JOURNAL OF MATERIALS SCIENCE 25 (1990) 2181–2184

Dielectric properties of the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$ $(0.00 \leqslant x \leqslant 0.15)$

H. S. TEWARI, OM PARKASH, V. B. TARE*, DEVENDRA KUMAR‡
*School of Materials Science and Technology, *Department of Metallurgical Engineering, and ‡Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varansi 221005, India*

The dielectric behaviour of the compositions with $x \leqslant 0.15$ in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$ sintered and cooled in air has been studied. Space-charge polarization which arises due to the presence of chemical inhomogeneities at the micro-level contributes significantly to their dielectric constant. The composition with $x = 0.05$ exhibits temperature and frequency-independent dielectric constant and very small dielectric loss.

1. Introduction

Strontium titanate doped with rare earth ions exhibits relaxor behaviour with increased permittivity [1, 2]. On heating in atmospheres having very low partial pressure of oxygen, it becomes semiconducting and potentially useful as a barrier layer capacitor material [3, 4]. Calcium titanate doped with yttrium also shows interesting dielectric and electrical properties which depend on the sintering atmosphere [5]. For example, on doping with > 1 mol % of yttrium and sintering in a nitrogen atmosphere it becomes semiconducting, showing dielectric relaxor behaviour characteristic of grain boundary layers. Doping with rare earth or yttrium facilitates the loss of oxygen from the material during sintering, making it semiconducting. During cooling of the ceramic from the firing temperatures, oxygen is regained. However, because of insufficient time, complete reoxidation of the grains does not occur. Oxidation is thus restricted to only grain boundaries, resulting in an insulating layer surrounding the semiconducting grains. This gives rise to barrier-layer relaxator behaviour as mentioned above.

On replacing Ca^{2+} by Y^{3+}, charge compensation is achieved by creating an appropriate number of oxygen vacancies in the calcium sublattice as represented by the formula $Ca_{1-(3x/2)}V_{Ca_{x/2}}Y_xTiO_3$ [5] where V_{Ca} represents a vacant calcium site. Recently we synthesized the solid solution $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$ for all values of x in the range $0.05 \leqslant x \leqslant 0.99$ [6]. This represents a valence-compensated solid solution where simultaneous replacement of La^{3+} by Pb^{2+} and Co^{3+} by Ti^{4+} leads to internal charge compensation. In this system, compositions with $0.50 \leqslant x \leqslant 0.90$ were found to exhibit relaxator behaviour [7]. With this in view and interesting behaviour exhibited by yttrium-doped calcium titanate as mentioned above, we attempted to synthesize the valence-compensated solid solution $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$ for $x \leqslant 0.50$. X-ray diffraction studies showed the formation of solid solution only in the compositions with $x \leqslant 0.15$ [8]. In this paper we report the dielectric behaviour of these compositions which are sintered and cooled in air.

2. Experimental procedure

Compositions with x = 0.00, 0.01, 0.03, 0.05, 0.10 and 0.15 were prepared by the ceramic method starting with calcium carbonate, yttrium oxalate, titanium dioxide and cobalt oxalate all having purity better than 99.5%. The detailed method of preparation has been reported earlier [8]. Formation of a single phase was confirmed by X-ray diffraction (XRD). For dielectric measurements, sintered pellets with thickness in the range 1.0 to 2.0 mm and diameter 11 to 12 mm were polished and coated with air-dried silver paint. Capacitance and dielectric loss were measured as a function of frequency in the range 100 Hz to 1 MHz at steady temperatures between 300 and 525 K employing a Hewlett-Packard 4192 A LF impedance analyser. Microstructures of freshly fractured surfaces of the pellets as well as polished and chemically etched surfaces of the sintered cylindrical pellets were observed using a Philips PSEM 500 scanning electron microscope.

3. Results and discussion

All the compositions synthesized were found to be single-phase materials having a crystal structure similar to $CaTiO_3$. The lattice parameters of all the compositions as reported earlier [8] are given in Table I. Density and porosity of the sintered pellets are also given in Table I. All the samples are found to have a bulk density > 90% of the theoretical density.

