DIELECTRIC RELAXATION FROM A NETWORK OF CHARGED DEFECTS IN

DILUTE $\text{CeO}_2\text{:Y}_2\text{O}_3$ SOLID SOLUTIONS

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Solid solutions of Y_2O_3 in CeO_2 are examined by the thermal depolarization (or ITC) method of dielectric relaxation. For concentrations ≤ 1 m/o Y_2O_3 , two peaks are observed. The lower temperature peak, Peak 1, is interpreted as due to the relaxation of nn YV_0 pairs (where V_0 = oxygen vacancy), and is analogous to the well-known CaV_0 pair obtained with Ca^{2+} doping. The upper peak, Peak 2, on the other hand, is a broad peak whose position is a function of concentration. It is not due to simple dipoles, but originates in the network of alternately charged $(\text{YV}_0)^+$ pairs and isolated Y' defects by redistribution of vacancies.

1. INTRODUCTION

The role of divalent and trivalent cation dopants in producing good ionic conductivity in the fluorite oxides, such as ceria, is well known [1]. For Ca^{2+} doping, for example, the oxygen vacancy (V_0) introduced for charge compensation associates with the Ca^{2+} ion, at relatively low temperatures, to produce a CaV_0 neutral pair, as shown in Figure 1. Such a pair behaves as an electric and an elastic dipole, giving rise both to dielectric and anelastic relaxation [2], while dissociation of the pair produces free V_0 's which are the charge carriers for the electrical conductivity. Trivalent dopants, M^{3+} , generally produce a higher conductivity than the divalents for the same dopant concentration. They are also of great theoretical interest because only one V_0 is produced for every two M^{3+} ions, i.e., for every molecule of M_2O_3 . Recently, we have made a detailed study of Y_2O_3 -doped CeO_2 [3] and shown that, in the dilute range, Y^{3+} ions are randomly distributed. The electrical behavior is explained by an association reaction in which the doubly charged mobile vacancies, V_0 , migrate to single Y' ions to form charged $(\text{YV}_0)^+$ pairs which are compensated by the remaining Y' ions. (Kröger-Vink notation is used here.) This formation of a network of alternately charged defects in the temperature range where association is nearly complete is unique to such systems and does not occur in any other widely studied ionic materials.

The purpose of the present work is to study dielectric relaxation of Y_2O_3 -doped ceria by the thermal depolarization (often called ITC [4]) method. In so doing, we first observed an enormous high-temperature peak, which was due to the grain-boundary effect, i.e., the presence of a low conductivity layer at the

grain boundaries which also gives rise to an extra arc in complex-impedance plots [5]. This peak is so large that it obscures any smaller dipole-type peaks. We have analyzed this peak elsewhere, and developed two methods for its elimination: i) the insertion of a thin inert dielectric material, and ii) rapid quenching from the polarization temperature after a short polarization time [6]. In the present work, we have used these methods to eliminate the grain-boundary peak, making possible the observation of residual effects due to the point defects present. Unexpectedly, we observe a new peak that is not capable of interpretation by con-

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Figure 1. Diagram of half the unit cell of a fluorite-type oxide containing a nn MV_0 pair (where $\text{M} = \text{M}^{2+}$ or M^{3+}).

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ventional dipole models.

2. EXPERIMENTAL METHODS

Samples were prepared by chemical coprecipitation of Y_2O_3 and CeO_2 . The powder was then dried and taken through a calcining step, then pressed and sintered at 1500°C for 4 days. For further details, see [3]. All Y_2O_3 concentrations quoted are in mole %.

Thermal depolarization measurements were made on disk-shaped samples. The sample was polarized at a temperature T_p , then cooled quickly to -80K . The field was then removed and the sample was heated at a constant rate while measuring the depolarization current $I(T)$ by means of a sensitive electrometer. Details of the apparatus will be reported elsewhere [6].

3. RESULTS AND DISCUSSION

Depolarization curves are given in Figure 2, for samples containing 0.05 to 2.5% Y_2O_3 . It shows that below 2.5% two peaks are obtained. The low temperature peak occurs at -64°C and is nearly a single Debye peak up to 0.5% Y_2O_3 . The second, or higher temperature, peak on the other hand moves down from -1.8°C to -31°C as doping increases from 0.05 to 1%. Also its height, relative to the first peak, decreases with increasing concentration. Data for higher con-

Figure 2. Thermal depolarization curves for five $\text{CeO}_2\text{:Y}_2\text{O}_3$ compositions.

centrations (6, 8 and 10% Y_2O_3) continue to show a single broad peak which moves back to higher temperatures as the Y_2O_3 concentration increases (not shown).

3.1 The Low-Temperature Peak (Peak 1)

The following evidence shows that this peak originates in simple YV_0 pairs:

- The peak height varies linearly with the Y_2O_3 concentration and is comparable to the peak for CaO doping, where CaV_0 pairs have been well established.
- A similar peak is observed by anelastic methods [7]; further, the anelastic relaxation time is $\frac{1}{2}$ the dielectric relaxation time, as expected for the nn pair model [2,8].
- The activation energy for this peak is 0.64 eV, representing the jump of a V_0 bound to an Y^{3+} . This value is quite consistent with the activation energy for motion of a free V_0 , which is 0.61 eV [3].

