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Electrical conduction in titania-doped lanthanum chromite ceramics

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The direct and alternating current electrical conductivities of lanthanum chromite ceramic doped with 1 to 3 wt % TiO_2 have been measured at temperatures from 20 to 200° C. The sample containing 3 wt % TiO_2 has been studied in detail because of all the samples it showed the highest sintered density and electrical conductivity. Alternating current conductivity, σ_{ac}, measurements taken over the frequency range 10 kHz to 1 MHz were found to follow a power law of the form $\sigma_{ac} \propto \omega^n$, where ω is the frequency and $0.5 < n < 1$, indicative of a hopping conduction mechanism. In addition, a dispersion in the dielectric constant was observed. The dispersion peak frequency has been found to be thermally activated with an activation energy of 0.423 ± 0.002 eV. The results are successfully interpreted in terms of a model proposed by Pike, wherein a classical hopping of charge carriers (over a potential barrier) between the localized states is considered. The direct current conductivity activation energy predicted from this model is found to be consistent with the experimentally obtained value.

Introduction

Lanthanum chromite ceramics have found a wide range of applications, such as electrodes for magneto-hydro-dynamics (MHD) power generation and refractory materials for high-temperature furnaces. Their electrical properties play an important role in deciding their suitability for such applications. The literature available [1–6] on MHD electrode materials has so far reported direct current (d.c.) conductivity data on some of these materials. It has been established that the charge transport takes place via a thermally activated hopping mechanism between the localized states [7].

The disorder, in atomic configuration and/or composition, is thought to create localized electronic states. Since charge carriers are localized, alternating current (a.c.) techniques are often employed to probe their behaviour. Quite extensive work has been performed on amorphous materials [8], thin films and glasses [9–11]. Recently, dielectric dispersion has been demonstrated in strontium-substituted lanthanum chromite [12]. In the present work an attempt has been made to investigate the electrical properties, particularly the a.c. properties, of $LaCrO_3$ doped with titania. Titania has been added to improve the sinterability of the pure $LaCrO_3$ [13].

2. Experimental procedure

Batches of $LaCrO_3$ doped with 1 to 3 wt % TiO_2 were prepared starting from reagent grade La_2O_3, Cr_2O_3 and TiO_2 employing usual ceramic techniques. Pre-firing was performed at 1400° C for 12 h in a nitrogen atmosphere. The pressed tablets of 14 mm diameter and 4 mm thickness were sintered in air at 1500° C for 4 h. The sample with 3 wt% TiO_2 (Sample LCT-3) sintered to the highest density of any of the compositions (92% of the theoretical density). The densities were measured by the Archimedes method. [14]. Conductivity measurements were made by putting indium amalgam contacts on each face of the tablets. D.c. conductivity data at different temperatures (20 to 200° C) were taken using a two-probe method by measuring the steady-state current at a constant field of 25 V cm^{-1}.

The a.c. conductivity properties, over the frequency range from 10 kHz to 1 MHz at temperatures between 20 and 200° C, were measured using an impedance bridge (Siemens Model R 2077).

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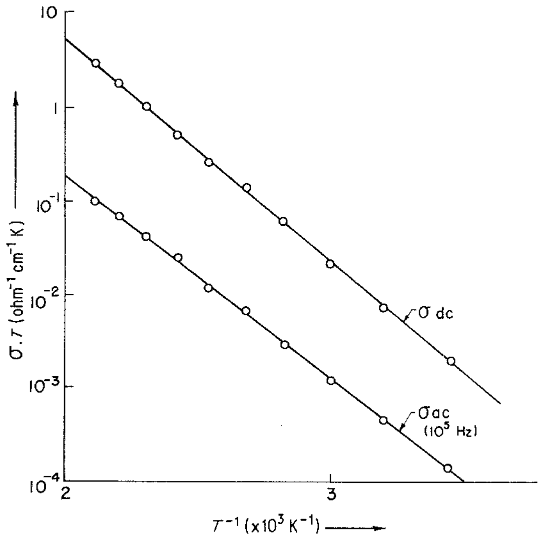

Figure 1 Arrhenius plots for the d.c. and a.c. conductivity variations with temperature of Sample LCT-3.

