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Electrical Transport in Rare-Earth Oxides*

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Sesquioxides and nonstoichiometric oxides of rare-earths (Ln) exhibit electrical conductivities in the range 10^{-9}–10^{-1} Ω^{-1} cm^{-1}. The sesquioxides exhibit mixed conduction with some contribution from ionic conductivity and major contribution from electronic conductivity. Seebeck coefficient data as well as the oxygen partial pressure dependence of conductivity indicate that LnO_x compounds are mixed valence semiconductors where oxides with $1.50 \leqslant x \leqslant 1.75$ are *p*-type semiconductors and oxides with $1.75 < x \leqslant 2.00$ are *n*-type semiconductors. The conductivity of LnO_x (Ln = Pr or Tb) goes through a maximum at $x \approx 1.75$; Seebeck coefficients are sensibly constant with temperature and approach zero value at $x \approx 1.75$. Employing the conductivities and Seebeck coefficients, transport parameters have been calculated. The mechanism of conduction in these oxides can be understood in terms of the hopping model and the small polaron theory. Fully ionised cation vacancies seem to be the predominant defects contributing to the defect structure in rare-earth sesquioxides.

Introduction

Rare-earth oxides with filled or partially filled inner 4*f*-shells of the lanthanide ions are likely to be narrow band materials and the electrical conduction in these oxides would undoubtedly involve the 4*f*-electrons (*1*). In the literature there are a few reports on the electrical conductivity of rare-earth oxides. Noddack and Walch (*2*) measured the resistivities of a few rare-earth oxides and found the conduction to be predominantly electronic in nature. Eyring and Baenziger (*3*) have reported some preliminary measurements of the resistivities of a few praseodymium oxides, while Honig and coworkers (*4*) have studied both the electrical resistivities and Seebeck coefficients of a few oxides. Some evidence has been presented by Tare and Schmalzried (*5*) for the presence of ionic conductivity in rare-earth sesquioxides.

We have presently examined the semiconduction of several rare-earth sesquioxides and the nonstoichiometric oxides of praseodymium and terbium in some detail. We have measured the conductivities of a few oxides at different partial pressures of oxygen in order to establish the defect equilibria. Seebeck coefficient measurements have been carried out to find out the sign of the charge carriers. Employing the experimentally measured values of conductivity and Seebeck coefficients, we have explained the mechanism of conduction with the aid of the hopping model and the polaron theory.

Experimental

Eu_2O_3, Ho_2O_3, Y_2O_3, and the other sesquioxides (all of better than 99.99% purity) obtained from American Potash Co. were ignited to constant weight and stored in a desiccator before use. Lindsay (American Potash Co.) 99.99% pure Pr_6O_{11} and "Tb_4O_7," ignited to constant weight were used in the investigation. C–Pr_2O_3 and C–Tb_2O_3 were prepared by the reduction of Pr_6O_{11} and Tb_4O_7 in a stream of dry hydrogen for 6 hr at 600 and 900°C, respectively (*6*, *7*). PrO_2 was prepared by leaching Pr_6O_{11} with 1.6*N* acetic acid for five days and TbO_2 by leaching Tb_4O_7 with 0.1*N* HCl for 24 hr (*8*). Pr_7O_{12} was prepared by heating Pr_6O_{11} in vacuum (~ 10^{-5} mm Hg) at 490°C for 4 hr (*8*). Lattice constants were calculated from the X-ray patterns recorded with a GE XRD diffractometer using CuKα radiation. The lattice constants agreed well with the literature data (*9*).

The electrical conductivities of polycrystalline pellets (pressed at 9000 psi and sintered at 950°C) of the various oxides were measured with a cell fabricated in this laboratory (*10*, *11*). A GR-1608A

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impedance bridge fitted with a GR-1232A tuned amplifier and null detector was employed for the measurements. The pellets were coated with duPont silver paint to obtain good electrical contact. The conductivity values reported are reliable and reproducible. The conductivities of the pellets did not vary appreciably with the pressure employed in the preparation.

