatures, <500 K. Arrows in the low-temperature data (Fig. 1) show the direction in which they were generated, i.e., increasing or decreasing temperature modes. The upward arrow numbered 1 represents the initial experiment starting from near room temperature. At about 700 K the slope of the conductivity curve increases and the results become highly reproducible. The results for the decreasing temperature mode, however, are significantly lower, as shown by the arrow numbered 1 for the downward mode. Subsequent heating of the sample gives σ data as shown by the upward arrows numbered 2 and 3. Again, the low-temperature results obtained during a downward mode are lower (by about one order of magnitude), as shown in Fig. 1.

Table II. E_g Values for UO_2

E_g (eV)	Reference	Remarks
1.9	This work	714–1267 K
2.3	9	Above 1400 K
1.8	9	Below 1400 K
2.1	10	Above 1430 K
2.5	11	—
2.6	4	1173–1473 K, low P_{O_2}

4. DISCUSSION

The activation energy for the niobia-doped UO_2 samples is indicative of an intrinsic behavior. It gives a value for $E_g = 1.9$ eV, which is in agreement with previously reported values for the high-temperature (intrinsic) conductivity of UO_2 (Table II). Apparently the addition of niobia as a dopant extends the intrinsic range down to a much lower temperature, ∼714 K, than had been previously observed [10].

This observation and the exceptionally low conductivity values at low temperatures, <500 K, suggest an inpurity compensation mechanism. The addition of Nb_2O_5 can be represented by

$$\mathrm{Nb_2O_5} \longrightarrow 2\,\mathrm{N\dot{b}_u} + 5\,\mathrm{O_0} \qquad (6)$$

with $\mathrm{N\dot{b}_u}$ representing an $\mathrm{Nb^{+5}}$ on a $\mathrm{U^{+4}}$ lattice point, in accordance with the Kröger-Vink notation. The electrical neutrality condition requires that

$$[\dot{h}] = 2[O_i''] + [\mathrm{N\dot{b}_u}], \qquad (7)$$

where $\dot{h}$ represents an electron hole and O_i'' is the doubly charged interstitial oxygen. The total concentration of O_i'' is

$$[O_i'']_{\mathrm{total}} = [O_i'']_{\mathrm{int}} + [O_i'']_{\mathrm{ext}}, \qquad (8)$$

i.e., it is the sum of the intrinsic and extrinsic contributions. The intrinsic concentration can be calculated from

$$1/2\,\mathrm{O_2} \xrightarrow{K_i} O_i'' + 2\dot{h}, \qquad (9)$$

where K_i is the equilibrium constant for the formation of an interstitial oxygen ion. Equation (8) can, therefore, be written as

$$[O_i'']_{\text{total}} = \frac{K_i P_O^{1/2}}{[\dot{h}]^2} + \frac{1}{2}[\mathrm{N\dot{b}_u}]. \tag{10}$$

At low temperatures K_i is small and we can use the approximation that

$$[O_i'']_{\text{total}} \simeq \frac{1}{2}[\mathrm{N\dot{b}_u}]. \tag{11}$$

The equilibrium constant of Eq. (9) can now be written as

$$K_i = \frac{[\dot{h}]^2\,[\mathrm{N\dot{b}_u}]}{2P_O^{1/2}}, \tag{12}$$

which rearranges to

$$[\dot{h}] = \frac{(2\,K_i)^{1/2} P_{O_2}^{1/4}}{[\mathrm{N\dot{b}_u}]^{1/2}}. \tag{13}$$

