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Synthesis, structure and electrical conduction behaviour of the $Ca_{1-x}La_xSn_{1-x}Co_{1-x}O_3$ system

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Abstract

The possibility of formation of a solid solution in the system $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ has been explored up to $x = 0.20$. Formation of a solid solution was studied using X-ray diffraction. It has been thus found that a solid solution forms in this system up to $x = 0.10$. A.c. and d.c. conductivities were measured to elucidate the electrical conduction behaviour in this system.

Keywords: Synthesis; Structure; Electrical conduction

1. Introduction

Alkaline earth titanates with the general formula $MTiO_3$ (where M = Pb, Ba, Sr or Ca) are an important class of materials used in a number of electronic devices [1–3]. These materials seldom find applications in undoped or pure form. Their properties are modified by suitable substitutions in M or Ti sites. There are two types of substitutions, isovalent and heterovalent. For the past few years, we have been studying the effect of heterovalent substitutions on M as well as on Ti sites simultaneously, i.e. $M_{1-x}A_xTi_{1-x}B_xO_3$ (where M = Ba, Sr, Pb or Ca; $A = La^{3+}$ or Y^{3+}; $B = Co^{3+}$ or Ni^{3+}). These systems have been studied extensively in recent years [4–6]. These represent solid solutions between a semiconductor, e.g. $LaCoO_3$ [7,8], and an insulator ($MTiO_3$) or between a metal, e.g. $LaNiO_3$ [9], and an insulator. It has been found that solid solutions form over a wide range of compositions in the $M_{1-x}La_xTi_{1-x}Co_xO_3$ systems. These systems exhibit interesting electrical and dielectric properties. Samples with $x \leq 0.50$ exhibit dielectric relaxor behaviour in the system $Pb_{1-x}La_xTi_{1-x}Co_xO_3$ [10]. Grain boundary barrier layers form for compositions $0.20 < x < 0.40$ in the system $Sr_{1-x}La_xTi_{1-x}Co_xO_3$ imparting very high values of the dielectric constant [11]. In the $Ba_{1-x}La_xTi_{1-x}Co_xO_3$ system, compositions with $x = 0.01$ and 0.05 exhibit a very diffuse ferroelectric to paraelectric transition [12]. Electrical properties of these materials have also been studied extensively [13,14].

Because of the interesting and useful properties exhibited by the above titanate systems, it was considered worthwhile to investigate analogous stannate systems. In the present work, we attempted to synthesize compositions in the system $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ which correspond to the solid solution between $CaSnO_3$ and $LaCoO_3$. In this paper we describe the synthesis and structural and electrical transport properties of the $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ system.

2. Experimental

Attempts were made to prepare the compositions with $x = 0.01, 0.05, 0.10, 0.15$ and 0.20 in this system by conventional ceramic powder processing method. Calcium carbonate, lanthanum oxalate, tin dioxide and cobalt oxalate all having purity better than 99.5% were used as starting materials. Appropriate quantities were mixed and ground for 6 h in an agate mortar using acetone. The dried powders were calcined at 1475 K for 12 h in a platinum crucible in air. The resulting powders were ground and mixed with a few drops of 1% polyvinyl alcohol solution as a binder and pressed into thin cylindrical pellets in a hydraulic press. The pellets were heated slowly to 675 K and

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kept at this temperature for 2 h to burn off the binder. The temperature was then raised to 1625 K slowly and samples were fired at this temperature for 12 h. X-ray diffraction (XRD) patterns of the finely ground powder of the sintered product of all samples were recorded using Cu Kα radiation in a Philips automatic X-ray diffractometer (model PW 1050/70).

The d.c. resistivity of all the samples coated with high temperature silver paint was measured by two-probe methods using a Keithley 616 digital electrometer in the temperature range 300–675 K.

A.c. conductance G, capacitance C and dielectric loss D of all the single-phase materials coated with silver paint which matured at 975 K for 15 min were measured using an HP-4192A LF impedance analyser as a function of temperature and frequency (0.10–1000 kHz) in the temperature range 300–500 K.

3. Results and discussion

XRD patterns of the compositions with $x = 0.01$, 0.05 and 0.10 reveal the formation of a single phase. This is indicated by the absence of XRD lines characteristic of constituent oxides or other compounds between constituent oxides. However, XRD lines characteristic of constituent oxides are present in the compositions with $x = 0.15$ and 0.20. This shows that a solid solution forms only in the compositions with $x \leq 0.10$. XRD data of these samples could be indexed on the basis of an orthorhombic unit cell similar to that of $CaSnO_3$ [15]. Lattice parameters are given in Table 1.