Accordingly, we believe that the nn pair model of Figure 1 applies to YV_0 pairs as well as to CaV_0 pairs. While the YV_0 pairs carry a net charge, they also possess the necessary dipole moment for such a relaxation process.

3.2 The Higher-Temperature Peak (Peak 2)

At the lower concentrations, this peak is much larger and considerably broader than Peak 1. It would be difficult to explain it in terms of any other point-defect reorientation model. Further we have observed no such peak for CaO -doped CeO_2 .

An interesting feature is that the maximum temperature, T_m , decreases for concentrations up to 2.5% Y_2O_3 and then increases again for higher concentrations. This is just the way that the activation enthalpy of the conductivity, H_σ , varies with concentration [3]. It is, therefore reasonable to regard the relaxation rate, τ^{-1} , as controlled by a vacancy migration process.

For an explanation, we turn to the unique aspect of Y^{3+} doping, viz., the creation of a network of defects, $(\text{YV}_0)^{\cdot}$ and Y' , of alternating charge. An applied electric field can be expected to alter the distribution of vacancies among the Y^{3+} ions leading to a relaxation within this network. It is then reasonable to take τ^{-1} as controlled by a vacancy conduction mechanism, and since it involves redistribution of charge, to be given by [9]:

$$\tau^{-1} = \sigma / \epsilon_0 \epsilon \quad (1)$$

where σ is the conductivity, ϵ_0 the permittivity of vacuum and ϵ the dielectric constant. Since

$$\sigma = (A/T) \exp(-H_\sigma/kT) \quad (2)$$

where A is the preexponential constant, we can find an expression for the peak temperature, T_m ,

by differentiating the conventional expression [4] for the depolarization current, $I(T)$, and inserting Equations (1) and (2). The result is

$$(H_{\sigma}/kT_m) = (A/b\epsilon\epsilon_0) \exp (-H_{\sigma}/kT_m) + 1 \quad (3)$$

where b is the heating rate. Using our earlier results for A and ϵ , we can calculate H_{σ} from T_m at each composition and compare it with the experimental values of H_{σ} from the conductivity measurements. This comparison is shown in Figure 3. (Since H_{σ} is not a monotonic function of composition, the % Y_2O_3 is marked next to each point on the graph.) The straight line, drawn at a 45° slope, shows that the agreement is very good and indicates that Equation (1) is indeed valid.

In order to interpret the peak heights, a more specific model is required. We assume, for simplicity, that the alternating network of $(YV_0)^{\bullet}$ and Y' defects form a regular lattice of the NaCl type, with half-cell spacing of R_0 . However, as in the case of ordered AB alloys, wrong pairs will be present in order to increase the configurational entropy. Such pairs, as illustrated in Figure 4, constitute large dipoles which can be reoriented in the presence of an electric field. The energy of formation of such a wrong pair in a lattice is (in c.g.s. units):

$$\Delta E = 4e^2(\alpha_M - 1)/\epsilon R_0 \quad (4)$$

where e is the electronic charge and α_M the Madelung constant for this "lattice." The number of wrong pairs can be calculated in terms of ΔE . It is then straightforward to show that the

Figure 3. Comparison of H_{σ} from conductivity experiments with values calculated from depolarization peak temperatures using Equation (3).

Figure 4. Model of network of Y' and $(YV_0)^{\bullet}$ defects showing a wrong pair.

ratio, β , of relaxation strengths of Peak 2 to Peak 1 is given by:

$$\beta = (R_0/r_0)^2 \exp (-\Delta E/kT_p) \quad (5)$$

where r_0 is the nn cation-anion separation and T_p is the polarization temperature.

Table 1 gives the ratios β for four compositions as calculated from Equations (4) and (5), and compares the results with the ratio of areas under the peaks, β (expt.), as obtained from Figure 2. It should be noted that all runs were not done in the same way. For example, the 0.05% Y_2O_3 run was done by the fast quenching method while the 0.15% Y_2O_3 was done with an inert dielectric insert (see the Introduction); this results in a more complete polarization and a correspondingly larger Peak 2 in the latter case. The results for β (calc.) and β (expt.) agree in order of magnitude, which is probably all one can expect for such a crude model. For the higher concentrations (0.5 and 1%), the role of wrong pairs at greater distances should increase, which may explain why, for these higher concentrations, the calculated β 's are so small relatively to the experimental quantities.

Table 1. Ratio β of Peak 2 to Peak 1 Relaxation Strengths for Various Y_2O_3 Concentrations.

mole % Y_2O_3	β (calc.)	β (expt.)
0.05	21	10.4
0.15	4.2	11.3
0.5	0.9	3.6
1.0	0.45	1.6

It may be concluded that the network of defects of alternating charge present in dilute $\text{CeO}_2\text{-Y}_2\text{O}_3$ solid solutions provides a novel source of dielectric relaxation which appears as our Peak 2. A more refined calculation of the width and magnitude of this peak would be most desirable.

4. ACKNOWLEDGMENT

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