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Structural, dielectric and electrical properties of $ACu_3Ti_4O_{12}$ (A = Ca, Sr and Ba)

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Polycrystalline compounds of a general formula $ACu_3Ti_4O_{12}$ (A = Ca, Sr, Ba) were synthesized by a high-temperature solid-state reaction technique. Crystal structure of the compounds at room temperature studied by an X-ray diffraction (XRD) technique was found to be cubic. Detailed studies of dielectric constant (ε) and loss tangent ($\tan\delta$) of the compounds as a function of frequency (100 Hz to 1 MHz) and temperature (125 K to 600 K) did not show any ferroelectric phase transition. The ac and dc conductivity studied over a wide range of temperature provided activation energy of the compounds. Variable range phonon-assisted quantum mechanical tunneling technique of correlated barrier hopping (CBH) model has been applied to interpret the temperature and frequency dependent ac conductivity. Using these theoretical models, various model parameters have also been calculated. The temperature variation of resistivity shows that the compounds have negative temperature coefficient of resistance (NTCR).

1. Introduction

Since the discovery of high dielectric constant ($>10^4$) at transition temperature, and low loss ($\sim 10^{-3}$) and zero or small spontaneous polarisation at/near transition temperature (T_c) in some ferroelectric perovskites, such as $BaTiO_3$ [1], $LiNbO_3$ [2], $PbTiO_3$ [3], PZT [4], etc. of a general formula ABO_3 (A = mono or divalent, B = tri to pentavalent ions), a large number of simple and/or complex charged neutral or charged deficient compounds of a general formula $(A_1 \ldots A_n)(B_1 \ldots B_n)O_3$ have been examined in the past in search of high dielectric constant and low dielectric loss materials for some electronic applications. In most of the materials studied so far, the relative dielectric constant (ε_r) and loss tangent ($\tan\delta$) were found to follow the Debye equations and Curie-Weiss laws, and hence they are temperature and frequency dependent. For some important applications, such as, capacitor in the control electronic circuit of space craft, pyroelectric detector etc., temperature and frequency independent high ε and low $\tan\delta$ are very important. Our extensive studies on many ferroelectric materials, for example, pure and complex perovskite (PbLa)(ZrTi)O_3 [5] and tungsten-bronze with a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$ [6] showed diffuse phase transition (DPT) in them with temperature and/or frequency independence of dielectric constant in the range of 10^2–10^3 and $\tan\delta$ in the range of 10^{-2}–10^{-3}. Recently temperature independent high dielectric constant ($\sim 10^4$) was reported in a higher order perovskite, $(CaCu_3)Ti_4O_{12}$, by Ramirez *et al.* [7] and Subramanian *et al.* [8] in the temperature range of 100 K to 550 K. This compound has centrosymmetric structure at room temperature with cubic space group Im3 and cell parameter: $a = 7.3730$ Å. We find that it is very unusual and unexpected to observe such a high dielectric constant (~ 10000) in low temperature region of non-ferroelectric material. Because of such incredibly high dielectric constant and some other discrepancies, we proposed to study the dielectric and electric properties not only of $CaCu_3Ti_4O_{12}$, but also other members of the family in greater details. Therefore, we have carried out extensive studies on structural, dielectric (dielectric constant and loss) and electrical (ac and dc conductivity) properties of a large number of perovskite compounds of higher order of a general formula $(A'A''_{n-1})B_nO_{3n}$ ($n = 4$; A′ = Ca, Sr, Ba; A″ = Cu, Ag, B = Ti, Zr, Sn). In this paper, we report our studies on some aspects of crystal structure, and detailed dielectric and electrical properties of the $ACu_3Ti_4O_{12}$ (A = Ca, Sr, Ba) compounds.

