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Hopping Conduction in a Mixed Valence Oxide System: $Pr_{1-y}Gd_yO_{1.5+\delta}$

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The electrical conductivity of σ-phase $Pr_{1-y}Gd_yO_{1.5+\delta}$ ($y = 0.0$, 0.1, 0.2, and 0.4) was measured as a function of temperature and oxygen partial pressure. The dependence of the electrical conductivity of $Pr_{1-y}Gd_yO_{1.5+\delta}$ on the composition was determined by combining gravimetric and conductivity data. The results are consistent with the small-polaron model of localized charge carriers hopping between two adjacent Pr ions in different valence states. The following equation was quantitatively examined: $\sigma = ns(1-s)pek_h$, where n is the concentration of total Pr ions, s is the fraction of Pr^{4+} ions in total Pr ions, p is the probability that cationic positions are occupied by mixed valence ions, and k_h is a constant characteristic of the charge-transfer process between different valence states. It was found that k_h increases slightly with increasing δ. This dependence is discussed in terms of the observed activation energy and the degree of delocalization of the 4f electrons.

Introduction

Nonstoichiometry introduced into transition-metal oxides generates formally two cationic states, M^{n+} and $M^{(n+1)+}$. For example, metal-excess oxide is formed by removing oxygen from the lattice, and electrons are left behind in the crystal. If an electron is localized in the vicinity of cationic site, it is equivalent to a lower valence cation M^{n+} and carries a unit charge by hopping from a M^{n+} ion to an adjacent $M^{(n+1)+}$ ion. In the case of a metal-deficient oxide, an oxygen takes two electrons from the lattice to form an oxygen ion at the lattice position, and two electron holes enter the crystal. An electron hole localized in the vicinity of a cationic lattice site is equivalent to a higher-valence cation $M^{(n+1)+}$ and carries a charge by hopping from a $M^{(n+1)+}$ ion to an adjacent ion.

For hopping conduction, Heikes and Johnston (*1*), and Honig (*2–4*) have given the following expression of conductivity:

$$\sigma = ns(1-s)pek_h, \qquad (1)$$

where n is the total cation concentration in mixed valence states, p is the probability that cationic positions are occupied by mixed valence ions when the oxide is a solid solution, s is the fraction of $M^{(n+1)+}$ ions in mixed valence cations, and k_h is a hopping-rate constant which has a dimension of mobility. The expression for k_h is given by the random-walk theory and the absolute reaction-rate theory as follows (*2–7*):

$$k_h = (zed^2/kT)\,\tau_o^{-1}\exp(\Delta S^{\ddagger}/k)\exp(-E_a/kT), \qquad (2)$$

where τ_o^{-1} is a frequency factor, E_a is the activation energy for charge transfer, $\Delta S^{\ddagger}$ is the entropy of activation, z is the number of nearest-neighbor cations ($z = 12$ for bixbyite structure), and d is the jumping distance of charge carriers.

The proportionality between σ and $s(1-s)$ has been found to hold qualitatively for intermediate phases of praseodymium oxide PrO_x and terbium oxide TbO_x (*2*, *8*, *9*). However, such data do not suffice to verify Eq. (1)

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quantitatively since each mixed system consists of a series of intermediate phases of narrow composition range and different crystal structure. As pointed out by Honig (*2*, *3*), to verify Eq. (1) it is necessary to carry out the conductivity measurement on an oxide system that has a wide nonstoichiometric composition range.

In the range $1.500 < x < 2.000$, the praseodymium oxide system PrO_x has two wide solid-solution regions of α (fluorite structure) and σ (bixbyite structure) phases, in addition to several intermediate phases such as ι ($PrO_{1.714}$) and β ($PrO_{1.833}$). The σ-phase oxide is stable when $1.6 < x < 1.7$ above 900°C (*10*). It has been found by the authors that substitution of Pr by Gd in PrO_x increases the σ-phase region. The present work aims to measure the electrical conductivity of solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$ ($y = 0.0$, 0.1, 0.2, and 0.4) as a function of temperature and oxygen partial pressure in order to examine the relationship represented by Eqs. (1) and (2).