Seebeck coefficients, β, were measured with an apparatus fabricated in this laboratory (*12*) which is a slightly modified version of the cell employed by Czanderna (*13*) and Honig and coworkers (*4*). Corrections were made for the platinum wires attached to the samples employing procedures reported in the literature (*13, 14*). In any case, these corrections do not significantly affect the present results except in the case of $TbO_{1.5}$; further, we have found high β in $TbO_{1.52}$. The uncertainty in temperature determination was ±0.5° and in the thermal emf, about ±2%. Even though the uncertainty in the determination of the Seebeck coefficient is around ±12% (and possibly more in cases where the value is very small) the general reproducibility of the results was very good; the values quoted are the results of many repeated experiments.

Dielectric constants were determined by measuring the capacitance of the oxide pellets over a wide range of frequencies, employing a GR716C capacitance bridge and a Boonton Q-meter. The measurements were made at room temperature and the dielectric constants at zero (ϵ_0) and high frequency (ϵ_∞) were obtained by an extrapolation procedure. The uncertainty in the determination is ±5%.

The restrahlen frequencies were determined by taking the infrared absorption spectra of the samples in the form of nujol mulls employing a Perkin Elmer 521 and Beckman IR-11 spectrometers.

Results and Discussion

Rare-Earth Sesquioxides

The electrical conductivity data of a few rare-earth sesquioxides, Ln_2O_3, are shown as a function of temperature in Fig. 1. Conductivities, σ, at two temperatures along with the activation energies for conduction, E_a, are given in Table I. The conductivities are generally low, particularly so in the heavier rare-earth sesquioxides. The conductivity of Y_2O_3 is in between that of Ho_2O_3 and of Yb_2O_3. All the sesquioxides showed decrease in conductivity with decrease in oxygen partial pressure in the temperature range 400–900°C indicating the presence of p-type electronic conduction.

Most of the sesquioxides, especially those of the heavier rare-earths show breaks in the $\log\sigma$ vs $1/T$ plots around 550–600°C. La_2O_3, Pr_2O_3, and Tb_2O_3 show such breaks at still lower temperatures, T_B. These breaks in the conductivity curves do not correspond to any phase transformations. Phase transformations are noticed at much higher temperatures in some of the sesquioxides and the $\log\sigma - 1/T$ plots show distinct changes in slope at the transformation temperatures (*10, 15, 16*). The change in slope was seen at all values of p_{O_2} studied (0.10–760 mm Hg) and hysteresis effects were negligible. The actual values of conductivity were somewhat more sensitive to p_{O_2} below T_B.

From Table I we see that whereas the conductivity decreases down the rare-earth series, E_a above the break temperature, T_B, increases. The variation of

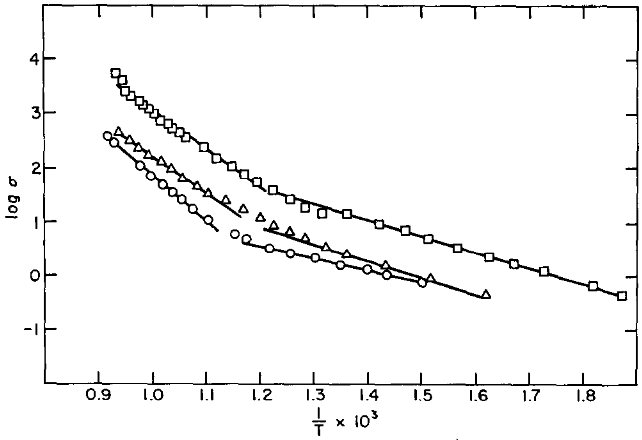

FIG. 1. Plots of electrical conductivity ($m\mu\Omega^{-1}\cdot cm^{-1}$) against the reciprocal of absolute temperature (p_{O_2} = 150 mm Hg; squares, Sm_2O_3; triangles, Eu_2O_3 and circles, Yb_2O_3.