Typical plots of dielectric constant, ε and fractional dielectric loss, D as a function of temperature at 1, 10 and 100 kHz are shown in Figs 1 to 3. The behaviour of the samples with x = 0.00 and 0.01 is quite similar. The value of ε remains constant with temperature up to a particular temperature, T_a, at all the frequencies after which it increases very rapidly up to 525 K at 100 kHz. The value of ε slightly decreases with frequency, the difference increasing with increasing

0022-2461/90 $03.00 + .12 © *1990 Chapman and Hall Ltd.*

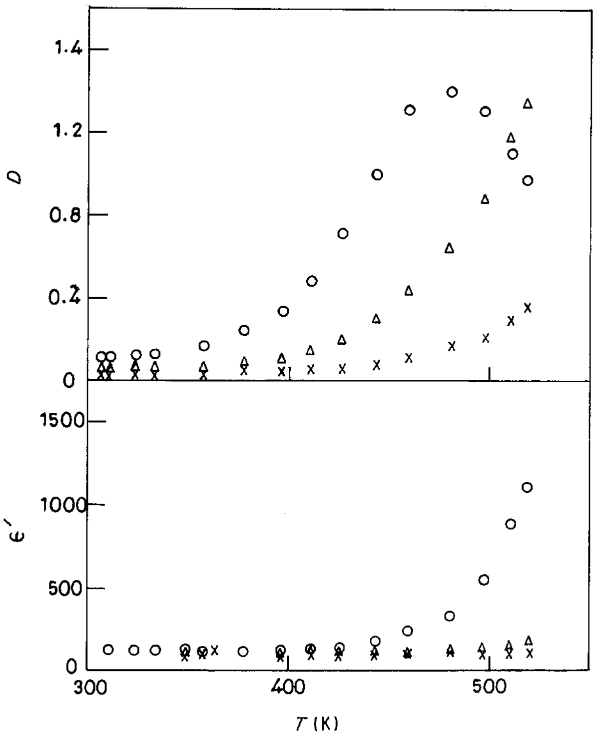

Figure 1 Plots of ε and D against temperature at (○) 1, (△) 10 and (x) 100 kHz for the composition with x = 0.01 in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$.

temperature beyond T_a. All these features indicate the predominant contribution of interfacial polarization to the observed dielectric constant of these materials.

The behaviour of the compositions with x = 0.03, 0.10 and 0.15 is essentially similar (Fig. 3). There is a continuous increase of dielectric constant with temperature above room temperature. Both the dielectric constant and dielectric loss depend strongly on frequency, their magnitude decreasing with increasing frequency. This shows that space charge polarization contributes more significantly to the observed dielectric parameters in these compositions. This is due to the increasing conductivity of these samples with increasing concentration of cobalt ions, which are primarily reponsible for the conduction process. The space-charge polarization in these materials arises due to the chemical heterogeneities present in them at the micro-level as a result of the slow diffusion-controlled thermochemical ceramic process used for their preparation. The values of ε and D at 1 kHz and 300 K for the various compositions are given in Table I.

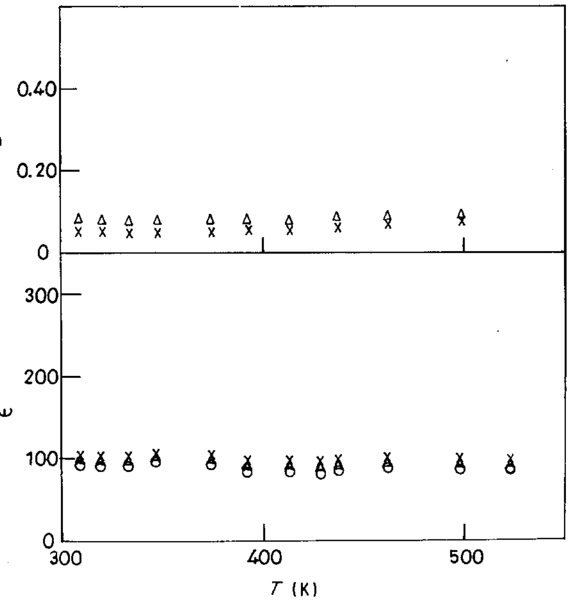

Figure 2 Plots of ε and D against temperature at (○) 1, (△) 10 and (x) 100 kHz for the composition with x = 0.05 in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$.