3. Results

3.1. Temperature variation of d.c. and a.c. conductivities, σ_{dc} and σ_{ac}.

The temperature dependence of the d.c. conductivity and the a.c. conductivity at 10^5 Hz for 3 wt% titania additions is given in Fig. 1. A linear relationship between $\log \sigma T$ and T^{-1} is observed for the temperature range of 20 to 200° C. Activation energies, E_A, for conduction were calculated from the relation expression for the conductivity, σ, [7]

$$\sigma = \frac{A}{T} \exp\left(-E_A/kT\right) \qquad (1)$$

where A is constant and k is Boltzman's constant.

For the Sample LCT-3 under investigation, the values of activation energies for d.c. and a.c. conductivities are found to be 0.469 ± 0.002 eV, respectively.

For lower concentrations of TiO_2, a decrease in the d.c. conductivity and an increase in its activation energy is observed.

3.2. Frequency variation of a.c. conductivity

Fig. 2 shows the variation of a.c. conductivity with frequency, ω, for Sample LCT-3 composition at different temperatures. The a.c. conductivity, σ_{ac}, is found to follow a power law

$$\sigma_{ac}(\omega) \propto \omega^n. \qquad (2)$$

Within the investigated range of temperature and frequency, the exponent n is found to have a value between 0.5 to 1.

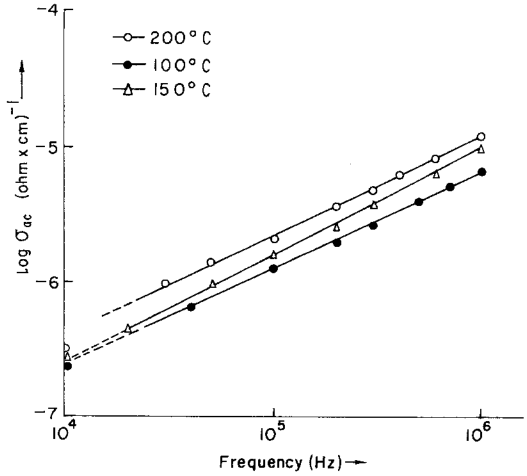

Figure 2 Frequency dependence of a.c. conductivity for Sample LCT-3 at selected temperatures.

3.3. Frequency and temperature variation of dielectric loss tangent, tan δ

Fig. 3 shows the dielectric dispersion cuves at different temperatures for Sample LCT-3. The peaks in the dielectric loss tangent $\tan \delta$, are found to be shifted towards higher frequencies on increasing the specimen temperature.

The Arrhenius plot of $\log \tan \delta$ at the peak frequency, f_{max}, against T^{-1} yields a straight line (see Fig. 4) giving an activation energy of 0.423 ± 0.002 eV for the dielectric relaxation process involved.

4. Discussion

The rise in the d.c. conductivity and the fall in its activation energy on the addition of titania indi-

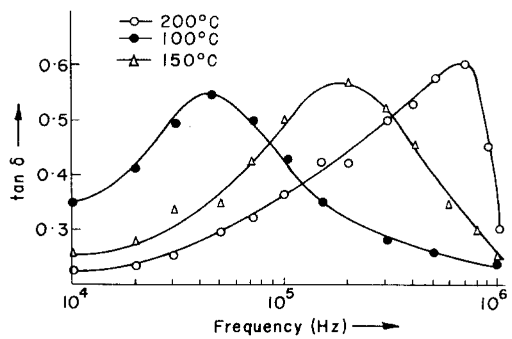

Figure 3 Frequency dependence of tan δ for Sample LCT-3 at selected temperatures

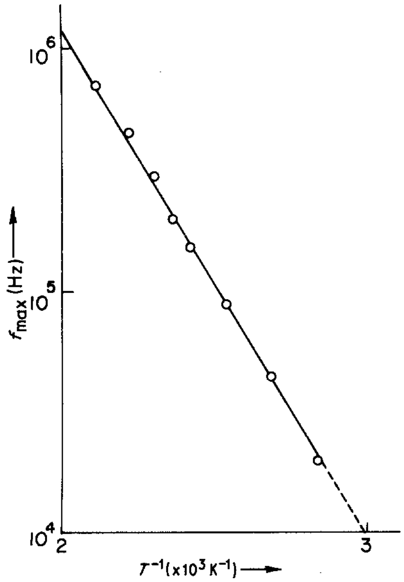

Figure 4 Temperature dependence of f_{max} for Sample LCT-3.

cate that the number of charge carriers increases with the titania content.