TABLE I

ELECTRICAL CONDUCTIVITY DATA OF RARE-EARTH SESQUIOXIDES (Ln_2O_3)[a]

Ln	T_B,°C	E_1,eV[b] ($T < T_B$)	E_2,eV ($T > T_B$)	$\sigma_{400^\circ C}$ ($\times 10^{+9} \Omega^{-1} \cdot cm^{-1}$)	$\sigma_{650^\circ C}$ ($\times 10^{+9} \Omega^{-1} \cdot cm^{-1}$)
La	270	0.7	1.05	230	1700[c]
Pr[d]	320	0.4	0.95	300	3450
Nd	—	—	1.15	25	1450
Sm	560	0.6	1.28	20	880
Eu	570	0.6	1.35	5	150
Gd	560	0.5	1.57	5	130
Tb[d]	280	0.4	0.95	3	200
Ho	575	0.7	1.61	5	160
Yb	605	0.5	1.61	3	50
Y	—	—	1.10	—	55

[a] DC conductivity measured at $p_{O_2} \approx 150$ mm Hg.

[b] Approximate values only since the conductivity is small at $T < T_B$.

[c] Values are for the hexagonal (A) form. In all the other cases, the oxides are in cubic (C) form (defect fluorite structure).

[d] Measured in dry hydrogen to prevent oxidation.

σ and E_a in the rare-earth series may be associated either with impurity effects or the variation in the ionic contribution to conductivity. We feel that ionic conductivity is more plausible in view of the following observations:

(i) The difference between σ_{dc} and σ_{ac} (at 10 KHz) is appreciable at $T > T_B$; σ_{ionic} thus estimated (*17*) is about 30% at ~ 700°C in Y_2O_3 and Nd_2O_3 in agreement with other independent estimates. The percentage of σ_{ionic} values are similar in other sesquioxides as well (*20*).

(ii) Continued electrolysis of sesquioxides at $T > T_B$ slightly reduces the conductivity.

(iii) Galvanic cell measurements of Tare and Schmalzried (*5*) clearly establish ionic conductivity to be appreciable in Sm_2O_3 at high temperatures.

These observations seem to suggest that the change in the slope of the conductivity-temperature plot at T_B could arise from the onset of ionic conductivity. We therefore feel that rare-earth sesquioxides are most likely to be mixed conductors with some contribution from ionic conductivity and major contribution from electronic conductivity. We shall presently examine some aspects of electronic conduction in these sesquioxides.

In order to examine the electronic conduction and the associated defect chemistry in these sesquioxides, the conductivity of Ho_2O_3 was measured (*18*) at different oxygen partial pressures in the range 2–100mm Hg at a few temperatures (in the 400–700°C range). The data established that σ was proportional to $p_{O_2}^{+1/5.3}$ in this pressure range. Schwab and Bohla (*19*) have recently found a $p_{O_2}^{+1/5.5}$ dependence of conductivity in Eu_2O_3 in the same pressure range. In Y_2O_3, Tallan and Vest (*20*) have observed a $p_{O_2}^{+1/5.33}$ dependence of conductivity. All these results show that the p-type electronic conduction in rare-earth sesquioxides arises from oxygen excess. The observed oxygen pressure dependence in the sesquioxides can be explained by a mechanism involving cation vacancies which would be consistent with the known crystal structures of these sesquioxides (*7*, *10*, *21*). Oxygen can enter the crystal structure of a sesquioxide creating metal ion vacancies and holes according to the equation,

$$3/4 O_2 (g) \rightleftharpoons 1.5\, O_O^{2-} + \square_{Ln} + 3h^+, \qquad (1)$$

where O_O^{2-} is an oxygen ion at its lattice site, $\square_{Ln}$ is a cation vacancy and h^+ is a hole. Since $[h^+]/3 = [\square_{Ln}]$, we find that

$$\sigma \propto [h^+] \propto p_{O_2}^{+1/5.3} \qquad (2)$$

as indeed observed experimentally in the case of Ho_2O_3 and Y_2O_3. Apparently, the p_{O_2} dependence arises from fully ionized vacancies,; in Eu_2O_3 however, the $p_{O_2}^{+1/5.5}$ dependence of conductivity implies some contribution from trapped holes.