Experimental

Praseodymium oxide and gadolinium oxide supplied by Shin-etsu Chemical Co. were used as starting materials. Purity of the oxides was 99.99%. Each oxide was dissolved with G.R. grade nitric acid in an appropriate ratio so that a desired composition could be obtained. Then, an excess amount of G.R. grade oxalic acid solution was added and the resulting oxalate precipitate was separated by filtration, oven-dried, and decomposed into oxide in air at 900°C. Then, the oxide sample was ground in an agate mortar, cold-pressed at a pressure of 7 ton/cm^2 and sintered at 1300°C for 23 hr. The dimensions of the sintered sample were 10 × 6 × 5 mm.

A standard four-probe dc technique was employed for the electrical conductivity measurement. Both the current and potential probes consisted of 0.2-mm Pt wires held in shallow grooves on the surface of the sample. The electrodes were coated with Engelhard No. 6926 Pt paste to obtain good electrical contact.

Desired partial pressures of oxygen were obtained by using pure oxygen gas and Ar/O_2 gas mixtures. The gas was circulated by means of a magnetic piston pump.

Nonstoichiometry was determined as a function of temperature and oxygen partial pressure by the microgravimetric method using a Cahn RG electro-balance. The existence range of the homogeneous phase was determined by means of X-ray diffraction and microgravimetric analysis.

Results and Discussion

The conductivity was measured for both increasing and decreasing partial pressures of oxygen. Agreement between both runs was good. Figures 1, 2, 3, and 4 show the results of conductivity measurement of nonstoichiometric $Pr_{1-y}Gd_yO_{1.5+\delta}$ ($y = 0.0$, 0.1, 0.2, and 0.4). Nonstoichiometry on the abscissa in these figures was calculated from the data of the gravimetric study. It was found that $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ has the widest homogeneous nonstoichiometric composition range.

As shown in Fig. 4, the slope of plots of conductivity vs oxygen pressure is positive in a region rich in Pr^{3+} ions and negative in a region rich in Pr^{4+} ions. The maximum conductivity appears at a composition where

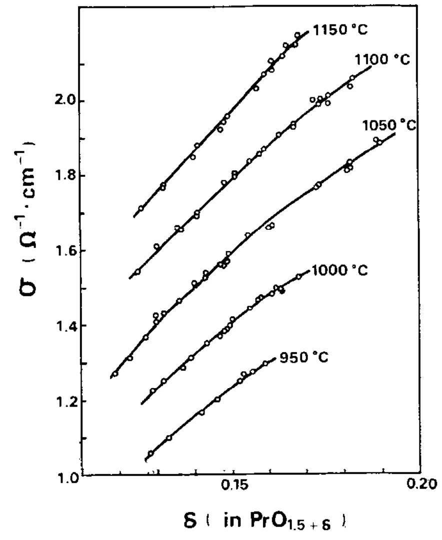

FIG. 1. Isothermal plot of σ vs δ for $PrO_{1.5+\delta}$.

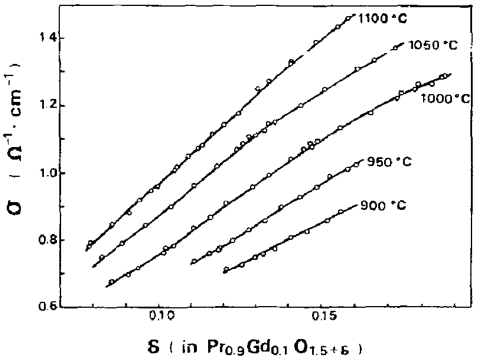

FIG. 2. Isothermal plot of σ vs δ for $Pr_{0.9}Gd_{0.1}O_{1.5+\delta}$.

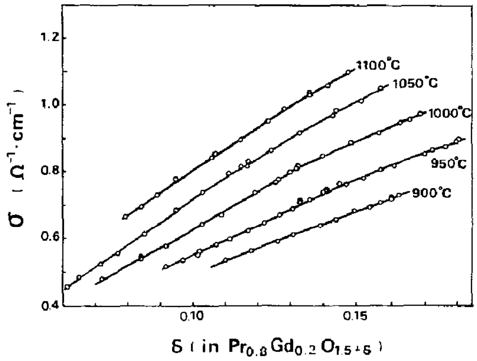

FIG. 3. Isothermal plot of σ vs δ for $Pr_{0.8}Gd_{0.2}O_{1.5+\delta}$.

the amount of Pr^{3+} ions is roughly equal to that of Pr^{4+} ions.

