ELSEVIER

Ceramics International 26 (2000) 13–17

CERAMICS
INTERNATIONAL

Effect of processing route on the dielectric behavior of $(Sr_{0.50}Ca_{0.15}La_{0.35})(Ti_{0.65}Co_{0.35})O_3$ ceramic

R.K. Dwivedi[a], Om Parkash[a,*], Devendra Kumar[b], L. Pandey[c], K.K. Srivastav[a]

[a] *School of Materials Science and Technology, Institute of Technology, Banaras Hindu University, Varanasi-221005, India*
[b] *Department of Ceramic Engineering, Institute of Technology, Banaras Hindu University, Varanasi-221 005, India*
[c] *Department of Post Graduate Studies and Research in Physics, Rani Durgavati University, Jabalpur, India*

Received 15 October 1998; received in revised form 26 October 1998; accepted 3 December 1998

Abstract

Dielectric properties of valence compensated perovskite oxide $Sr_{0.50}Ca_{0.15}La_{0.35}Ti_{0.65}Co_{0.35}O_3$ prepared by a conventional solid state reaction and by a novel semi-wet route have been studied. A peak is observed in $\in_r$ vs T plots of both the samples whose position depends on frequency. The behaviour resembles that of relaxor ferroelectric in both the cases. However, the temperature of peak maxima depends on the processing route. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: C. Dielectric properties; C. Ferroelectric properties; D. Perovskites

1. Introduction

In the last decade extensive research work has been carried out on simultaneously substituted valence compensated perovskite systems by Parkash et al. [1–3]. Some of the systems have exhibited very interesting dielectric properties. The $Sr_{1-x}La_xTi_{1-x}Co_xO_3$ system is one of such systems which has shown barrier layer characteristics with a high value of dielectric constant. The compositions within the range $0.20 \leqslant x \leqslant 0.40$ in this system have been found to exhibit very diffuse maxima in the dielectric constant vs temperature plots whose peak position is frequency dependent [3,4]. This behaviour is very much similar to the behaviour of relaxor materials e.g. lead magnesium niobate [5]. The composition with $x = 0.35$ has been found to exhibit the maximum value of dielectric constant [4] ($\in_r = 10^5$). It has been reported that such a high value of dielectric constant is due to interfacial space charge polarization which arises due to microheterogeneities caused by either random distribution of Sr^{2+} and La^{3+} on dodecahedral sites or Ti^{4+} and Co^{3+} on octahedral sites and also by formation of barrier layers at the grain–grain-boundary interfaces [6,7].

Titanate ceramics show a very unusual non-linear behaviour due to variation of the resistivity from bulk region to grainboundary region. A high temperature process such as sintering reversibly converts an electrically conducting sample into an insulating one. Samples with highly resisting barriers (grainboundaries) and low ohmic grains are being used as non-linear devices, such as varistors, PTCR and barrier layer capacitors. The high value of dielectric constant may be attributed to barrier layer formation at the grain–grain boundary interfaces depending on the thermodynamic conditions during processing. At high temperature neutral oxygen at regular oxygen sites leave the lattice and produces oxygen vacancies. At temperatures >1000°C, these oxygen vacancies are doubly ionised by emitting two electrons into conduction band according to

$$O_o^x \rightarrow 1/2\ O_2 + V_o^{\bullet\bullet} + 2e'' \qquad (1)$$

where O_o^x and others are written according to the formalism of Kroger and Vink. At lower temperatures i.e. during cooling at temperatures <1000°C the oxygen vacancies may become singly ionised. The change in ionization is expressed as

$$V_o^{\bullet\bullet} + e' \rightarrow V_o^{\bullet} \qquad (2)$$

and further becomes neutral

$$V_o^{\bullet} + e' \rightarrow V_o^x \qquad (3)$$

---

* Corresponding author.
E-mail address: oparkash@banaras.ernet.in (O. Parkash).

PII: S0272-8842(99)00012-7

Initially these reactions take place at the grain boundaries making grain boundaries isolated from the grains i.e. insulating grain boundaries.