When oxygen was initially let into the evacuated conductivity cell containing the pellet of Eu_2O_3 or

Ho_2O_3, there was a marked decrease in the conductivity. It appears that at low pressures of oxygen, Eu_2O_3 and Ho_2O_3 may act as *n*-type semiconductors. Schwab and Bohla (*19*) and Tallan and Vest (*20*) have similarly found evidence for the *n*-type behavior of Eu_2O_3 and Y_2O_3 at low values of p_{O_2}. Tare and Schmalzried (*5*) report *n*-type conduction in Sm_2O_3 on the basis of emf measurements at low p_{O_2}. Thus, it appears that most of the rare-earth sesquioxides lose oxygen at low p_{O_2} and high temperatures to produce anion vacancies ($\square_O$) and free electrons:

$$O_O^{2-} \rightleftharpoons 1/2O_{2(g)} + \square_O + 2e^-. \qquad (3)$$

This would give rise to a $p_{O_2}^{-1/6}$ dependence of conductivity. The conductivity data of Schwab and Bohla (*19*) on Eu_2O_3 seem to conform to this behavior.

Except for Pr_2O_3, no Seebeck coefficient data are available for the rare-earth sesquioxides. We have measured the Seebeck coefficients of a few sesquioxides in the range 400–800°C at $p_{O_2} \approx 140$ mm Hg (Fig. 2). As expected, these oxides are *p*-type semiconductors in this temperature range. The β values are relatively small at temperatures less than 600°C, but increase markedly above this temperature. Some of the rare-earth chalcogenides are known to exhibit a similar behavior (*22*). It is possible that ionic conductivity might be contributing significantly to β at high temperatures (above T_B). Measurements on Eu_2O_3 in an atmosphere of nitrogen at ~ 800°C showed a decrease in β (Fig. 2), but no change in sign. Studies at still lower values of p_{O_2} may reveal a change in the sign of β.

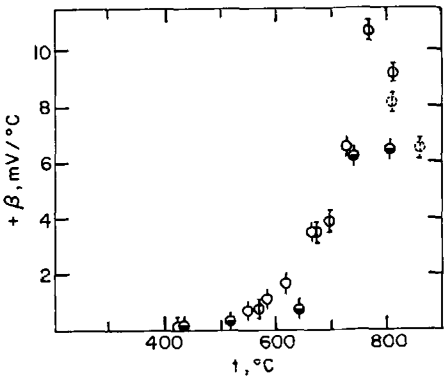

FIG. 2. Plots of Seebeck coefficient against temperature for various Ln_2O_3 measured in air (p_{O_2} = 140 mm Hg; ϕ: Y_2O_3; ϕ: Ho_2O_3; Φ: Eu_2O_3; ϕ: Eu_2O_3 in nitrogen atmosphere.)

Nonstoichiometric Oxides of Praseodymium and Terbium

Phase equilibria in the praseodymium–oxygen (*23*, *24*) and terbium–oxygen (*6*, *25*) systems as well as the crystallography of the Ln_nO_{2n-2} ($n \geqslant 4$) phases have been reported in the literature. Semiconduction in some of the equilibrium compositions of praseodymium and terbium oxides have been carefully studied in this laboratory. Among these oxides, the intermediate phase close to the composition $LnO_{1.75}$ (Ln = Pr or Tb) exhibits the highest electrical conductivity and the lowest activation energy for conduction. We shall not presently descuss the experimental data on σ as a function x since the essential features have already been presented earlier by Honig and coworkers (*4*). It is interesting that the conductivities of all the LnO_x compositions fall on the $\sigma - x$ curves showing maxima at $x \approx 1.75$, immaterial of whether they are ordered (uniphasic) compounds with narrow homogeneity ranges or disordered (and biphasic) phases. Apparently, the main factor that governs the conductivity maximum at $x \approx 1.75$ is the stoichiometry (Ln^{+3} and Ln^{+4} concentrations) rather than the defect structure.