D.c. resistivity data of the compositions with $x = 0.00$ and 0.01 are not included in this paper because of their humidity-sensitive behaviour at and above room temperature. Plots of the logarithm of d.c. resistivity vs. $1000/T$ are shown in Fig. 1 for the compositions with $x = 0.05$ and 0.10. It is noted that the resistivity of these compositions decreases linearly with increasing temperature. This shows that the resistivity data obey the Arrhenius relationship:

$$\rho = \rho_0 \exp(E_a/kT) \qquad (1)$$

where E_a is the activation energy for conduction. Values of E_a obtained by least-squares fitting of the resistivity data are given in Table 2. It is found that E_a decreases with increasing x (or cobalt concentration). This shows that conduction is predominantly due to cobalt ions as all other ions having inert gas configuration are not expected to participate in the conduction process [16].

Table 1
Lattice parameters of the samples in the $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ system

Composition x	a (Å)	b (Å)	c (Å)
0.01	5.5216	7.918	5.672
0.05	5.5382	7.918	5.672
0.10	5.5718	7.950	5.788

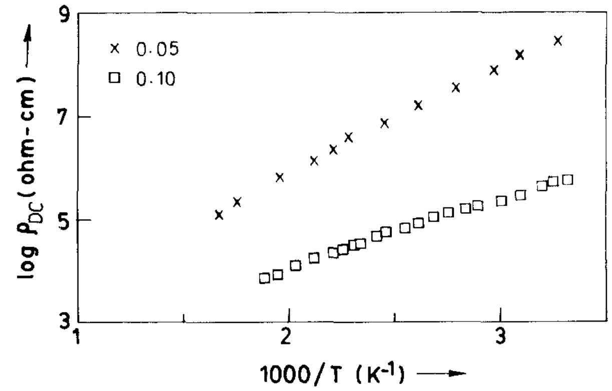

Fig. 1. Variation in d.c. resistivity with temperature for the compositions $x = 0.05$ and 0.10 in the $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ system.

Table 2
Activation energies for d.c. conductivity (E_a), AC conductivity (E_1 and E_2) at 100 kHz and activation energy W for hopping for samples of the system $Ca_{1-x}La_xSn_{1-x}Co_xO_3$

Composition x	E_a (eV)	E_1 (eV)	E_2 (eV)	$W = E_a - E_2$ (eV)
0.05	0.41	0.03	0.17	0.24
0.10	0.29	0.11	0.23	0.06

In order to understand the mechanism of conduction in these materials, a.c. conductivity was measured as a function of frequency and plots of $\log \sigma_{AC}$ vs. $\log f$ at a few temperatures are shown in Fig. 2. A.c. conductivity is independent of frequency in the lower frequency range for the compositions with $x = 0.05$ and 0.10. This represents the d.c. contribution to the total conductivity [17]. For these samples, a.c. conductivity values in the lower frequency range exactly match our measured d.c. conductivity values of the samples. These samples exhibit a frequency dependence of a.c. conductivity above a particular frequency. This frequency shifts to the higher frequency side with increase in temperature. Above this frequency, the a.c. conductivity varies according to the relation

$$\sigma_{AC} = A\omega^s \qquad (2)$$

where $\omega = 2\pi f$ is the angular frequency and s is a weak function of frequency at a given temperature. The values of s at different temperatures are calculated and are found to be less than unity in each case.

Plots of $\log \rho_{AC}$ vs. $1000/T$ for these samples at 100 kHz are shown in Fig. 3. We have plotted data for 100 kHz because any contribution due to electrode and space charge polarization processes will not be

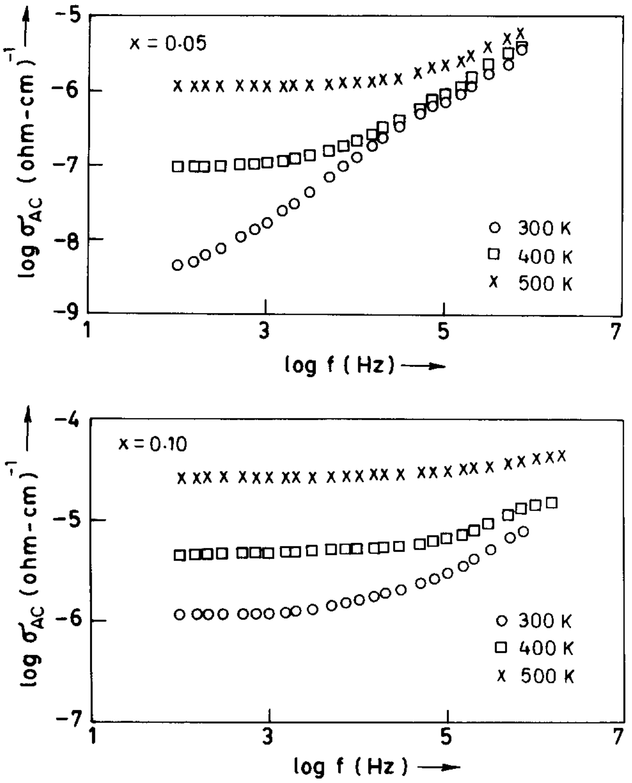

Fig. 2. Variation in a.c. conductivity with frequency at various temperatures for samples with $x = 0.05$ and 0.10 in the $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ system.

