

Dielectric properties of the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$

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Abstract. Dielectric behaviour of samples of the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ with $x \leq 0.20$ has been studied in the temperature range 300–525 K as a function of frequency. The strong dispersion of ϵ and D observed in these materials indicate the significant contribution of interfacial polarisation to the observed dielectric properties. The interfacial polarisation arises due to the presence of microscopic chemical heterogeneities arising out of the slow diffusion-controlled solid state sintering process used for their preparation.

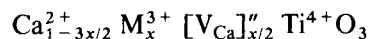
Keywords. Dielectric constant; dielectric loss; interfacial polarisation; microscopic chemical heterogeneities; Ca–La–Ti–Co oxide.

1. Introduction

Calcium titanate doped with yttrium shows interesting electrical properties which depend on the sintering atmosphere (Neirman and Burn 1984). For example, on doping with > 1 mol% Y and sintering in a nitrogen atmosphere, CaTiO_3 becomes semiconducting showing dielectric relaxator behaviour characteristic of grain boundary layers. During sintering, oxygen is lost from these ceramics according to the reaction



where all the species are represented according to the Kröger Vink notation of defects. On cooling from the firing temperature, reoxidation of the products takes place. However, sufficient time is not available for the reoxidation of the grains. Only grain boundaries are reoxidized and become insulating, thus enveloping the semiconducting grains. This gives rise to barrier layers at grain/grain boundary interfaces imparting very high dielectric constant to the resulting materials. On replacing divalent calcium by trivalent yttrium or rare-earth ions, charge neutrality is achieved by creating an appropriate number of vacancies at calcium sites in CaTiO_3 as represented by the formula



where $\text{M}^{3+} = \text{Y}^{3+}$ or rare-earth ion and $[\text{V}_{\text{Ca}}]''$ represents a vacant Ca^{2+} site.

Recently we prepared two valence-compensated solid solutions, (i) $\text{Pb}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $0.10 \leq x \leq 0.95$ (Parkash *et al* 1987), and (ii) $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x \leq 0.40$ (Parkash *et al* 1988a). The compositions for $x \leq 0.50$ in the system (i) (Parkash *et al* 1988b) and all the compositions in the system (ii) (Parkash *et al* 1988c) are found to exhibit dielectric relaxator behaviour. In view of this and the

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interesting electrical and dielectrical properties shown by the Y-doped CaTiO_3 system, we synthesized a few compositions in the valence compensated solid solution, $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$ for $x \leq 0.50$ (Parkash *et al* 1988d). All these compositions are single phase materials. In this paper, we report the dielectric properties of these materials.

2. Experimental

Compositions with $x = 0.05, 0.10, 0.20, 0.30$ and 0.50 were prepared by the ceramic method using calcium carbonate, lanthanum oxalate, titanium dioxide and cobalt oxalate. All these materials were of reagent grade with purity better than 99.5%. The details of method of preparation have already been reported (Parkash *et al* 1988d). X-ray diffraction patterns of the sintered samples were taken in an X-ray diffractometer (JEOL) using Cu-K_α radiation to check the formation of single phase materials. Bulk density of these materials was determined by the water displacement method and the percentage porosity was calculated from the values of true density and bulk density. For the measurements of dielectric properties, the sintered pellets were polished, washed with *iso*-propanol to remove any moisture and dried. Air-dried silver paint was used as electrode. Capacitance and dielectric loss, D , are measured as a function of temperature in the frequency range 1 kHz–1 MHz using an impedance analyzer (HP 4192A LF). Measurements on the samples with $x = 0.30$ and 0.50 were not possible because of their high conductivity. For microstructural studies, polished pellets were etched using 10% HCl+2–3 drops of 40% HF. The etched surfaces were coated with gold and micrographs were taken using a scanning electron microscope (JEOL PSM-800).