Equation (13) shows that the addition of Nb_2O_5 to uranium dioxide decreases the hole concentration and hence the conductivity. Furthermore, if the decrease in hole concentration is significant, the intrinsic electronic equilibrium must be taken into account, i.e.,

$$[\dot{h}] = \frac{K_e}{[e']}, \tag{14}$$

where $[e']$ is the concentration of electrons and K_e is the equilibrium constant for the formation of a hole and an electron. Substituting for $[\dot{h}]$ in Eq. (13) in terms of its value from Eq. (14) gives

$$[e'] = \frac{K_e}{(2\,K_i)^{1/2}} \cdot P_{O_2}^{-1/4}\,[\mathrm{N\dot{b}_u}]^{1/2}. \tag{15}$$

At a low P_{O_2}, for example, $P_{O_2} \sim 10^{-20}$ atm, and a favorable ratio of K_e/K_i, the above relationship indicates that n-type or intrinsic conductivity can be achieved.

While the results of the 0.5 mol% Nb_2O_5-doped samples can be explained in terms of impurity compensation, those of the 0.5 mol% TiO_2-, 0.4

mol% Cr_2O_3-, and 0.5 mol% La_2O_3-doped samples present anomalies. On the basis of an impurity compensation scheme, the addition of TiO_2 is not expected to give rise to a conductivity change, yet the present results show a decrease in the conductivity at the low temperatures. At temperatures above about 830 K, the results of the TiO_2-doped and the undoped samples are not significantly different. The activation energy for the titania-doped UO_2, however, is nearly a factor of two higher than that for undoped uranium oxide. There is evidence to suggest that the incorporation of Ti^{+4} in uranium dioxide is not substitutional [12], and hence these results cannot be easily interpreted in terms of impurity compensation in the manner presented above. Indeed, it is possible to explain the observed nonlinearity and low values of the conductivity in this case in terms of a hop mechanism. Like the titania-doped samples, those of La_2O_3-doped UO_2 showed a decreased conductivity, relative to the undoped UO_2, at the lower temperatures. The activation energy was found to be the same as that for the TiO_2-doped UO_2.

At temperatures above about 500 K, the results of the 0.4 mol% Cr_2O_3-doped samples are essentially the same as those of the undoped UO_2. However, at a higher concentration, 0.8 mol%, the conductivity increases by roughly a factor of two (Fig. 2). The results of the gadolynia-doped samples, also plotted in Fig. 2, show a corresponding increase in conductivity with dopant concentration. At 500 K, the ratios of the conductivities of the 3, 2, and 1 mol% Gd_2O_3-doped samples are 3.25:2:1. The activation energies for these three compositions (Table I) are the same and are reasonably close to that of the undoped uranium dioxide. These observations are also consistent with the impurity compensation model since a lower valency ion, e.g., Gd^{+3}, is incorporated in UO_2 according to

$$Gd_2O_3 = 2\,Gd'_u + 3\,O_0. \qquad (16)$$

The condition of electrical neutrality is now

$$[\dot{h}] = 2[O''_i] + [Gd'_u]. \qquad (17)$$

By analogous reasoning to that presented for the Nb^{+5} doping, we can approximate

$$[\dot{h}] \simeq [Gd'_u]. \qquad (18)$$

Substituting this in the expression for K_i gives

$$[O''_i] = \frac{K_i\,P_O^{1/2}}{[Gd'_u]^2}. \qquad (19)$$

Thus the addition of Gd^{+3} decreases the concentration of interstitial oxygen and, therefore, increases the hole concentration.

The activation energy for the extrinsic conductivity of the undoped UO_2, 0.13 eV, is in reasonable agreement with corresponding values reported by Bates et al. [9] (0.17 eV) and by Wolfe [13] (0.13 eV). Recent results [10] using identically prepared samples gave an activation energy of 0.14 eV for the extrinsic portion of the conductivity of uranium dioxide. Other investigators, however, reported activation energies which are approximately a factor of two higher than the value calculated from the present data. Lee [5], who found a dependence of E_A on x in UO_{2+x}, reported a value of 0.31 eV for the composition with $x \sim 0$. Nagels et al. [14] found a similar dependence on composition and reported a value of 0.34 eV for stoichiometric uranium oxide.

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