2. Experimental

The polycrystalline samples of $ACu_3Ti_4O_{12}$ (A = Ca, Sr and Ba) compounds were prepared by a high-temperature solid-state reaction technique using high purity carbonates; $CaCO_3$ (99%, M/s. Sarabhai Chem., India), $SrCO_3$ (99%, M/s Burgoyne Urbridges and Co.), $BaCO_3$ (99.5%, M/s. Sarabhai Chem., India) and oxides; CuO (99%, M/s. Loba Chem., India) and TiO_2 (99%, M/s. S.d. Fine Chem., India) in a suitable stoichiometry. The thoroughly mixed powders were calcined at 1000°C for 24 h. The process of calcination and grinding was repeated until the formation of desired compounds was confirmed by XRD studies. The fine powder of the compounds was pressed into pellets of 9.5 mm diameter and 1.5–2 mm thickness at a pressure of 7×10^7 kg/m^2 using a hydraulic press. The pellets were sintered in an air atmosphere at 1060°C for

TABLE I Comparison of some observed [o] and calculated [c] d-values of some reflections of $ACu_3Ti_4O_{12}$ (A = Ca, Sr, Ba) compounds at room temperature

$CaCu_3Ti_4O_{12}$			$SrCu_3Ti_4O_{12}$			$BaCu_3Ti_4O_{12}$		
hkl	d (Å)	I/I_o	hkl	d (Å)	I/I_o	hkl	d (Å)	I/I_o
211	3.0100 (o) 3.0100 (c)	11	211	3.0126 (o) 3.0122 (c)	17	211	3.0978 (o) 3.0978 (c)	22
220	2.6046 (o) 2.6067 (c)	100	220	2.6077 (o) 2.6086 (c)	100	220	2.6848 (o) 2.6828 (c)	100
310	2.3316 (o) 2.3315 (c)	15	310	2.3341 (o) 2.3332 (c)	13	310	2.4023 (o) 2.3995 (c)	29
222	2.1300 (o) 2.1284 (c)	11	222	2.1300 (o) 2.1300 (c)	11	222	2.1880 (o) 2.1905 (c)	24
321	1.9716 (o) 1.9705 (c)	11	321	1.9750 (o) 1.9720 (c)	10	320	2.1046 (o) 2.1045 (c)	21
400	1.8488 (o) 1.8432 (c)	34	400	1.8477 (o) 1.8446 (c)	34	322	1.8405 (o) 1.8404 (c)	39
422	1.5066 (o) 1.5055 (c)	48	422	1.5084 (o) 1.5061 (c)	43	420	1.6967 (o) 1.6967 (c)	44

12 h. X-ray diffraction patterns of the compounds were recorded at room temperature with a Philips X-ray Powder diffractometer with Co K_α radiation ($\lambda = 1.7902$ Å) over a wide range of Bragg angles 2θ ($20° \leq 2\theta \leq 80°$) at a scanning rate of 2°/min.

The dielectric constant (ε) and loss tangent ($\tan\delta$) of the compounds were measured as a function of frequency (100 Hz to 1 MHz) in a wide range of temperature (125 K to 600 K) using a HIOKI-3532 LCR HiTester (Japan) and a laboratory-fabricated sample holder. The frequency and temperature dependence of ac conductivity was calculated using the dielectric data. The dc conductivity was obtained as a function of temperature (273 to 600 K) and electric field (2.5 to 70 kV/m) using a laboratory-fabricated experimental set up consisting of a Keithley 617 programmable electrometer, PID temperature controller, sample holder and furnace.

3. Results and discussion

The sharp and single peaks of the XRD patterns (Fig. 1) of all the compounds, which are quite different (in position and intensity) from those of ingredient carbonates and oxides, suggest the formation of single-phase compound. All the peaks were indexed and cell parameters were determined using interplanar spacing d using computer software "POWDmult". Least-squares refined cubic cell parameter a of $ACu_3Ti_4O_{12}$ (A = Ca, Sr and Ba) (Table II) was found to be consistent with that reported [7]. A good agreement between the observed and calculated d values of these compounds suggests the correctness of lattice parameters and crystal structure (Table I).