3. Results and discussion

X-ray diffraction (XRD) data indicated the formation of single phase materials in all the samples. The XRD data for all the five compositions could be indexed on the basis of a pseudo-cubic unit cell similar to CaTiO_3 (Murdoch 1951). The lattice parameters as reported earlier are given in table 1. The bulk as well as X-ray densities and the percentage porosities for all the samples are also given in table 1.

Typical scanning electron micrographs of the samples with $x = 0.05, 0.10$ and 0.30 are given in figure 1. The average grain size calculated by the linear intercept

Table 1. Structure, lattice parameter, a , bulk density, X-ray density and percentage porosity for various samples in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$. The structure in all cases is pseudo-cubic.

| x | a (Å) | X-ray density | Bulk density | Percentage porosity |
|------|---------|---------------|--------------|---------------------|
| 0.05 | 15.273 | 4.22 | 4.01 | 5.0 |
| 0.10 | 15.280 | 4.38 | 4.18 | 4.0 |
| 0.20 | 15.374 | 4.62 | 4.30 | 7.0 |
| 0.30 | 15.277 | 5.03 | 4.92 | 2.0 |
| 0.50 | 15.329 | 5.61 | 5.57 | 1.0 |

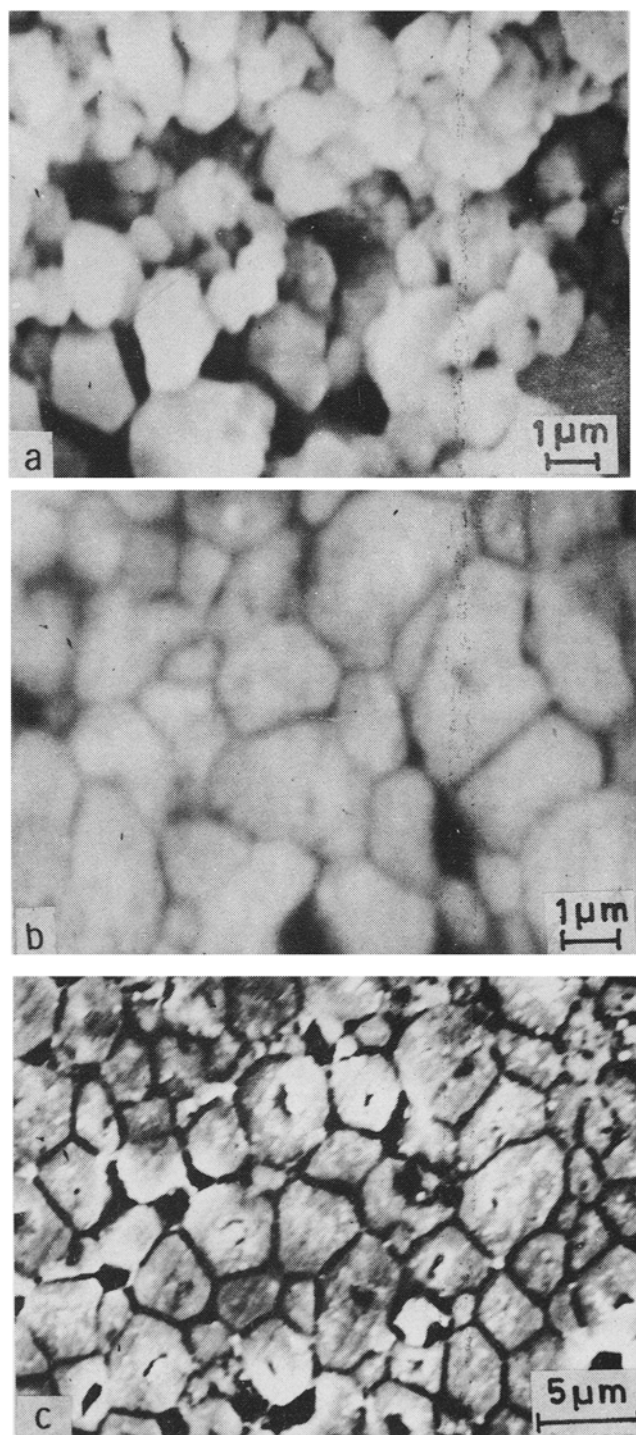


Figure 1. Scanning electron micrographs of samples with (a) $x=0.05$, (b) $x=0.10$ and (c) $x=0.30$.