The fraction of Pr^{4+} ions s is related to δ and y using the electroneutrality condition; namely,

$$s = 2\delta/(1 - y). \qquad (3)$$

Since the bixbyite structure contains 32 cation sites per unit cell, the total Pr ion concentration of $Pr_{1-y}Gd_yO_{1.5+\delta}$ is expressed as

$$n = 32(1 - y)/a_o^3 \qquad (4)$$

where a_o is the lattice parameter. For $Pr_{1-y}Gd_yO_{1.5+\delta}$, the probability p of total Pr ions occupying the cationic positions is

$$p = 1 - y. \qquad (5)$$

Inserting Eqs. (3), (4), and (5) into Eq. (1), one can obtain an expression for k_h. The results calculated from Eq. (2) are shown in Fig. 5. The order of magnitudes of k_h were 10^{-3} cm^2 $V^{-1}\cdot sec^{-1}$. Such small values are in accordance with the small-polaron condition derived from the optical-phonon mode (*5*, *6*).

The plot of $\ln \sigma T$ vs $1/T$ at constant δ values exhibits a good linearity, as shown in Fig. 6. Such a linearity indicate that the hopping-rate constant k_h possesses an activation energy and that Eq. (4) is applicable to the present system. If the electronic conduction of $Pr_{1-y}Gd_yO_{1.5+\delta}$ is caused by the so-called band electrons, which are nearly free, the mobility at higher temperatures does not increase exponentially with temperature but should be proportional to $T^{-3/2}$. Therefore, it is concluded that the conduction of nonstoichiometric $Pr_{1-y}Gd_yO_{1.5+\delta}$ would be caused by hopping.

As already shown in Fig. 5, k_h can be regarded as nearly constant in the observed composition range. As the first approximation, a simple model whereby electrons are exchanged between two adjacent cations in

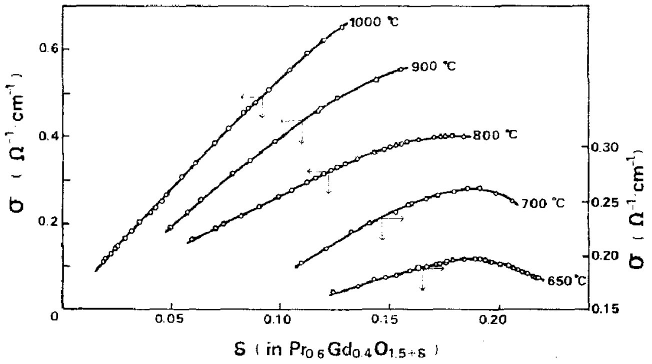

FIG. 4. Isothermal plot of σ vs δ for $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$.

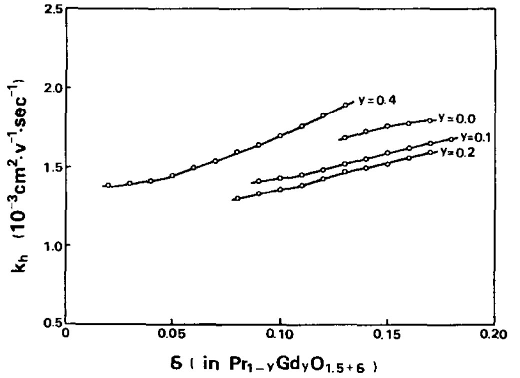

FIG. 5. The plot of k_h vs δ at 1000°C for different solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$.

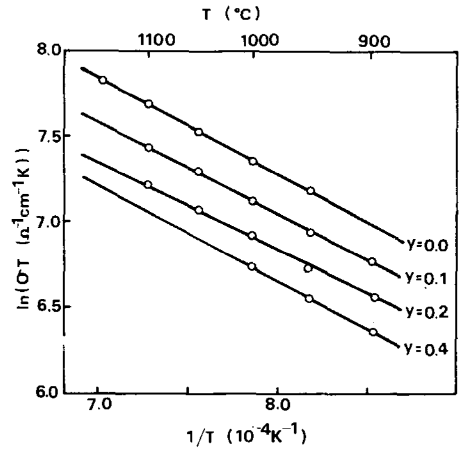

FIG. 6. The plot of $\ln\sigma T$ vs $1/T$ at $\delta = 0.13$ for different solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$.