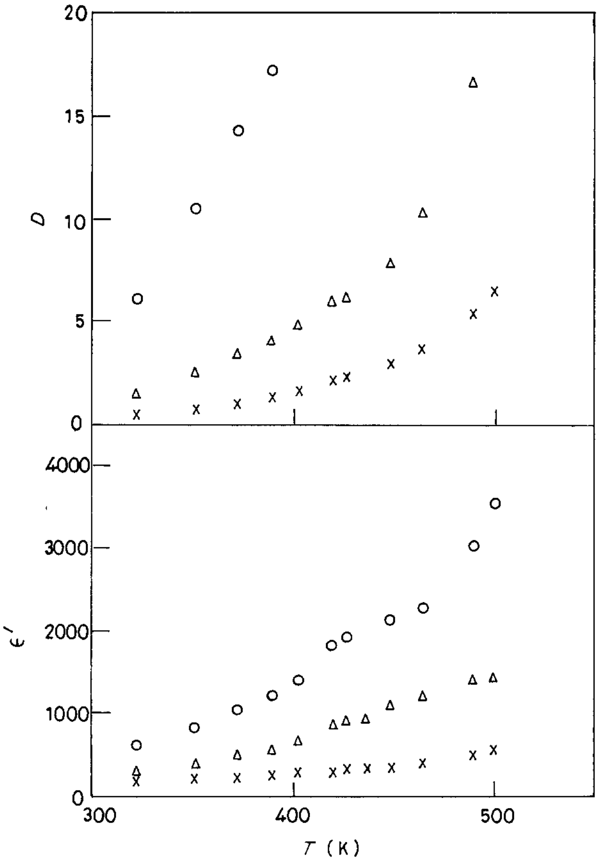

Figure 3 Plots of ε and D against temperature at (○) 1, (△) 10 and (x) 100 kHz for the composition with x = 0.10 in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$.

The behaviour of the composition with x = 0.05 is entirely different from all other compositions (Fig. 2). ε remains independent of temperature and frequency over the entire range of temperature (300 to 525 K). The dielectric loss is also very low compared with that of the other compositions. It is worth mentioning that in this composition alone, splitting of the strongest XRD line occurs indicating the presence of distortion from the cubic symmetry [8]. The almost temperature- and frequency-independent value of the dielectric loss in this sample indicates a very wide distribution of relaxation times [9]. The reason for the anomalous

TABLE I Lattice parameter a, bulk density ϱ, porosity, dielectric constant ε and dielectric loss D (at 1 kHz and 310 K) for various compositions in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$

x	a (nm)	ϱ (g cm^{-3})	Porosity (%)	ε	D
0.00	1.5319	2.89	28	84	0.68
0.01	1.5259	3.60	11	123	0.11
0.03	1.5274	3.73	8	519	0.67
0.05	1.5249	3.96	4	94	0.01
0.10	1.5272	4.15	1	568	5.34
0.15	1.5266	4.24	1	200	5.64

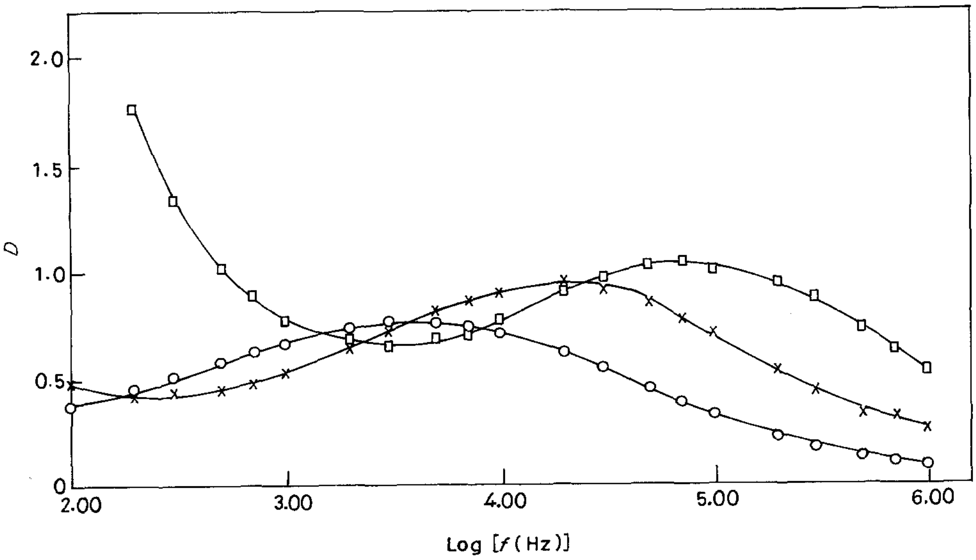

Figure 4 Plots of D against frequency (○) at 310, (x) 400 and (□) 485 K for the composition with $x = 0.03$ in the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$.

behaviour of this composition is not clear at the moment.