method is in the range 2–4 μm for all the samples. The fine-grain size of these materials can now be explained. Doping of CaTiO_3 with rare earth ions like La^{3+} facilitates the loss of oxygen (Neirman and Burn 1984). Similarly, the presence of acceptor ions such as Fe, Co, Ni etc. at the Ti site also results in oxygen deficient materials in order to maintain charge compensation (Newnham 1983). Therefore, the simultaneous presence of La^{3+} and Co^{3+} in CaTiO_3 will promote the loss of oxygen. There may be segregation of the charged oxygen vacancies at the grain boundaries. These oxygen vacancies may form dipoles with $[\text{Co}_{\text{Ti}^{4+}}^{2+}]''$ or $[\text{Co}_{\text{Ti}^{4+}}^{3+}]'$ ions which inhibits grain growth.

Plots of ϵ vs. T and D vs. T at 1, 10 and 100 kHz are shown in figures 2–4 for compositions with $x=0.05$, 0.10 and 0.20 respectively. For the composition with $x=0.05$, the dielectric constant is found to vary very little with temperature within the temperature range of measurements. The variation decreases with increasing frequency. D remains constant up to a particular temperature and thereafter starts increasing rapidly.

In the samples with $x=0.10$ and 0.20, both ϵ and D increase with temperature at all the three frequencies. The variation with temperature decreases with increasing frequency. A small hump is observed in the D vs. T plot of the sample with $x=0.20$ (figure 4b) at 1 kHz around 400 K. The room temperature values of ϵ and D at 1, 10 and 100 kHz for all the three samples are given in table 2.

Both dielectric constant and dielectric loss strongly depend on frequency with their magnitude decreasing with increasing frequency. This indicates the significant contribution of interfacial polarisation to the observed dielectric properties of these materials. These materials are prepared by a slow diffusion-controlled solid state sintering process which gives rise to microscopic chemical heterogeneities in local regions. Different microscopic regions have different conductivities because of different compositions giving rise to interfacial polarisation. The strong frequency dependence of dielectric constant and dielectric loss is attributed to the slow

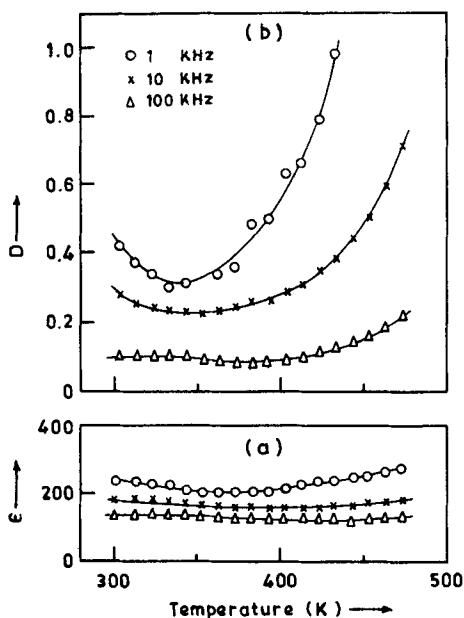


Figure 2. Plots of (a) ϵ and (b) D vs. temperature for the sample with $x=0.05$ in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