different valence states is applicable to the present system. If we assume that k_h is constant, the conductivity σ should exhibit a parabolic dependence upon δ. Thus, the existence of a maximum in conductivity data shown in Fig. 4 can be qualitatively explained. Precise examination of Fig. 4 reveals that conductivity reaches a maximum at about $\delta = 0.18$, instead of $\delta = 0.15$, where the amount of Pr^{3+} ions is equal to that of Pr^{4+} ions. This implies that k_h cannot be considered to be independent of δ. Actually, Fig. 5 shows that k_h increases slightly with δ. This is interpreted as discussed below.

Equation (2) is rewritten in the form:

$$-kT\ln k_h(kT/zed^2) = E_a - T(k\ln\tau_o^{-1} + \Delta S^{\ddagger}). \tag{6}$$

In order to examine whether τ_o^{-1} changes with δ, $-kT\ln k_h$ (kT/zed^2) was plotted against T using the observed values for several different δ values. Figure 7 gives the plots. Clearly, the plot exhibits a good linearity, and the slope of the lines is constant. This implies that the preexponential frequency term $\tau_o^{-1}\exp(\Delta S^{\ddagger}/k)$ in the hopping process is nearly independent of δ. The slope of the lines yields $\tau_o^{-1}\exp(\Delta S^{\ddagger}/k) \simeq 10^{12}$ sec^{-1}.

On the other hand, the extraporation of lines to $T = 0$ yields the activation energy, E_a, corresponding to a given value of δ. Figure 8 shows the relationship between E_a and δ. As seen in the figure, E_a decreases gradually with increase of δ. A similar dependence was also observed for CeO_{2-x} by Blumenthal *et al.* (*11*, *12*), who found that E_a increases with increase of x. The dependence of k_h on δ is a result of the gradual decrease of E_a with δ.

The activation energy for hopping would be reduced if the delocalization degree of 4*f* electrons in mixed valence states is increased with an increase of δ. The overlap integral J

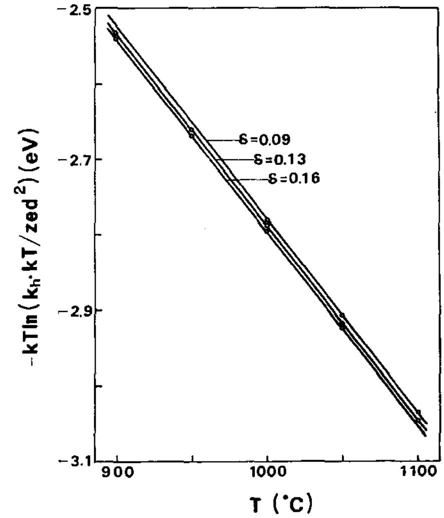

FIG. 7. The plot of $-kT\ln k_h(kT/zed^2)$ vs T for several different nonstoichiometric compositions of $Pr_{0.9}Gd_{0.1}O_{1.5+\delta}$.

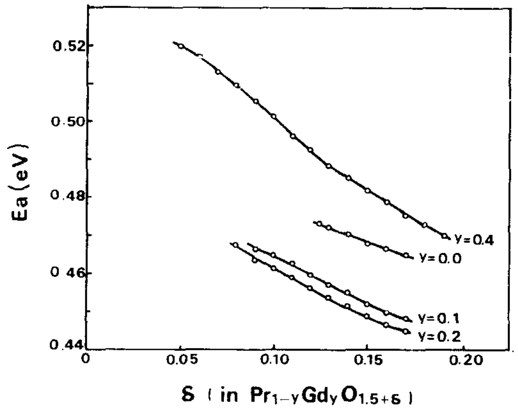

FIG. 8. The dependence of activation energy E_a on δ in $Pr_{1-y}Gd_yO_{1.5+\delta}$.

between two adjacent cations can be taken as a measure of delocalization degree. The value of J depends on the lattice parameter a_0 and decreases exponentially with the increase of a_0 *(7)*. Measurement of lattice parameters of quenched $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$ ($\delta = 0.0$, 0.075, 0.12, and 0.157) by the X-ray diffraction method *(13)* revealed (see Fig. 9) that Vegards' law is obeyed in this system and a_0 decreases linearly with the increase of δ. Therefore, it is presumed that an increase of J with nonstoichiometry δ causes the decrease of activation energy.