The a.c. conductivity data may be analysed by the new hopping model proposed by Pike [15] which has explained the a.c. conductivity results obtained for many oxides and amorphous materials. In this model, the carrier motion in characterized by an activation energy, W, which is equivalent to the height of the potential barrier separating the sites above the ground state (Fig. 5). Pike and Rockstad [16] took the site potential to be coulomb-like in shape and related the barrier height, W, to the site separation, R. The a.c. conductivity to a first approximation may then be expressed as

$$\sigma_{ac}(\omega) = \left(\frac{\pi^2 N^2 \epsilon}{24}\right)\left(\frac{3e^2}{\omega W_m}\right)^6 \frac{\omega^n}{\tau_0^{1-n}}, \quad (3)$$

where ϵ is the dielectric constant, W_m is the energy of the impurity ionization level measured from the ground state, τ_0 is the characteristic relaxation time, e is the electronic charge and N is the density of defect states. It is now possible to estimate τ_0 involved in the hopping process using the following equation [17]

$$\frac{\partial}{\partial T}\left[\log\{\sigma_{ac}(\omega)\}\right] = \left\{\frac{6k \log\left[1/(\omega\tau_0)\right]}{W_m}\right\}. \quad (4)$$

Substituting the value of

$$\frac{\partial}{\partial T}\left[\log\{\sigma_{ac}(\omega)\}\right] = 12 \times 10^{-3}\,\mathrm{K}^{-1}$$

from Fig. 6 at $\omega = 2\pi \times 10^5$ Hz and $T = 373$ K and estimating W_m from [18] gives

$$1 - n = 6kT/W_m. \quad (5)$$

τ_0 is computed to be 2.3×10^{-11} sec. Applying the value of $n \approx 0.6$, as calculated from Fig. 2, in the above equation, W_m is calculated to be 0.48 eV. The value of τ_0 so obtained is larger than expected. It has been suggested that for classical hopping there is a dependence of τ on the site separation, R. If the separation is large, screening by free carriers may increase the relaxation time [15, 16].

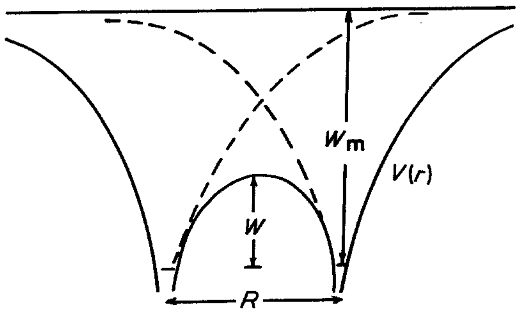

Figure 5 The model of overlapping coulomb-like shaped site potentials. Charge transport between localized states via hopping over the potential barrier separating two identical sites of carrier localization of separation distance R. W_m is the ionization energy level, i.e. the energy difference between the ground state of the potential well and the ionized state and W is the height of the potential barrier characterized by the activation energy.

The values of $\sigma_{ac}(\omega)$ and ϵ at a temperature of 100° C and frequency of 10^5 Hz are approximately $1.58 \times 10^{-6} (\Omega\,\mathrm{cm})^{-1}$ and approximately 100, respectively. From these values and from the preceding values of W_m and τ_0, N is calculated from Equation 3 to be $3.6 \times 10^{16}\,\mathrm{cm}^{-3}$.

According to Seager and Pike [18], the activation energy for d.c. conductivity is the critical barrier height W_0 for which an infinite hopping path exists. It has been expressed by

$$W_0 = W_m - \left(\frac{3e^2}{\epsilon}\right) S N^{1/3} \quad (6)$$

where S is a constant and has a theoretical value of about 1.15.

From Equation 6, W_0 is computed to be about 0.478 eV. This value of activation energy for d.c. conduction is very close to the experimentally-observed value of approximately 0.469 eV.