Conduction in PrO_x and TbO_x may be treated as a simple electron diffusion problem generally encountered in hoppers. Here, the mobility and diffusivity are related through a transition probability. At sufficiently high temperatures (*4*, *26*), we have

$$\begin{aligned} \sigma T &= C\tau^{-1} cs(1-s)\exp(-\Delta H/kT) \\ &= (n_e + n_p)\, e\mu(T), \end{aligned} \qquad (4)$$

where C is a collection of constants, τ_0^{-1} is the transition probability at infinite temperature, c is the charge carrier density, s is the concentration of available sites to which the charge carrier can jump and ΔH is the enthalpy change accompanying the transfer of a charged particle. Considering that the nonstoichiometric rare-earth oxides to be hoppers, the conductivity given by Eq. (4), should be proportional to the product $[Ln^{3+}][Ln^{4+}]$. Stated differently, σ would be proportional to the product $(x-1.5)(2-x)$. Thus, in LnO_x, σ should go through a maximum around $x = 1.75$ at a given temperature as found experimentally.

In praseodymium (*4*) and terbium oxides where x is between 1.5 and 1.75, we would expect *p*-type conduction. For compositions near LnO_2 most of the cations will be present as Ln^{4+} ions with occasional Ln^{3+} ions; since the charge carriers in these oxides are electrons, we expect conduction to be of *n*-type. Midway between the extremes of $LnO_{1.5}$

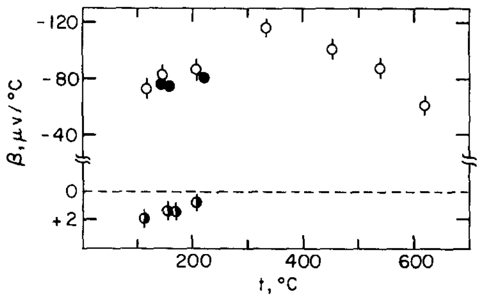

FIG. 3. Plot of Seebeck coefficient against temperature for TbO_x in air ($p_{O_2} = 140$ mm Hg; open circles, $x = 1.81$; shaded circles, $x = 2.00$; half-shaded circles, $x = 1.50$).

and LnO_2 we would expect a change from *p*- to *n*-type behavior. This prediction is in agreement with the Seebeck coefficient data on PrO_x reported by Honig and coworkers (*4*) and on TbO_x obtained presently.

We have measured the Seebeck coefficients in four ordered narrow homogeneity phases, $TbO_{1.5}$, $TbO_{1.52}$, $TbO_{1.81}$ and TbO_2, over a range of temperatures. The results are presented in Fig. 3. We see that β is positive for $TbO_{1.5}$ and $TbO_{1.52}$ typical of *p*-type semiconductors and negative in the case of the other two oxides indicating *n*-type behavior. In the case of $TbO_{1.5}$ (when the stoichiometry is nearly exact) β is very small (~ 2 $\mu V/°C$ around 200°C), but when x is slightly higher (~ 1.52) β increases markedly ($\sim +200$ μV/°C at $\sim$ 200°C). A similar behavior has been noted by Honig and coworkers (*4*) in $PrO_{1.5}$. This may be because, at the stoichiometric composition $TbO_{1.5}$, we would expect a rapid change from a large negative to a large positive value of β; we note here that at $x < 1.5$ the oxide would be *n*-type. The expected high values of β are indeed found in stoichiometric sesquioxides of other rare earths (Fig. 2). We also note from Fig. 3 that within experimental error β is essentially independent of temperature for a given composition, a behavior typical of hoppers; $TbO_{1.81}$, however, shows a slight maximum around 350°C, the cause of which is not clear.