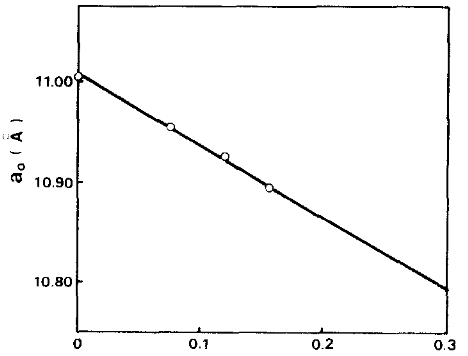

FIG. 9. The relationship between a_0 and δ for $Pr_{0.6}Gd_{0.4}O_{1.5+\delta}$. o, observed. ——, calculated by the following equation: $a_0 = (1 - y - 2\delta)a_{PrO_{1.5}} + 2\delta(2a_{PrO_2}) + ya_{GdO_{1.5}}$, where a_0, $a_{PrO_{1.5}}$ a_{PrO_2}, and $a_{GdO_{1.5}}$ are the lattice parameters of $Pr_{1-y}Gd_yO_{1.5+\delta}$, $PrO_{1.5}$, PrO_2, and $GdO_{1.5}$, respectively.

The activation energy E_a passes through a minimum with increasing y, as shown in Fig. 10. Since a_0 decreases with increasing y at fixed δ values, the decrease of E_a observed in the lower Gd concentration region is considered to be mainly due to the increase of delocalization of $4f$ electrons. As shown in Fig. 11, the fact that the plots of E_a vs a_0 for the samples with $y < 0.2$ fall on essentially the same line supports this conclusion.

The increase of E_a at higher Gd concentrations may be attributed to a decrease in the

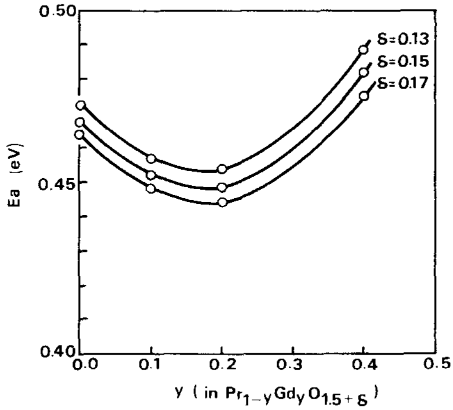

FIG. 10. The dependence of activation energy E_a on y in $Pr_{1-y}Gd_yO_{1.5+\delta}$ for different δ values.

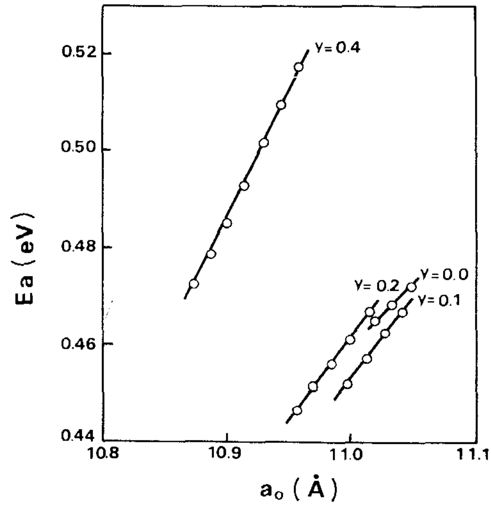

FIG. 11. The dependence of activation energy E_a on lattice parameter a_0 for various solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$.

delocalization of the praseodymium 4*f* electrons by perturbation from the Gd nearest neighbors.

Conclusion

The dependence of the electronic conductivity of solid solutions of $Pr_{1-y}Gd_yO_{1.5+\delta}$ ($y = 0.0$, 0.1, 0.2, and 0.4) on nonstoichiometry δ can be interpreted in terms of the hopping of localized charge carriers between two adjacent Pr ions. The hopping-rate constant k_h was found to increase slightly with increasing δ. This dependence results from a decrease in the hopping activation energy as a result of increasing delocalization of the 4*f* electrons.

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