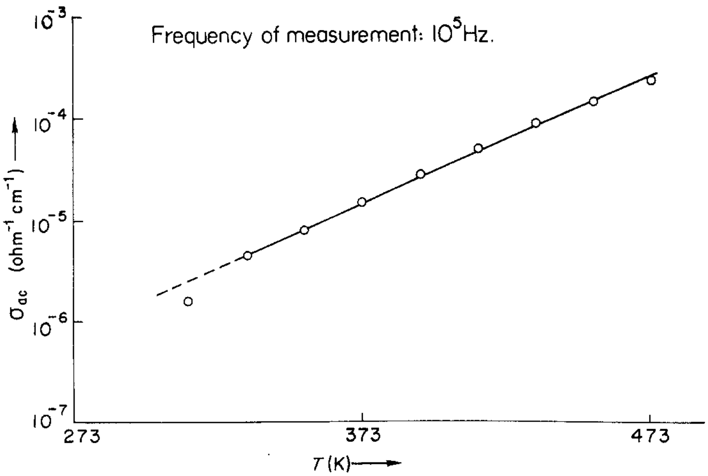

Figure 6 Temperature dependence of a.c. conductivity for Sample LCT-3.

The model proposed by Pike also predicts the occurrence of a thermally activated dielectric relaxation with an activation energy, W, given by

$$\tau \propto \exp\left(-\frac{W}{kT}\right), \tag{7}$$

and the value obtained is $W \approx 0.423 \pm 0.002$ eV, which is very close to the activation energy for a.c. conductivity at 10^5 Hz of 0.436 ± 0.002 eV. The difference may be accounted for by the fact that the constant of proportionality, which has been assumed to be approximately 1, is indeed a function of both the site separation, R, and the radius of the localized wave function [15].

In order to ascertain the extent to which loss peaks could be described by a Debye process, ϵ'' (the imaginary part of the dielectric constant) was plotted against ϵ' (the real part of the dielectric constant) following the Cole–Cole [19] formalism. Relatively well-defined semicircles are obtained (Fig. 7) whose centres are found to be depressed slightly below the real axis. The complex dielectric constant, ϵ^*, is then given by [19] the Debye equation

$$\epsilon^* = \epsilon_\infty + [(\epsilon_s - \epsilon_\infty)/\{1 + (j\omega\tau)^{1-\alpha}\}], \tag{8}$$

where ϵ_∞ and ϵ_s are the high frequency and static values of the dielectric constant, respectively, and α represents the angle shown in Fig. 7. The general interpretation of the inclined semicircle is that there is a distribution of relaxation times in the material and that α gives a measure of this distribution. The value of α is about 0.16 found in this study implies a fairly narrow distribution extending over one or more orders of magnitude [20]. This distribution in τ is reflected in the frequency spread in the tan δ peaks, illustrated in Fig. 3.

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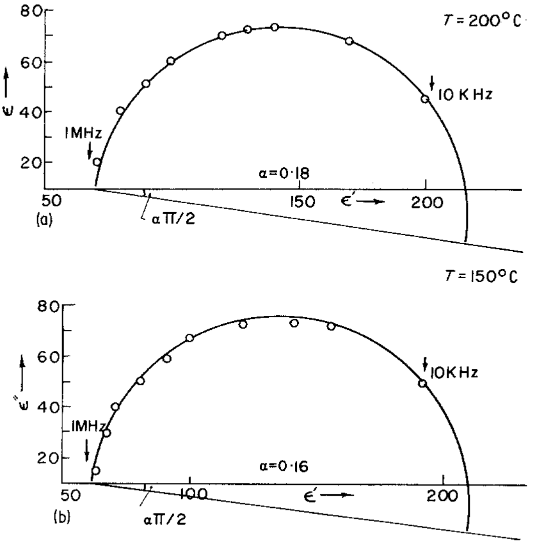
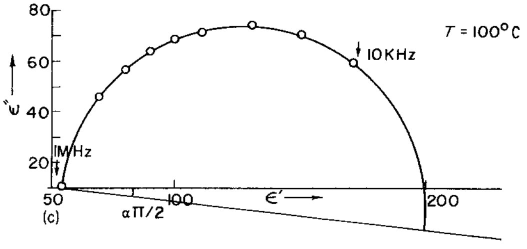


Figure 7 Cole–Cole plots for Sample LCT-3 at selected temperatures.



oratory for providing the laboratory facilities for carrying out the work.

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