The variation of D with $\log f$ for the composition with $x = 0.03$ is shown in Fig. 4. A peak is observed in the value of D at a certain frequency. This peak frequency shifts to a higher frequency with increasing temperature. This is characteristic of Debye relaxation in which a peak is observed when $\omega\tau = 1$ where $\omega = 2\pi f$ and τ is the relaxation time. With increasing temperature, the relation $\omega\tau = 1$ will be satisfied for higher values of ω as τ decreases with increasing T. Similar behaviour is observed for $x = 0.01$. No peak is observed in D against $\log f$ plots of the composition with $x = 0.10$ and 0.15. In these samples the value of D decreases with f at all temperatures.

Preliminary results of complex plane impedance analysis of these samples (unpublished results) show that there are two contributions to their observed dielectric behaviour, one due to grains and the other due to grain boundaries. The grain boundary contribution dominates in the frequency ranges 1 to 10 kHz and 1 to 100 kHz for $x = 0.01$ and 0.03, respectively.

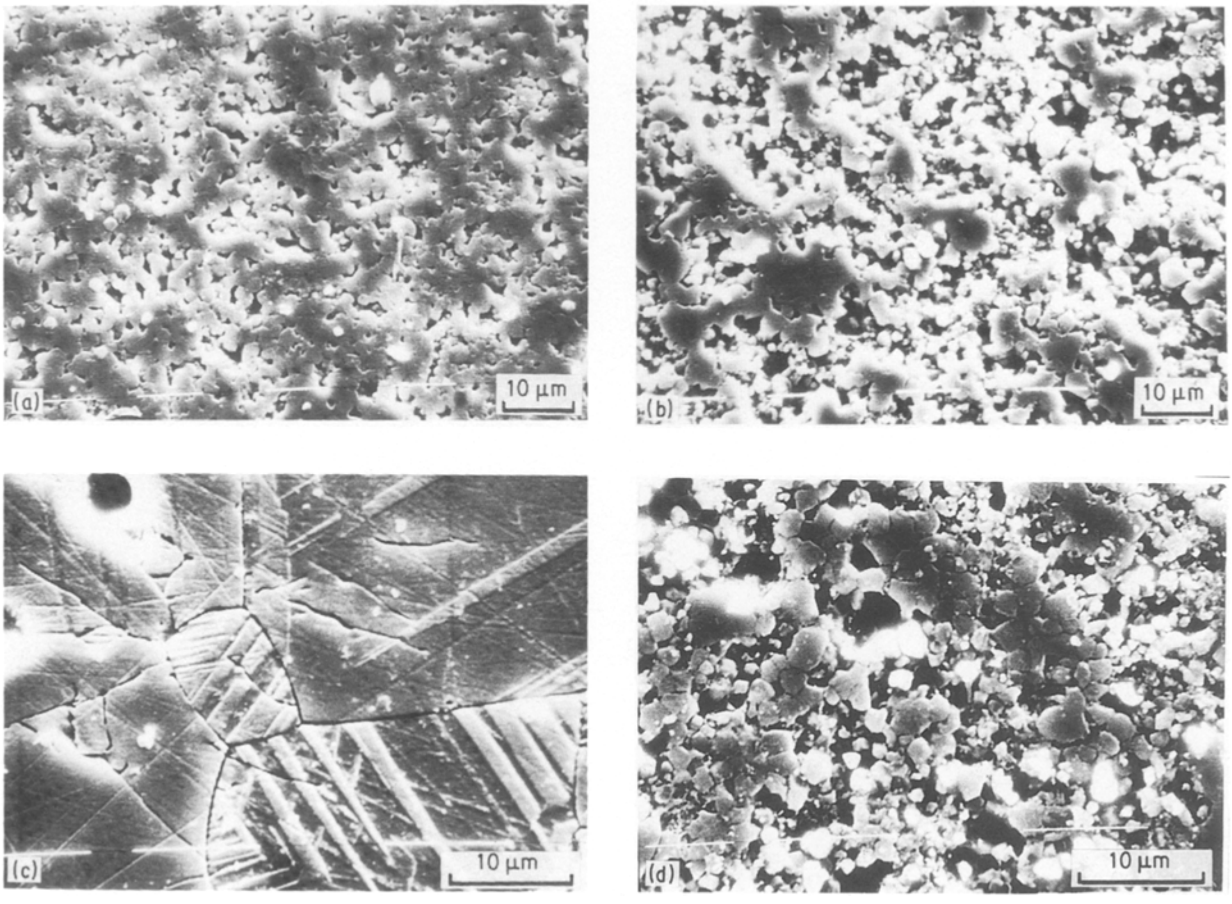

Figure 5 Scanning electron micrographs of the system $Ca_{1-x}Y_xTi_{1-x}Co_xO_3$ with x = (a) 0.01, (b) 0.03, (c) 0.05 and (d) 0.10.

The bulk contribution dominates in the higher frequency range. The relaxation peaks observed in D against $\log f$ plots are therefore due to the grain boundary process. This is in conformity with the microstructural results, which indicate that grain boundaries have a local structure which is different from the bulk structure.

Scanning electron micrographs of the various samples are shown in Fig. 5. It is observed that the grain size for the compositions with $x = 0.01$, 0.03 and 0.15 is small (2 to 3 μm). The composition with $x = 0.05$ has grains of size 20 to 30 μm. The micrograph of this composition (Fig. 5c) shows the presence of domain structure in some of the grains. The average grain size in all other compositions is rather small. As mentioned in