It has been the object of extensive research to find some compositions with greater diffuseness of dielectric peak and a reasonably high value over the working temperature range close to room temperature. In view of very important and useful dielectric and electrical characteristics, the composition $Sr_{1-x}La_xTi_{1-x}Co_xO_3$ with $x=0.35$ (SLTCO) has been investigated in detail [7]. It is well known that calcium substitution in $BaTiO_3$ lowers its transition temperature, T_c [8]. Since the size of Ca^{2+} (0.97Å) lies in between Sr (1.36Å) and Ti (0.61Å) in $SrTiO_3$, the probability of occupancy of Ca on Ti along with the Sr site can not be ruled out in Ca doped $SrTiO_3$ samples which leads to the compositional fluctuation. It would be interesting to see the effect of calcium substitution at the strontium site in the valence compensated SLTCO system. The composition $Sr_{0.50}Ca_{0.15}La_{0.35}Ti_{0.65}Co_{0.35}O_3$ (SLTCO) has been prepared by a conventional ceramic method. (CM sample). In order to avoid the occupancy of Ca^{2+} on B site this composition (SLTCO) has been also prepared by a semiwet route (SW sample) where it is assumed that $(SrCaLa)CO_3$ precursor ensures occupancy of Ca^{2+} on A site. A semi-wet route has been exploited by Mishra et al [9] for the synthesis of various electronic ceramic systems to get compositionally homogeneous products. In this paper we are reporting the effect of substitution of Ca^{2+} and processing route on the dielectric properties of SLTCO materials.

2. Experimental

For preparing the sample via the ceramic method (CM), appropriate amounts of pure strontium carbonate (99.5%), calcium carbonate, lanthanum oxalate, titanium dioxide (99%) and cobalt oxalate were weighed and ball milled for 6 h in acetone followed by drying in air. The mixed powders were calcined at 1200°C for 6 h in a covered platinum crucible. The calcined powder was ground and mixed for half an hour using mortar and pestle. This powder was cold pressed in a hydraulic press using PVA (2% solution) as binder, into cylindrical pellets of 12 mm diameter and approximately 1.5 mm thickness. The compacts were then sintered at 1300°C for 6 h followed by cooling to 800°C with cooling rate 5°C/m. Samples having 90% of theoretical density were obtained.

In the semi-wet method, first strontium carbonate, calcium carbonate and lanthanum oxalate were dissolved in HNO_3 separately to form nitrates. The nitrates were dissolved in distilled water with slight heating and mixed into each other in appropriate amounts. A super saturated solution of ammonium carbonate in distilled water was poured rapidly into the nitrate solution of strontium, calcium and lanthanum with continuous stirring, which leads to the co-precipitation of (SγCaLa) CO_3 as one precursor. An appropriate amount of this precursor, titanium dioxide and cobalt oxalate was mixed coventionally using ball mill. This powder was calcined at 1050°C for 6 h and subsequently ground and compacted into cylindrical discs of 12 mm diameter. The samples were then sintered at 1250°C for 6 h followed by the same cooling rate of 5°C/m to 600°C. The density of these samples was 96% of the theoretical. Sintered pellets were polished using abrasive papers of grade 1/0, 2/0, 3/0, and 4/0 respectively followed by diamond paste of 1 and 1/4 μm. Polished samples were etched using equal volume 2% HF and 5% HCl solution, washed with flowing tape water followed by isopropanol and subsequently coated with a thin film of Au–Pd alloy. Microstructures were studied by scanning electron microscope [SEM Jeol 800]. The grain size of sintered samples was obtained from these micrographs. Two pellets of each sample (CM and SW samples) were coated with Ag–Pd paste for dielectric characterization. Dielectric measurements on each sample were made using an impedance analyzer [HP 4192A LF] in the temperature range 300–500 K and frequency range 100 Hz–10 Mhz.