The variation of Seebeck coefficient with temperature in LnO_x can be understood from relation (5) generally applicable to electron-transfer materials (*1*, *27*):

$$\beta = -\frac{k}{e}\left[\ln\frac{c}{s} + \frac{S^*}{k}\right]. \tag{5}$$

Here e is the electronic charge and k is the Boltzmann constant. The entropy transported per particle, S^*, depends on the nature of the charge transfer process. Applying this to the case of LnO_x, we find that β should vary with x as,

$$\beta \approx -(k/e)\ln\{(x-1.5)/(2-x)\} \tag{6}$$

and β will depend on T only to the extent that S^* does. To a first approximation, therefore, β should be roughly independent of T. This theoretical prediction is in agreement with our experimental observations on TbO_x (Fig. 3) and in a very limited temperature range for Ln_2O_3 (Fig. 2). We find that the value of S^*/k is of the order of 0.2 in TbO_x; S^*/k in PrO_x has been reported to be 0.2 by Honig and coworkers (*4*).

The composition $LnO_{1.75}$ can be assumed to have a random distribution of Ln^{3+} and Ln^{4+} ions with a maximum of electronic disorder among the oxides of LnO_x systems. The configurational entropy due to the electronic disorder would therefore be maximum at this composition (*28*). It is possible to conceive of a slightly different model according to which the conductivity maximum would be at the composition $x = 1.71$ instead of $x = 1.75$. The phase $LnO_{1.71}$ may be described as consisting of parallel 'strings' of irregular LnO_6 octahedra in the $\langle 111 \rangle$ direction surrounded by contiguous sheaths of seven-coordinated cations (*24*, *25*). According to this model, the seven-coordinated cations with an average charge of +3.5 would be responsible for the conductivity. This would result in the conductivity maximum and zero value for β at a composition of $LnO_{1.71}$ rather than at $LnO_{1.75}$. Although the second model appears to be reasonable, it is difficult to make such subtle distinctions on the basis of the available experimental data. This is because, (i) stable $LnO_{1.75}$ phase is nonexistent, (ii) experimental uncertainties in the determination of β (particularly near zero) are large and most important of all, (iii) the cross-over point from *p*- to *n*-type behavior and the conductivity maximum are determined by the concentration of charge carriers, n_i, as well as their mobility, μ_i. Thus, β would be zero when $n_p\mu_p\beta_p = n_e\mu_e\beta_e$. Experimentally we find that the conductivity maximum is around the composition $LnO_{1.71}$ only at some temperatures while β is zero at this composition in both TbO_x and PrO_x. Oxygen partial pressure dependence of conductivity discussed next also throws some light on the cross-over from *p*- to *n*-type semiconduction in the PrO_x system.

In order to examine possible defect equilibria in the PrO_x system, electrical conductivities were measured at different partial pressures of oxygen. Preliminary measurements on Pr_6O_{11} at two oxygen partial pressures clearly indicated it to be an *n*-type semiconductor as expected (Fig. 4). We see that the

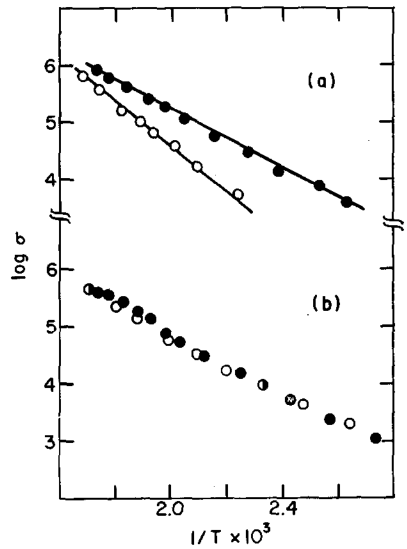

FIG. 4. Plot of electrical conductivity ($\mathrm{m}\mu\Omega^{-1}\cdot\mathrm{cm}^{-1}$) against the reciprocal of absolute temperature of Pr_6O_{11} (a) and Pr_7O_{12} (b). Open circles, $p_{O_2} = 140$ mm Hg; closed circles, $p_{O_2} = 0.2$ mm Hg.