Section 1, doping of calcium titanate with yttrium facilitates the loss of oxygen. Similarly the presence of acceptor atoms such as iron, cobalt and nickel at titanium sites also results in oxygen deficiency to maintain the electrical charge neutrality [10]. Therefore simultaneous presence of Y^{3+} and Co^{3+} in $CaTiO_3$ will promote the loss of oxygen. There will be segregation of the charged oxygen vacancies at the grain boundaries, which will attract acceptor ions such as Co^{2+} and Co^{3+} and form dipoles. The segregation of these impurity ions at the grain boundaries inhibit the grain growth [11].

We are synthesizing these materials by different methods in different atmospheres to study the effect of processing on their dielectric properties.

Acknowledgements

Financial support from the Department of Science and Technology, Government of India, New Delhi is gratefully acknowledged. We are grateful to the National Electron Microscope Facility at Banaras Hindu University for its help in scanning electron microscopy. Thanks are due to Dr Lakshman Pandey for useful discussions.

References

1. D. W. JOHNSON and L. E. CROSS, *Jpn J. Appl. Phys.* **6** (1967) 459.
2. J. BOUWMA, K. J. DEVRIES and A. J. BURGRAAF, *Phys. Status Solidi* (*a*) **35** (1976) 281.
3. S. WAKU, *Rev. Elec. Commun. Lab* **15** (1967) 689.
4. Y. TAKAHASHI, N. YAMAOKA and S. KAKUBARL, US Patent 3 933 668 (1976).
5. S. NEIRMAN and I. BURN, *J. Mater. Sci.* **19** (1984) 737.
6. O. PARKASH, CH. DURGA PRASAD and D. KUMAR, *J. Solid State Chem.* **69** (1987) 385.
7. *Idem, Phys. Status Solidi* (*a*) **106** (1988) 627.
8. H. S. TEWARI, O. PARKASH, V. B. TARE and D. KUMAR, *J. Mater. Sci. Lett.* **7** (1988) 1088.
9. A. MANSINGH, R. P. TONDON and J. K. VAID, *J. Phys. Chem. Solids* **36** (1975) 1267.
10. B. JAFFE, W. R. COOK Jr and H. JAFFE, in "Piezoelectric Ceramics" (Academic, London, 1971) Ch. 10.
11. A. TAWFIK and F. M. EI-MEKAWY, *Ind. Ceramique* **811** (1986) 780.

Received 8 August 1988
and accepted 16 August 1989