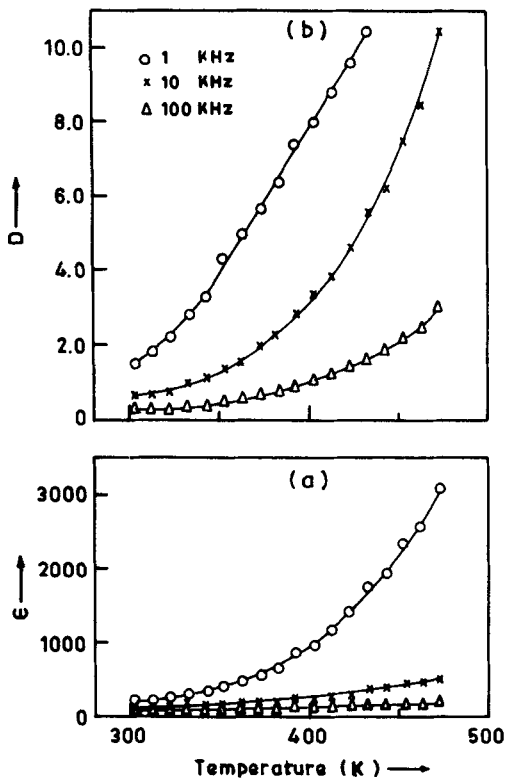


Figure 3. Plots of (a) ϵ and (b) D vs. temperature for samples with $x=0.10$ in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

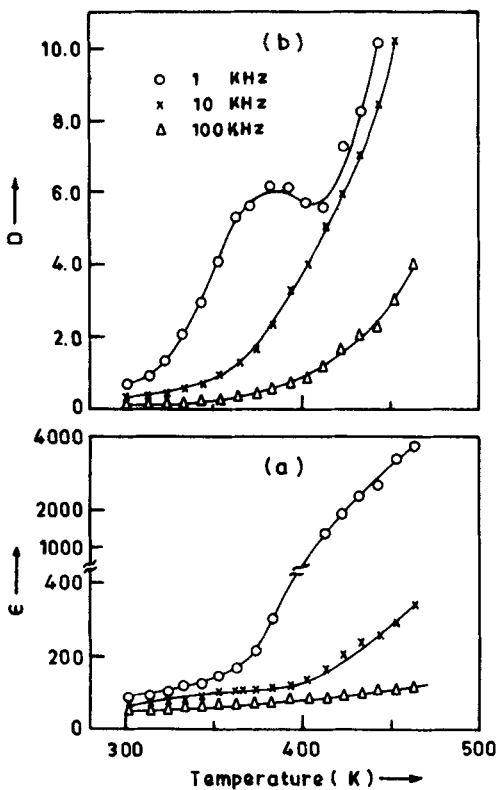


Figure 4. Plots of (a) ϵ and (b) D vs. temperature for samples with $x=0.20$ in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

Table 2. Room temperature values of ϵ and D at 1, 10 and 100 kHz for various samples in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

| x | ϵ | | | D | | |
|------|------------|--------|---------|-------|--------|---------|
| | 1 kHz | 10 kHz | 100 kHz | 1 kHz | 10 kHz | 100 kHz |
| 0.05 | 230 | 170 | 130 | 0.37 | 0.26 | 0.10 |
| 0.10 | 210 | 120 | 80 | 1.53 | 0.57 | 0.27 |
| 0.20 | 90 | 70 | 60 | 0.71 | 0.26 | 0.13 |