TABLE II Comparison of CBH model parameters, lattice constant a, dielectric parameters and other transport parameters for $ACu_3Ti_4O_{12}$ compounds (A = Ca, Sr and Ba)

Parameters	Ca	Sr	Ba
s	0.27	0.29	0.37
n	17.45	15.21	8.03
R_ω (Å) at 1 kHz	0.56	0.47	0.44
w (eV)	0.843	0.784	0.585
$N(E_F) \times 10^{26}$ $eV^{-1} \cdot cm^{-3}$	3.9	1.81	1.45
a (Å)	7.3730 (20)	7.3784 (20)	7.5880 (20)
ε_r (RT and 1 kHz)	478	550	521
$\tan\delta$ (RT and 1 kHz)	1.102	0.062	0.744
σ_{dc} (at RT)$(\Omega^{-1} \cdot m^{-1}) \times 10^{-6}$	0.41	0.01	3.42
E_{ac}(eV)	0.77	0.68	0.35
E_{dc} (eV)	0.75	0.67	0.38

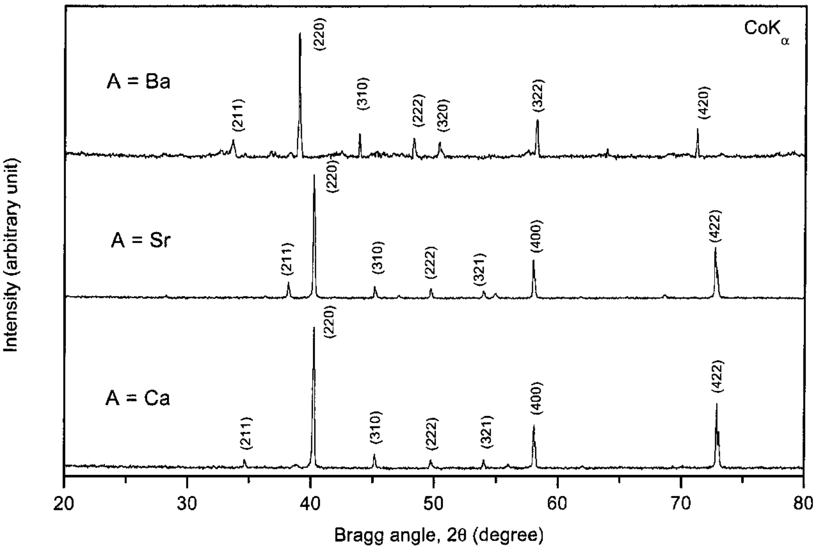
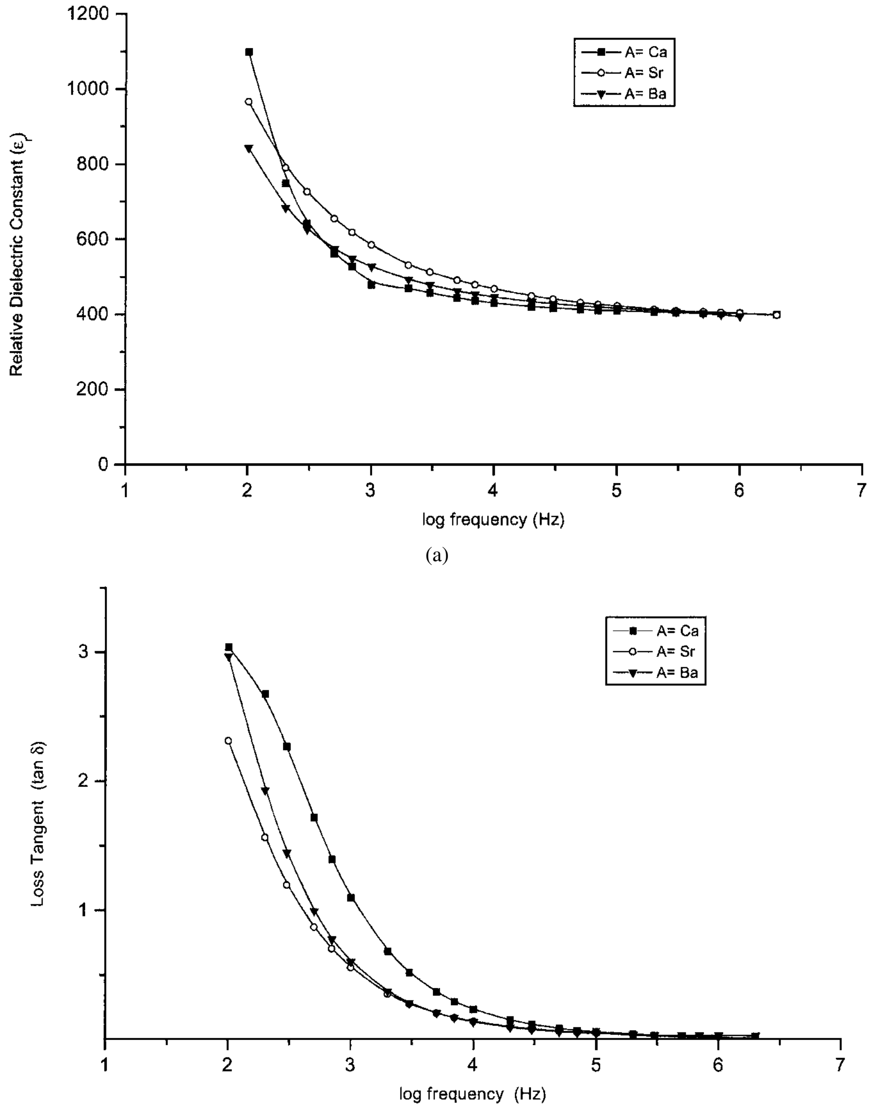


