

Electrical conduction behavior of high dielectric constant perovskite oxide $\text{La}_x\text{Ca}_{1-3x/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$

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Abstract

In the present work, an attempt has been made to synthesize La doped calcium copper titanate, $\text{La}_x\text{Ca}_{1-3x/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x \leq 0.50$) by solid state ceramic route and study its electrical conduction behavior. The nature of conduction is studied by measuring Seebeck coefficient α as a function of temperature. It is found to be negative above 500 K indicating that electrons are the majority charge carriers. Measurements of Seebeck coefficient at lower temperatures are not reliable because of high resistance of the samples. In order to understand the mechanism of conduction, dc and ac conductivity were measured as a function of frequency and temperature. Frequency dependence of ac conductivity shows that it occurs by hopping of charge carriers among localized sites.

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1. Introduction

Perovskite oxides such as BaTiO_3 , KNbO_3 or LiNbO_3 are ferroelectric exhibiting large value of dielectric constant [1]. High value of dielectric constant is desirable to miniaturize the capacitor required for integrated circuits. A problem with these materials is strong temperature dependence of their dielectric constant near ferroelectric to para-electric transition which is not desirable from device point of view. Compounds with the general formula $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ ($A = \text{Ca}, \text{Sr}$ and Ba) have been known since 1967 [2]. It has been recently discovered that $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits large value of dielectric constant which remains independent of temperature up to 300 °C [3–6]. Using impedance analysis, it has been shown that large value of dielectric constant is due to formation of barrier layers at grainboundaries [7–9]. Compounds with the formula $\text{A}_{2/3}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ where A is a rare earth element have also been studied [3]. In this paper, synthesis and electrical behavior of the system $\text{La}_x\text{Ca}_{1-3x/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ($x \leq 0.50$) in which calcium is partly replaced by lanthanum

is being reported. Electrical charge neutrality is maintained by vacancies in calcium sublattice. Dielectric behavior of these materials will be communicated elsewhere.

2. Experimental procedure

Compositions with $x = 0.0, 0.10, 0.20, 0.30$ and 0.50 in the system $\text{La}_x\text{Ca}_{1-3x/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$ were prepared by the conventional solid state ceramic route. Stoichiometric amounts of lanthanum oxalate, CaCO_3 , CuO and TiO_2 all of A.R. grade and purity >99.5% were used as starting materials. These were weighed accurately and mixed in an agate ball mill for 6 h using acetone as the mixing medium. The mixed powders were dried overnight and calcined at 1000 °C for 10 h in a platinum crucible in air and were then compacted in the form of cylindrical discs of thickness 1–2 mm and diameter 10–11 mm under an optimum load of 70 kN. These pellets were heated slowly to 600 °C and kept at this temperature for 1 h to burn off the binder, viz., 2% polyvinyl alcohol (PVA) solution and the temperature was then raised to 1050 °C and held there for 20 h. The heating rate was 5 °C/min and the cooling rate after sintering was 4 °C/min. One pellet of each composition with thickness ~6–8 mm was used for Seebeck coefficient measurements. A temperature gradient of 6–8 °C was maintained across the two faces of the pellet using an auxiliary heater. Another pellet (1–2 mm thickness) of each composition was polished and coated with Ag-Pd paint for ac and dc conductivity measurements.

dc resistivity measurements were carried out using two-probe method. All the measurements were made at steady temperatures maintained constant to within ± 1 °C. Measurements were made during both heating and cooling cycles. ac conductivity was measured using a Hioki 3532-50 LCR Hi Tester in the temperature range 300–500 K during heating and cooling cycles.

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3. Results and discussion

Powder X-ray diffraction (XRD) patterns of all the samples indicated formation of single phase materials as no XRD line characteristic of constituent oxides was present in them. XRD data for various compositions could be indexed on the basis of a cubic unit cell with space group $Im\bar{3}$ similar to $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ reported earlier [2,3]. Values of lattice parameters ‘ a ’ for various compositions are given in Table 1. It is noted that ‘ a ’ decreases with increasing value of x . It may be due to vacancies in Ca^{2+} sublattice as the ionic radii of La^{3+} (1.32 Å) and Ca^{2+} (1.35 Å) are almost equal [10]. Bulk density of all the samples determined by Archimedes principle is more than 93% of theoretical value.