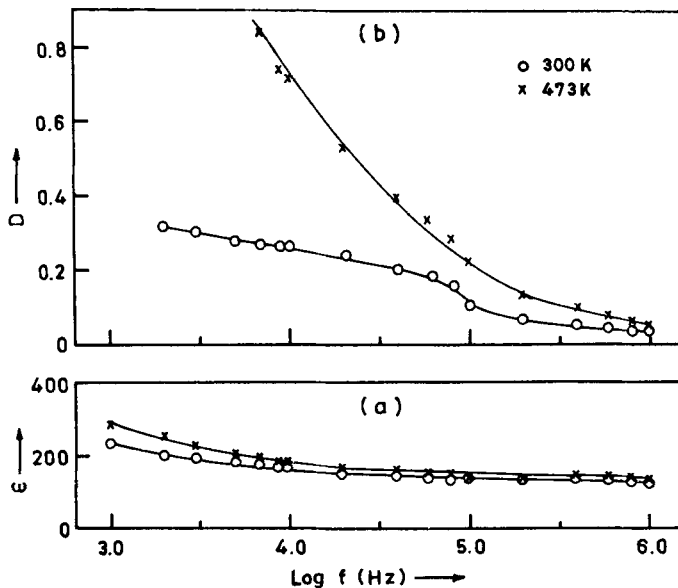


Figure 5. Plots of (a) ϵ and (b) D vs. $\log f$ for samples with $x=0.05$ in the system $\text{Ca}_{1-x}\text{La}_x\text{Ti}_{1-x}\text{Co}_x\text{O}_3$.

response of interfacial polarisation to the applied field. The high dielectric loss in these materials is due to the high d.c. conductivity for which the d -electrons of the cobalt ions are mainly responsible.

Variation of ϵ and D with the logarithm of frequency at a few selected temperatures are shown in figures 5 and 6 for samples with $x=0.05$ and 0.20, respectively. The behaviour of samples with composition $x=0.10$ is similar to that of those of composition $x=0.20$. ϵ varies very little with frequency in samples with $x=0.05$. Strong dispersion is observed in the samples with $x=0.10$ and 0.20. The dispersion decreases with increasing frequency. D shows a strong frequency dispersion in all the three samples. A peak is observed in the D vs. $\log f$ plot of the sample with $x=0.20$ around 9 kHz at ~ 473 K and is expected to occur at higher frequencies with increase in the temperature. Similar anomalies seem to occur in the D vs. $\log f$ plots of samples with $x=0.10$. This is a Debye-type relaxation in which a peak is observed when

$$\omega\tau = 1, \quad (2)$$

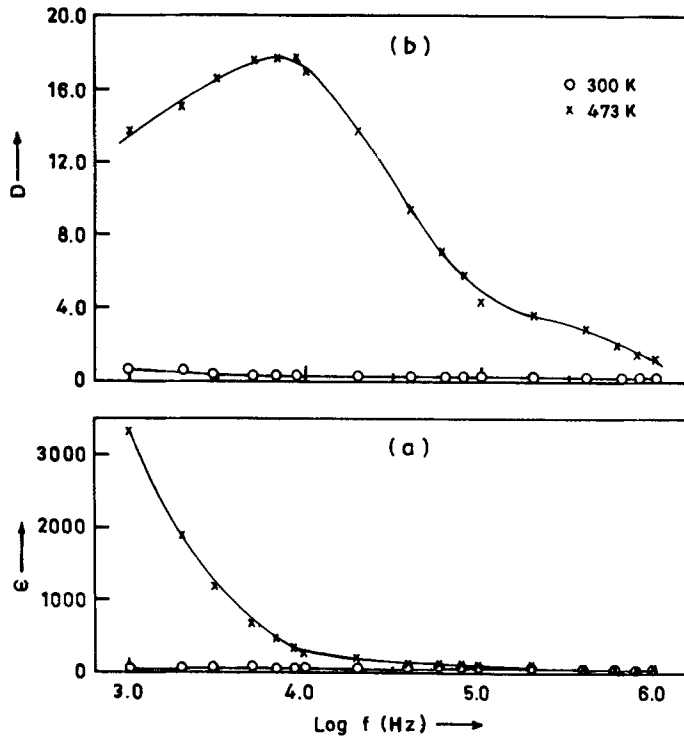


Figure 6. Plots of (a) ϵ and (b) D vs. $\log f$ for samples with $x=0.20$ in the system $Ca_{1-x}La_xTi_{1-x}Co_xO_3$.

where $\omega = 2\pi f$ and τ is the relaxation time. With increasing temperature, (2) will be satisfied for higher values of ω as τ decreases with increasing temperature.

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