3. Results and discussion

X-ray diffraction patterns of the CM sample, prepared by the ceramic method and SW sample, prepared by the semi-wet method, are shown in Fig. 1. These patterns have been indexed on the basis of a cubic unit cell and confirm the formation of a single phase in both of the samples. Lattice parameters, determined using HOCT software, are given in Table 1. Scanning electron micrographs, shown in Fig. 2, reveal the formation of faceted euhedral homogeneous grains in CM sample. In the SW sample, the grains are anahedral without sharp grain-boundaries. The average grain size and percentage porosity are given in Table 1. Both samples are found to have a density greater than 90%.

Dielectric measurements have been carried out from 300 to 500 K in the frequency range 100 Hz–10 MHz at several steady temperatures. The variation of dielectric constant with temperature at 1, 10 and 100 KHz for CM and SW samples is shown in Fig. 3 . Both samples show diffuse maxima in their ε_r vs T plots whose position shift to higher temperature with increasing frequency. This behaviour is similar to the one observed in an earlier SLTCO sample [4,7]. It has been observed that the calcium substituted CM sample has shown peaks in its dielectric constant vs temperature plots at around the same temperatures as has been reported in the unsubstituted reference sample SLTCO. It is reported

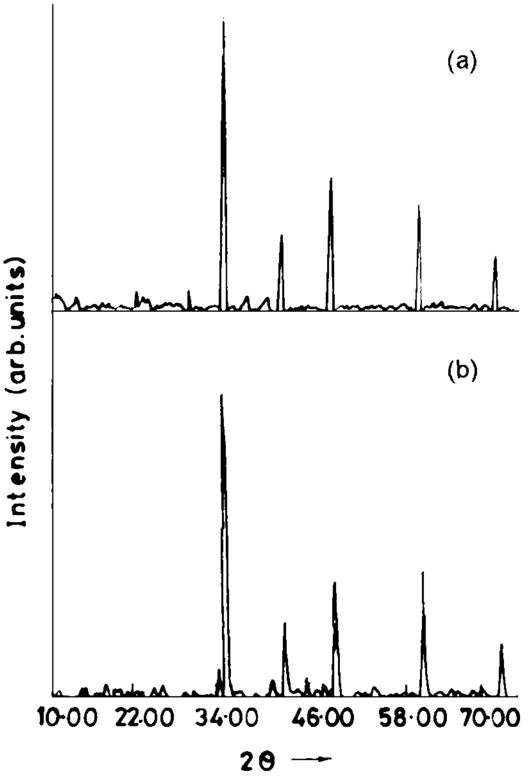

Fig. 1. X-ray diffiraction pattern of (a) CM-sample (b) SW-sample.

Table 1
Structure, lattice parameters, % porosity and grain size of the CM and SW samples

Sample	Structure	Lattice parameter(Å)	%Porosity	Grain size (μm)
CM-sample	Cubic	3.8535 ± 0.0008	8	4
SW-sample	Cubic	3.8813 ± 0.0018	4	3

that substitution of calcium in $BaTiO_3$ reduces its ferroelectric Curie temperature. In the present system substitution of calcium has not shown any change in the peak position in $\in_r$ vs T plots. This support our earlier observation from hysteresis loop measurements that this peak is not of ferroelectric origin. The diffused broad peaks in this sample may be due to orientation of the dipoles or clusters of different size which have shown different positions as a result of applied ac field.

Dielectric constant vs temperature plots of the SW sample, given in Fig. 3., show some major changes in its dielectric behaviour. These are (i) the temperatures at which the maxima of dielectric constant occur in this sample are lower as compared to the SLTCO sample (ii) the maxima are more diffused as compared to the SLTCO sample and (iii) the value of dielectric constant at room temperature is higher than for the SLTCO sample.

It is known that different sizes of dipoles as well as different levels of heterogeneity occur in these materials which interrupt the flow of the charge carriers at the interfaces and lead to the formation of barrier layer. It is assumed that dipoles in dielectrics usually interact with neighbouring dipoles. Orientation of the dipoles with applied electric field would be very much dependent on the dipole–dipole interaction. If this is weak, orientation will be easier and orientation will be difficult if this is strong. In the SW sample, it appears that dipole–dipole interaction is stronger and dipole relaxation response with applied field is slower which causes broadening in dielectric constant vs temperature plots.