dependence of σ of Pr_7O_{12} is not (where Ln^{+3}-Ln^{+4} concentrations are close) at all appreciable (Fig. 4). More detailed investigations on Pr_6O_{11} ($x = 1.833$) in the low pressure range ($p_{O_2} = 2$–15 mm Hg) indicated a $p_{O_2}^{-1/6}$ dependence of conductivity at ~200°C; this dependence can be interpreted in terms of anion vacancies (Eq. 3). The conductivity of the nonstoichiometric oxides in the composition range $1.68 < x < 1.72$, on the other hand, showed a dependence of $p_{O_2}^{+1/6}$; the $p_{O_2}^{+1/6}$ dependence is consistent with a cation vacancy mechanism. Although we can satisfactorily account for the oxygen pressure dependence of conductivity of LnO_x in terms of defect equilibria, we are presently unable to eliminate the equally plausible interpretation based on the presence of mixed valence; these two mechanisms are, of course, interdependent.

Small Polaron Model

Since band widths in rare-earth oxides are very small, we considered it interesting to examine the conduction in these compounds in terms of the polaron theory (*29–31*). The measure of the electron–phonon interaction in polaron materials is given by the dimensionless Fröhlich coupling constant (*29*), α_F^*:

$$\alpha_F^* = e^2(m^*/2\hbar^3\,\omega_l)^{1/2}(\epsilon_\infty^{-1} - \epsilon_0^{-1}), \tag{7}$$

where m^* is the effective mass of the charge carrier and ω_l is the longitudinal mode frequency. The dimension of the polaron, λ_F^*, defined by Feynman (*30*), is

$$\lambda_F^* = (\hbar/2m^*\,\omega_l)^{1/2}. \tag{8}$$

The effective mass of charge carriers in praseodymium and terbium oxides can be calculated from the experimental Seebeck coefficient data (*1*). Using the calculated m^* values, the experimentally determined values of the dielectric constants and the longitudinal mode frequency, the values of the coupling constants (α_F^*) were calculated for the oxides. The values of α_F^* in all the oxides is seen to be greater than unity (Tables II and III). The transition probability, τ^{-1}, could be calculated making use of the conductivity data and the charge carrier density (*1*); the drift mobility, μ_D, of the charge carriers was then calculated from τ^{-1}.

An estimate of Szigeti's effective charge, e^*, of the charge carrier was obtained from the equation (*32*)

$$e^* = (3\nu_0/(\epsilon_\infty + 2))\,[(\epsilon_0 - \epsilon_\infty)\pi M V']^{1/2} \tag{9}$$

where ν_0 is the observed restrahlen frequency, M is

TABLE II

ELECTRICAL TRANSPORT PARAMETERS FOR PrO_x AT 600°C

Compound	ϵ_0	ϵ_∞	ν_{obsd}, cm^{-1}	E_a, eV	V in cc per ion ($\times 10^{-24}$)	σ, $\Omega^{-1}\cdot$cm^{-1}	β, μV/°C	c	m^*/m	α_F^*	τ^{-1}, sec^{-1}	μ_D, cm²/V sec	λ_F^*, Å
Pr_2O_3	100	5.6	420	0.84	38.5	2.6×10^{-6}	+10	0.42	25	6.6[a] (1.3)	9.8×10^5	1.5×10^{-8}	0.83[a]
$PrO_{1.714}$	120	5.6	400	0.57	42.8	1.7×10^{-2}	+9	0.43	23	6.3 (1.3)	1.3×10^{10}	8.0×10^{-4}	0.85 (4.10)
$PrO_{1.833}$	60	15	640	0.81	41.0	8.4×10^{-2}	−50	0.59	19	5.0 (1.0)	5.4×10^{10}	2.5×10^{-3}	1.15 (4.89)

[a] Value in parenthesis indicates for the free electron mass.