Figure 1 Comparison of XRD patterns of $ACu_3Ti_4O_{12}$ compounds at room temperature.



(a)

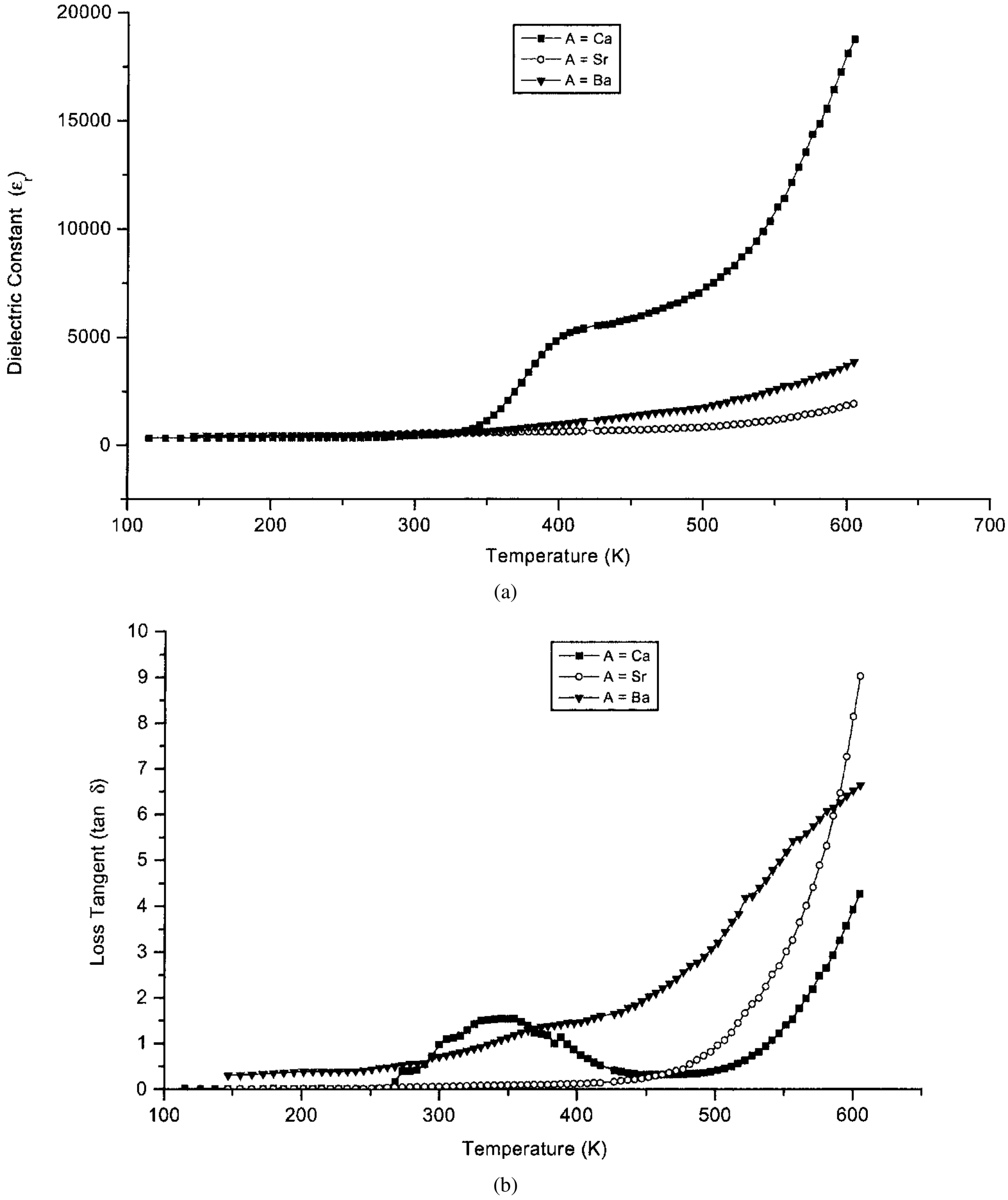
(b)