Plots of dissipation factor vs logf (frequency in cps) for the CM and SW samples are shown in Fig. 4. It has been observed in the SWsample that the position of the dielectric loss maxima is almost same for all temperatures while they shift towards high frequency with increasing temperature in the CM-sample. In this case

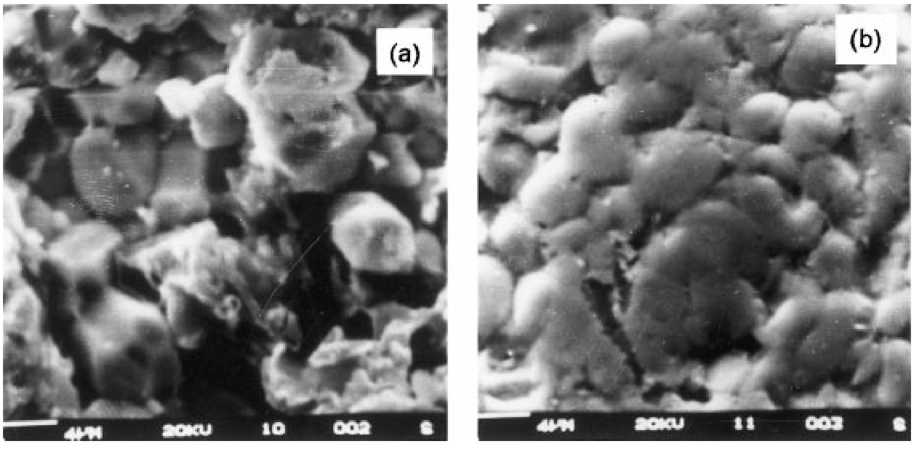

Fig. 2. Scanning electron micrograph of (a) CM-sample (b) SW-sample.

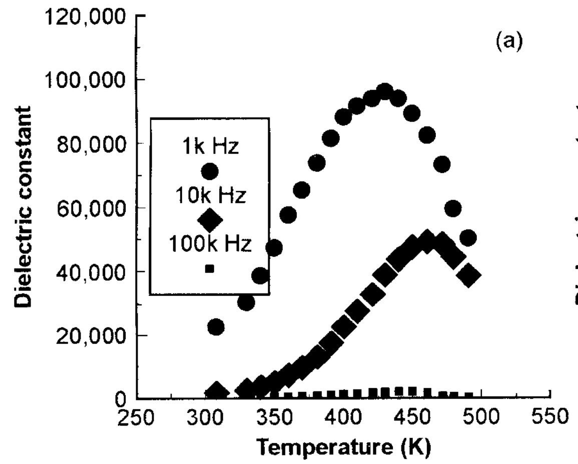

Fig. 3. Variation of dielectric constant with temperature in (a) the CM-sample (b) the SW-sample.

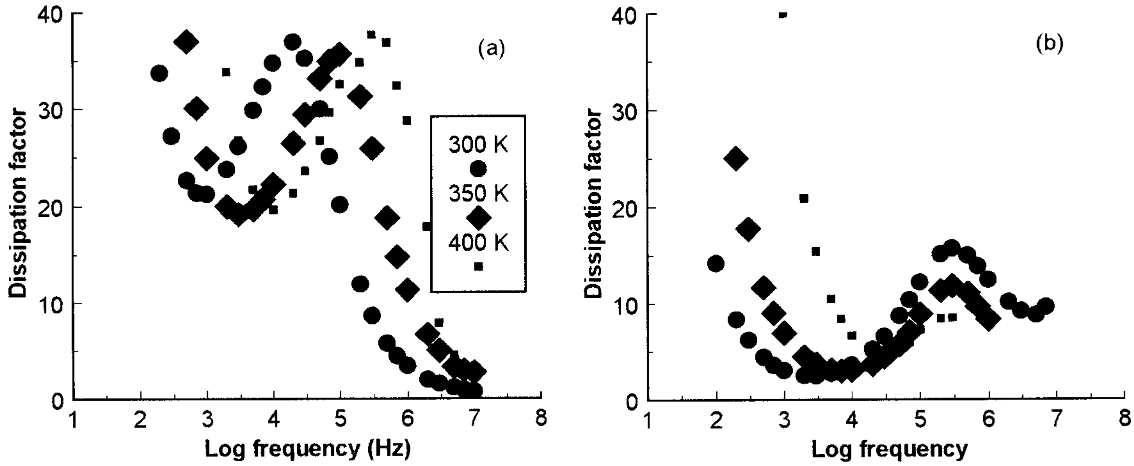

Fig. 4. Variation of dissipation factor with frequency in (a) the CM-sample (b) the SW-sample.

