Preparation and characterization of $Ca_{1-x}La_xTi_{1-x}Co_xO_3$ (0.00 < x ≤ 0.50) system

OM PARKASH†, Ch. DURGA PRASAD* and DEVENDRA KUMAR**

School of Materials Science and Technology, **Department of Ceramic Engineering, Institute of Technology, Banaras-Hindu University, Varanasi 221 005, India
*Present address: Naval Chemical and Metallurgical Laboratory, Bombay 400 023, India

Abstract. The possibility of the formation of solid solution in the system $Ca_{1-x}La_xTi_{1-x}Co_xO_3$ for $x \leqslant 0.5$ has been investigated. X-ray diffraction studies show that compositions with $x = 0.05$, 0.1, 0.2, 0.3 and 0.5 prepared by the ceramic method are single-phase materials. All the compositions have a structure similar to $CaTiO_3$ with a pseudo-cubic unit cell. Preliminary studies show that interfacial polarization contributes significantly to their dielectric constant.

Keywords. Calcium lanthanum titanium cobalt oxide; perovskite.

1. Introduction

Strontium titanate ($SrTiO_3$) and calcium titanate ($CaTiO_3$) doped with yttrium or rare earth elements exhibit interesting and useful dielectric and electrical properties when sintered in atmosphere having very low partial pressures of oxygen (Burn and Neirman 1982; Neirman and Burn 1984; Waku 1967). During the sintering of these materials, oxygen is lost making them semiconducting. On cooling, from the firing temperature, reoxidation of the product takes place. However, sufficient time is not given for the complete reoxidation of the grains. Only grain boundaries are reoxidized and become insulating enveloping the semiconducting grains. This imparts them a very high value of dielectric constant and makes them potentially useful materials for grain boundary barrier layer capacitors. On replacing divalent Ca^{2+} or Sr^{2+} by trivalent Y^{3+} or rare earth ions, charge neutrality is achieved by having an appropriate number of vacancies in the Ca^{2+} or Sr^{2+} sublattice in $CaTiO_3$ and $SrTiO_3$ respectively as represented by the formula $M^{2+}_{1-3x/2}M'^{3+}_x$ $V_{M^{2+}x/2}Ti^{4+}O_3$ ($M^{2+} = Ca^{2+}$ or Sr^{2+}, $M'^{3+} = Y^{3+}$ or rare earth ions) where $V_{M^{2+}}$ represents a vacant M^{2+} site.

Recently we prepared the solid solution $La_{1-x}Pb_xCo_{1-x}Ti_xO_3$ for values of x in the range $0.05 \leqslant x \leqslant 0.99$ and investigated its electrical and dielectric behaviour (Parkash et al 1987, 1988). It is found that compositions with $x \geqslant 0.5$ exhibit dielectric relaxator behaviour. This represents a valence-compensated substitutional solid solution where simultaneous replacement of La^{3+} by Pb^{2+} on dodecahedral site and Co^{3+} by Ti^{4+} on octahedral site in $LaCoO_3$ leads to internal charge compensation. Keeping in view the interesting properties exhibited by the above materials, we considered it worthwhile to investigate the possibility of formation of valence compensated solid solution $Ca_{1-x}La_xTi_{1-x}Co_xO_3$ (for

---

†To whom all correspondence should be addressed.

$x \leqslant 0.50$) and study its electrical behaviour. In this communication we report the results of our investigations in this direction.

2. Experimental

Samples with $x = 0.05$, 0.1, 0.2, 0.3 and 0.5 were prepared by the ceramic method using calcium carbonate, lanthanum oxalate, titanium dioxide and cobalt oxalate all having purity better than 99·5%. Appropriate quantities of these materials were accurately weighed and mixed in an agate mortar using acetone. The dried powders were calcined at 1523 K for 4 h and slowly cooled in the furnace. The calcined powders were mixed again and pressed as cylindrical pellets after addition of 1% PVA solution as a binder. The pellets were heated slowly in platinum crucibles at 673 K to drive off the binder. The temperature was raised to 1623 K and maintained at this temperature for 12 h and then furnace-cooled to room temperature. The process of grinding, mixing, pelletizing and firing at 1623 K for 12 h was repeated to ensure the chemical homogeneity of the resulting product. X-ray diffraction patterns of the resulting samples were taken using Cu-K$_\alpha$ radiation by employing X-ray diffractometer (JEOL).

3. Results and discussion

X-ray diffraction (XRD) patterns of all the samples did not show any lines characteristic of constituent oxides. This confirmed the formation of single phase materials for $x \leqslant 0.5$ in the system $Ca_{1-x}La_xTi_{1-x}Co_xO_3$. XRD data could be indexed on the basis of a pseudo-cubic unit cell similar to $CaTiO_3$. Lattice parameters of all the samples (table 1) remained almost constant with composition up to $x = 0.3$ except for the composition with $x = 0.2$ which shows a higher value of the lattice parameter.

Values of DC conductivity, σ_{DC}, and dielectric constant ε_r (at 1 kHz) measured at 300 K are also given in the table. It is observed that σ_{DC} and ε_r increase with x except for the composition with $x = 0.2$. It is noteworthy that this composition has an anomalous value of lattice parameter in this series. Dielectric constant of all the compositions is strongly frequency-dependent, decreasing with increasing frequency. This shows that there is significant interfacial polarization present in these materials. The dielectric constant of the compositions with $x = 0.3$ and 0.5 is very

Table 1. Lattice parameter and other details for various samples in the system $Ca_{1-x}La_xTi_{1-x}Co_xO_3$.

x	a A°	σ_{DC} (ohm-cm)$^{-1}$	ε_r at 300 K (1 kHz)
0·05	15·273	4.3×10^{-8}	91
0·1	15·280	1.2×10^{-7}	214
0·2	15·374	4.4×10^{-8}	88
0·3	15·277	5.0×10^{-6}	14370
0·5	15·349	2.0×10^{-5}	40700

The crystal structure in all cases was pseudo-cubic.

high. They may find applications as capacitor materials. Detailed studies on electrical properties are in progress.

Acknowledgement

References

Burn I and Neirman S 1982 *J. Mater. Sci.* **17** 3510
Neirman S and Burn I 1984 *J. Mater. Sci.* **19** 737
Parkash O, Prasad C D and Kumar D 1987 *J. Solid State Chem.* **69** 385
Parkash O, Prasad C D and Kumar D 1988 *Phys. Status Solidi* **106** 627
Waku S 1967 *Rev. Electr. Commun. Lab.* **15** 689