Figure 2 Variation of ε with frequency of $ACu_3Ti_4O_{12}$ compounds at room temperature. (b) Variation of $\tan\delta$ with frequency of $ACu_3Ti_4O_{12}$ compounds at room temperature.

The frequency dependence of ε and $\tan\delta$ of the above compounds is shown in Fig. 2a and b respectively. The dielectric constant of all the compounds decreases rapidly with increasing frequency. Above 10 kHz, dielectric constant becomes almost constant. Similar trend is also observed in loss tangent (Fig. 2b). At lower frequencies, we have different types of polarisations (i.e., atomic, interfacial, ionic and electronic) and at higher frequencies ($>$1000 kHz) dielectric constant has main contribution from the electronic polarisation.

Fig. 3a and b show the temperature variation of ε and $\tan\delta$ respectively at 1 kHz. We observed almost constant ε in all the $ACu_3Ti_4O_{12}$ compounds in the temperature range of 100–340 K, but above this temperature, ε increases rapidly only for $CaCu_3Ti_4O_{12}$. The dielectric constant of $CaCu_3Ti_4O_{12}$ was reported very high value ($\sim 10^4$) in the low temperature range (liquid helium temperature to room temperature) [7], but we did not get such type of results in other compounds in the liquid nitrogen region. Our extensive dielectric studies of other compounds of this family, such as $SrCu_3Ti_4O_{12}$ and $BaCu_3Ti_4O_{12}$ yielded low ε ($\sim$500) at 1 kHz at room temperature. The dielectric constant of $CaCu_3Ti_4O_{12}$ was found nearly constant ($\sim$500) from liquid nitrogen temperature to 340 K, and thereafter it increases to very high value (2×10^4 at 600 K). The value of dielectric constant ($\sim$550) of $SrCu_3Ti_4O_{12}$ is almost temperature independent upto 575 K and then increases very slowly. Among all three samples studied, $CaCu_3Ti_4O_{12}$ shows a $\tan\delta$ anomaly at around 350 K which is consistent with that reported [7, 8].