the maxima are well separated. According to Debye relaxation the loss peak occurs when applied field is in phase with the dielectrics and the condition $\omega\tau = 1$ is satisfied where $\omega = 2\pi f$, f being the frequency of the applied field. From these plots it is clear that for the SW-sample the relaxation time is nearly independent of temperature. In the CM-sample the relaxation times decrease with increasing temperature. It seems that various dipoles of different size might have got higher mobility in the CM-sample and they respond faster with Fig. 4 changing temperature. The relaxation time is very much temperature dependent. In the SW-sample Ca^{2+} ion is uniformly distributed on Sr sites and dipole–dipole interaction is stronger which causes their orientations difficult. Hence they are getting relaxed slowly with broad hump around their dielectric anomaly. The relaxation time is not much dependent on temperature.

4. Conclusions

Ca doping has not shown any effect on the position of dielectric maxima in SLTCO sample. Position of the dielectric maxima has been found to be dependent on processing method. Relaxation time in the CM-sample is temperature dependent while in the SW-sample, it is temperature independent.

Acknowledgements

Financial support from the Department of Science & Technology, Government of India, is gratefully acknowledged. We are also thankful to Head, Department of Ceramic Engineering, for extending XRD facility. We are also grateful to Sri L. K. Srivastav For doing SEM of our samples.

References

[1] Om Parkash, C.D. Prasad, D. Kumar, Dielectric properties of lanthanum lead cobalt titanium oxide $(La_{1-x}Pb_x)(Co1\text{-}_xT_{ix})O3$, $(0.50 \leqslant x \leqslant 0.90)$, Phys. Stat. Sol. (a), 116 (1988) 627.

[2] Om Parkash, H.S. Tewari, L. Pandey, R. Kumar, D. Kumar, Preparation, structure and dielectric properties of the system $Ba_{1-x}La_xTi_{1-x}Ni_xO_3$, J. Am. Ceram. Soc. 72 (1989) 1520.

[3] Om Parkash, C.D. Prasad, D. Kumar, Dielectric relaxor behaviour of the system $Sr_{1-x}La_xTi_{1-x}Co_xO_3$, $(x \leqslant 0.40)$, J. Mat. Sci. 25 (1990) 487.

[4] Shail Upadhyay, D. Kumar, Om Parkash, Effect of composition on dielectric and electrical properties of the $Sr_{1-x}La_xTi_{1-x}Co_xO_3$ system, Bull. Mat. Sci. 19 (1996) 513.

[5] V.V. Kirilov, V.A. Isupov, Relaxation polarization $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)—A ferroelectric with diffuse phase transition, Ferroelectrics 5 (1973) 3.

[6] I. Burn, S. Neirman. Dielectric properties of donor doped polycrystalline $SrTiO_3$, J. Mat. Sci. 17 (1982) 3510.

[7] R.K. Dwivedi, Om Parkash, C.C. Christopher, D. Kumar, Effect of processing route and parameters on the dielectric properties of the valence compensated composition $Sr_{0.50}Ca_{0.15}La_{0.35}Ti_{0.65}\text{-}Co_{0.35}O_3$, J. Mat. Sci. Lett. 15 (1996) 1865.

[8] B. Jaffe, W.R. Cook Jr., H. Jaffe, Piezoelectric Ceramics, Academic, New York, 1971.

[9] S.K. Mishra, A.P. Singh, D. Pandey. Thermodynamic nature of phase transition in $Pb(Zr_xTi_{1-x})O_3$ ceramics, Phil. Mag. 76 (1997) 213.