Plots of Seebeck co-efficient, α , versus temperature in the temperature range 500–800 K for all the samples are shown in Fig. 1. Measurements of Seebeck co-efficient below 500 K were not possible because of high resistance of the sample. This shows that electrons are the majority charge carriers above 500 K. Initially α decreases with increasing temperature. After a particular temperature, it levels off. Negative value of α increases sharply as x increases from 0.0 to 0.1 and thereafter, it does not change much with x .

dc resistivity measurements have been made in the temperature range 300–1000 K by the two-probe method. Plots of log of dc resistivity, ρ_{dc} , with inverse of temperature, $1000/T$ for compositions with x upto 0–0.5 are shown in Fig. 2. These plots are found to be linear upto 600 K obeying Arrhenius relationship.

$$\rho_{\text{dc}} = \rho_0 \exp\left(\frac{E_a}{kT}\right) \quad (1)$$

where E_a is the activation energy for conduction and k is the Boltzmann constant. The values of activation energies obtained by least square fitting of the resistivity data for various compositions in the temperature range 300–600 K are given in Table 1. It is noted that the resistivity decreases with increasing temperature upto 600 K and then becomes constant for all the samples. The values of activation energies of conduction for these samples in the temperature range 300–600 K lie in the range 0.57–0.78 eV. It is interesting to note from Figs. 1 and 2 that the temperatures at which α and ρ becomes independent of temperature are almost the same. As in the case of Seebeck co-efficient, resistivity drops rapidly as x increases from $x=0.0$ to 0.1. Thereafter, there is not much variation in resistivity with x .

Table 1

Lattice parameter ‘ a ’, % theoretical density, activation energy, E_a , for dc conduction in the temperature range 300–600 K for different compositions in the system $\text{La}_x\text{Ca}_{1-3x/2}\text{Cu}_3\text{Ti}_4\text{O}_{12}$

Composition	Lattice parameter, a (Å)	Theoretical density (%)	Activation energy, dc (eV)
$x=0.0$	7.39	93.4	0.78
$x=0.1$	7.36	98.5	0.62
$x=0.2$	7.35	98.7	0.61
$x=0.3$	7.34	96.8	0.59
$x=0.4$	7.31	98.3	0.57
$x=0.5$	7.30	96.2	0.59

If one studies ac conductivity as a function of frequency and electrode polarization is absent, then one gets two plateaus and two dispersion regions [11]. The low frequency plateau represents the total conductivity followed by a dispersion region in which grainboundaries contribution relaxes. This dispersion region is followed by a plateau which represents the contribution of grains to the total conductivity. The dispersion after this plateau in the highest frequency region represents the frequency dependence of bulk conductivity.

Typical variation of $\log \sigma_{\text{ac}}$ with $\log f$ at a few steady temperatures as well as $\log \sigma_{\text{ac}}$ with $1000/T$ at a few frequencies for compositions with $x=0.10$ and 0.50 are shown in Figs. 3 and 4, respectively. Similar behavior is observed in other compositions also. For $x=0.10$ one observes only one plateau in the low frequency range and a dispersion in the high frequency range. For $x=0.50$ one plateau and one dispersion region is observed at 300 K, two dispersion region connected by a plateau region are seen at 350 K while two plateaus connected by two dispersion regions are observed at 400 K. Two plateau and two dispersion regions do not appear at all temperatures because the ac conductivity could be measured only in a limited range of frequencies available in the instrument. Variation of $\log \sigma_{\text{ac}}$ with $1000/T$ shows two regions for both the samples. In the lower temperature region there is very little variation of conductivity with temperature but a strong dependence on frequency. In the higher temperature range conductivity varies exponentially with the temperature but with very weak frequency dependence.

The conductivity determined from the plateau of the curve, where only one plateau appears (in $\log \sigma_{\text{ac}}$ versus $\log f$) is more than one order of magnitude than the corresponding dc conductivity value determined at same temperature. This implies that this plateau represents the contribution of the grains which are expected to be more conducting as compared to grainboundaries as explained below. For sample with $x=0.50$, two plateaus and two dispersion region are observed only at 400 K. The value of conductivity obtained from the low frequency plateau is close to the value determined from dc conductivity. At other temperatures, the low frequency plateau will appear at lower frequencies. The dispersion after the single plateau observed at lower frequency (for $x=0.10$) represents the dispersion of bulk conductivity in this sample. In this region σ_{ac} varies as: $\sigma_{\text{ac}} = A\omega^s$, where A is constant at a given temperature and the exponent ‘ s ’ a weak function of frequency at a given temperature [12]. The value of ‘ s ’ determined from this dispersion region lies in the range 0.5–0.8 and it decreases with increase in temperature. This shows that conduction occurs due to correlated barrier hopping of electrons [13] among Cu^+ and Cu^{2+} as explained below.

The values of activation energies for conduction determined by us agree with the values reported by Sinclair et al. [7,14]. These authors reported the high dielectric constant of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is due to formation of barrier layers. There is a slight loss of oxygen during sintering in accordance with the reaction



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