For multi-component system, there is always some uncertainty for ascertaining the actual conduction mechanism. However, we attempted to obtain ac conductivity and activation energy E_{ac} using dielectric data and some empirical relations, $\sigma_{ac} = \varepsilon\varepsilon_o\omega\tan\delta$ and $\sigma_{ac} = \sigma_o\exp(-E_{ac}/kT)$. Using an established correlated barrier-hopping (CBH) model [9], different transport parameters were calculated. The variation of $\ln\sigma_{ac}$ with frequency and temperature (K^{-1}) is shown in Figs 4 and 5 respectively. As it is evident from the figures, $\sigma_{ac}(\omega)$ obeys a relation $\sigma_{ac}(\omega) = A(T)\omega^s$, where



(a)

(b)

Figure 3 Temperature variation of ε at 1 kHz of $ACu_3Ti_4O_{12}$ compounds. (b) Temperature variation of tan δ at 1 kHz of $ACu_3Ti_4O_{12}$ compounds.

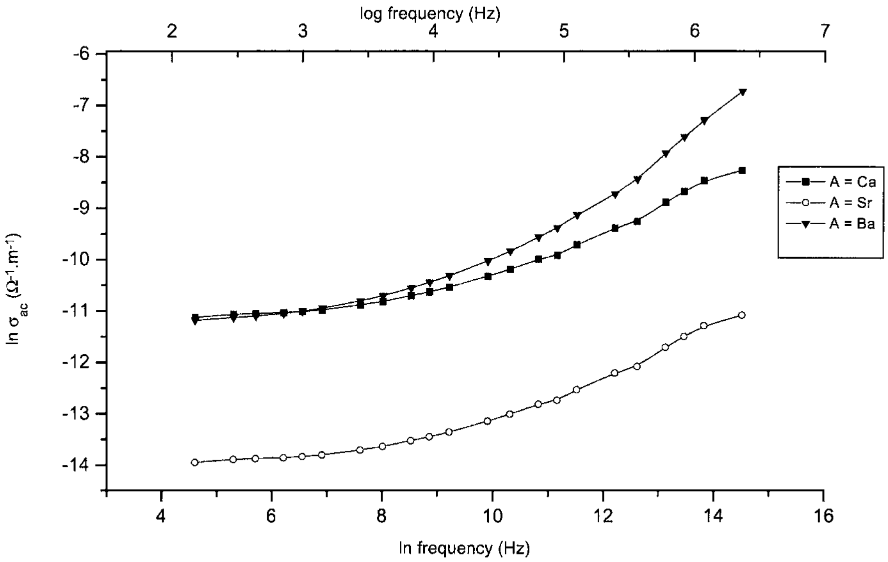


Figure 4 Variation of ln σ_{ac} with frequency at room temperature of $ACu_3Ti_4O_{12}$ compounds.

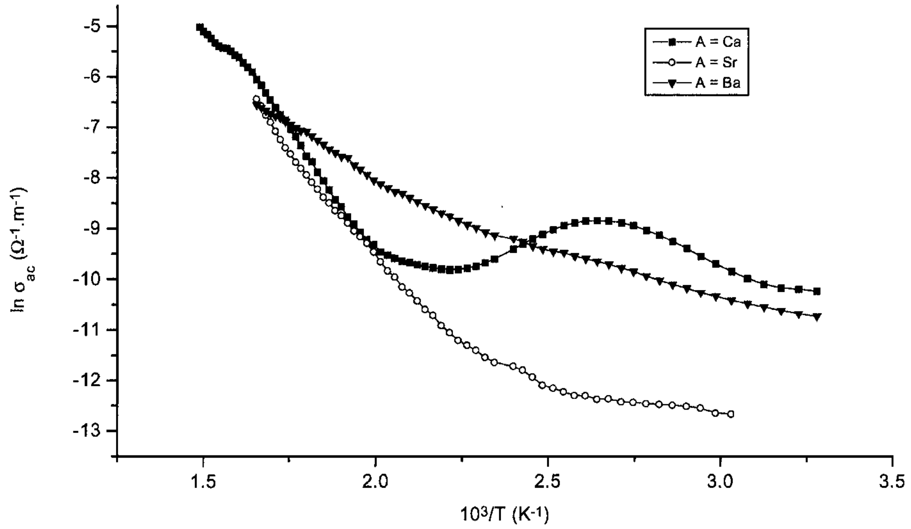


Figure 5 Variation of $\ln\sigma_{ac}$ with temperature (K^{-1}) at 1 kHz of $ACu_3Ti_4O_{12}$ compounds.