TABLE III

ELECTRICAL TRANSPORT PARAMETERS FOR TbO_x

T,°C	σ, $\mu\Omega^{-1}\cdot cm^{-1}$	β, $\mu V/°C$	c	m^*/m	α_F^*	τ^{-1}, sec^{-1}	μ_D, cm^2/V sec	λ_F^*, Å
$TbO_{1.5}$[a]								
200	0.3	+1	0.42	45	8.4[b] (1.3)	2.2×10^5	6.1×10^{-8}	0.96[b] (6.42)
TbO_2[c]								
200	2.5	−78	0.67	33	3.5 (0.6)	9.9×10^5	6.6×10^{-8}	0.45 (2.61)
$TbO_{1.81}$[d]								
200	6.3	−92	0.70	29	3.0 (0.6)	2.5×10^6	1.7×10^{-7}	0.62 (3.36)
300	44.7	−101	0.73	23	2.6	2.2×10^7	1.3×10^{-6}	0.70
400	177.8	−102	0.73	20	2.5	1.0×10^8	5.0×10^{-6}	0.75
500	609.5	−94	0.71	15	2.1	3.9×10^8	2.1×10^{-5}	0.87
600	1778.0	−78	0.67	17	2.3	1.2×10^9	4.5×10^{-5}	0.82

[a] $\epsilon_0 = 8.4$, $\epsilon_\infty = 4.5$, $\nu_{obsd} = 545\ cm^{-1}$, $E_a = 0.95$ eV, $V = 38.6 \times 10^{-24}\ cm^3$.

[b] Value in parenthesis indicates for the free electron mass.

[c] $\epsilon_0 = 840$. $\epsilon_\infty = 8$, $\nu_{obsd} = 440\ cm^{-1}$, $E_a = 0.5$ eV, $V = 35.5 \times 10^{-24}\ cm^3$.

[d] $\epsilon_0 = 285$, $\epsilon_\infty = 11.2$, $\nu_{obsd} = 540\ cm^{-1}$, $E_a = 0.66$ eV, $V = 37.5 \times 10^{-24}\ cm^3$.

the reduced mass of all the ions present in the crystal and V' is the volume of the unit cell. The ϵ_0 value is very high in many of the rare-earth oxides. Such large values have also been reported for other oxides like TiO_2 (*33*), $SrTiO_3$ (*34*), and $LaCoO_3$ (*35*).

The relevant experimental data and the calculated transport parameters for praseodymium and terbium oxides are presented in Tables II and III. For $TbO_{1.81}$ it has been possible to calculate all the transport parameters as a function of temperature which permits us to examine the applicability of the hopping model more closely. Hall data would have been valuable, but the small mobilities in these materials even at high temperatures would make such measurements less reliable.

The charge carrier density is higher in non-stoichiometric oxides than in stoichiometric oxides; in $TbO_{1.81}$ it is almost independent of temperature in the range studied (Table III). The effective mass of the charge carriers, m^*, is usually 20 to 40 times the free electron mass, indicating considerable interaction between the charge carriers and phonons; m^* is slightly lower in non-stoichiometric oxides. Such high m^* values have been encountered in the other oxides as well (*36*). For $TbO_{1.81}$, m^* shows a decreasing trend with rise in temperature; Fröhlich coupling constant (α_F^*) also shows a similar behavior.

Both τ^{-1} and μ_D are greater in the nonstoichiometric oxides compared to the stoichiometric oxides. In the oxides studied presently, μ_D is in the range 10^{-3}–$10^{-8}\ cm^2/V$ sec, which is in the region normally found in oxide semiconductors. In $TbO_{1.81}$, μ_D increases with temperature exponentially, the energy of activation being 0.5 eV. This monotonic increase in mobility can be taken to indicate hopping mechanism rather than 'polaron band' formation (*37*). The value of 0.5 eV noted above is comparable with the 0.6 eV obtained from the conductivity data. The polaron dimension is of the same order as the lattice parameter (small polarons) indicating that the charge carriers are localized at lattice sites. Szigeti's effective charge in the case of stoichiometric phases is not much different from the free electron charge, but considerably higher (~ 2 to 3e) in nonstoichiometric oxides.

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