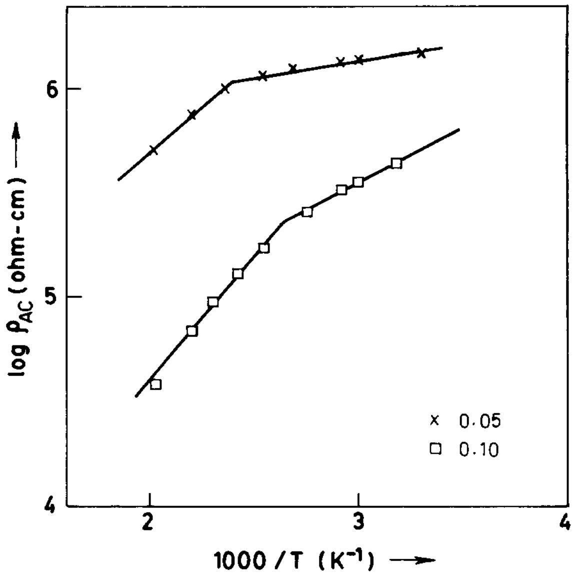

Fig. 3. Plots of a.c. resistivity vs. $1000/T$ at 100 kHz for samples with $x = 0.05$ and 0.10 in the $Ca_{1-x}La_xSn_{1-x}Co_xO_3$ system.

observed at this frequency. Two regions are observed in these plots: (i) a low temperature region where the slope is small (this region seems to shift to lower temperature with increasing x); (ii) a high temperature region with higher slope.

The activation energies E_1 and E_2 calculated from the slopes in the two temperature regions are given in Table 2. The frequency dependence of a.c. conductivity given by Eq. (2) may arise from the following mechanisms [18].

(I) Transport could take place by carriers excited into the localized states at the edges of valence or conduction band and hopping at energies close to it.

(II) Hopping of charge carriers could occur in the localized states near the Fermi level.

(III) Hopping of charge carriers among localized sites could give rise to a Debye-type loss similar to the thermally activated rotation of dipoles. These dipoles can point in two or more directions with different energies w_1 and w_2 ($\Delta w = w_1 - w_2$) with a jump time τ from the lower to the upper states. Both Δw and τ vary over a wide range including zero.

Although all three mechanisms predict a similar frequency dependence of a.c. conductivity, the temperature dependence of the a.c. conductivity will be different for the three mechanisms. For mechanism (I), the a.c. conductivity will increase with temperature similarly to carrier concentration, i.e. $\sigma_{ac} \propto \exp[-(E_F - E_A)/kT]$ and the d.c. conductivity will vary with temperature as

$$\sigma_{DC} \propto \exp[-(E_F - E_A + W)/kT]$$

where W is the activation energy for hopping of charge carriers [19] and E_A is the separation of the Fermi level from the valence band edge. In mechanism (II), the conductivity should be proportional to the temperature T if kT is small compared with the energy range over which $N(E_F)$ is constant and independent of temperature if kT is larger than the width of some well-defined defect band in which E_F lies. In mechanism (III), the a.c. conductivity is proportional to temperature T if charge compensation is large and independent of T if the compensation is small. Process (III) will operate in such systems where hopping of charge carriers is associated with a change in polarization.

In the present samples, the cobalt ions are predominantly in the trivalent state. These materials also contain a small concentration of Co^{2+} ions as explained below.

During sintering of the samples at high temperature, a slight amount of oxygen is lost according to the reaction

$$O_O \rightarrow (1/2)O_2 + V_O^{\bullet\bullet} + 2e' \qquad (3)$$

where all the symbols have been used in accordance with Kroger–Vink notation of defects. The electrons released in reaction (3) during the sintering process reduce Co^{3+} to Co^{2+} ions. The conduction is predominantly due to the presence of cobalt ions in these materials as mentioned earlier. The almost temperature independent a.c. conductivity in the low temperature region for $x = 0.05$ and 0.10 shows that conduction occurs by hopping of charge carriers among these localized sites according to mechanism (III). Co^{3+} and Co^{2+} ions on Sn^{4+} sites may form dipoles with vacant oxygen sites $V_O^{\cdot\cdot}$. These dipoles can change their orientation by electron hopping. In the higher temperature region (375–500 K), the observed exponential dependence of a.c. conductivity ($x = 0.05$ and 0.10) on absolute temperature shows that conduction occurs by process (I), i.e. as a result of the excitation of charge carriers at the valence band edge and hopping at energies close to it. The cobalt ions present in the divalent and trivalent states in our system gives rise to localized energy levels in the energy gap of $CaSnO_3$. The charge carriers trapped at such localized sites may form small polarons and the conduction would then occur as a result of thermally activated hopping of small polarons [20].

The values of activation energies W of hopping determined from the difference in activation energies of d.c. and a.c. conductivities in the higher temperature regions are given in Table 2.

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