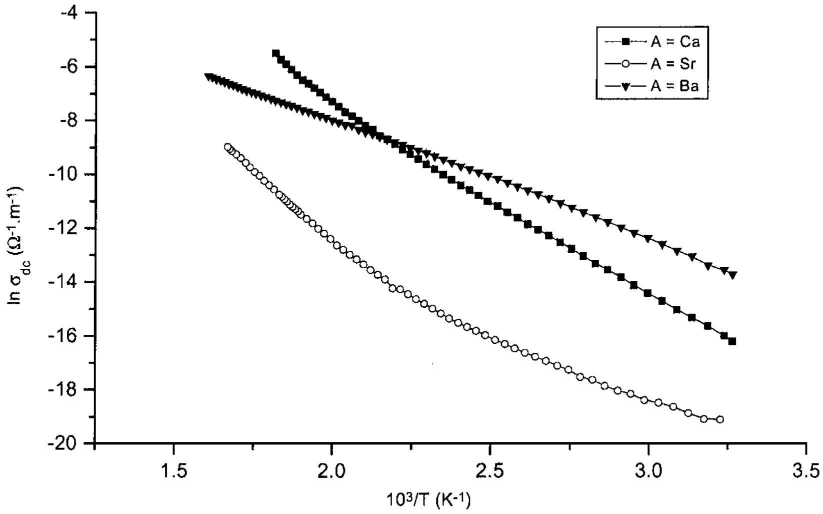


Figure 6 Variation of $\ln\sigma_{dc}$ with temperature (K^{-1}) of $ACu_3Ti_4O_{12}$ compounds.

the frequency exponent s was calculated from the slopes of the curves of Fig. 4. The value of s for all compounds was found lying within the range of 0.27 to 0.37 in the frequency band 1 kHz to 1 MHz. It is observed that s is temperature and frequency dependent. The frequency response of ac conductivity of $ACu_3Ti_4O_{12}$ (A = Ca, Sr and Ba) suggests that the exponent s increases with increasing frequency. We have calculated different transport or model parameters using this model. In the CBH model, the variable range phonon-assisted quantum mechanical tunneling of localized electrons between two sites, closed to Fermi level, has been considered. This model correlates the barrier height w with barrier width R_ω. Here the frequency dependent electrical conductivity in a wide frequency band limit Δ_o ($\Delta_o \gg kT$) for the hopping of localized electrons among different atomic sites is calculated using an empirical relation [9]:$\sigma_{ac}(\omega) = [\pi^3 g_o^2 (kT)^2 \varepsilon\varepsilon_o \omega R_\omega^6]/12$ where, $g_o = N\ (E_F)$ is the density of states at the Fermi level, k = Boltzmann constant, ε = relative permittivity of material at angular frequency ω and temperature T, and ε_o = free space permittivity. The barrier width R_ω at a particular frequency ω is given by $R_\omega = \frac{e^2}{\pi\varepsilon\varepsilon_o[w + kT\ln(\omega\tau_o)]}$ where; τ_o and e are the mean relaxation time and electronic charge respectively. Now the frequency exponent s can be written as $s = 1 - \frac{6kT}{w + kT\ln(\omega\tau_o)}$.

Again from the power law of ac conductivity $\sigma_{ac} = BT^n$ (where B = constant). The value of temperature exponent n can be calculated by $n = (1 - s)\ln(1/\omega\tau_o)$. It is observed (Fig. 4) that $\ln\sigma_{ac}$ of $SrCu_3Ti_4O_{12}$ is much lower compared to that of other two compounds of the family. But in all the cases, $\ln\sigma_{ac}$ increases with rise in frequency. Fig. 5 shows that $\ln\sigma_{ac}$ increases with rise in temperature. At high temperature, nature of variation of $\ln\sigma_{ac}$ with temperature for all these compounds is similar. Again, we have observed a broad σ_{dc} peak in $CaCu_3Ti_4O_{12}$, but no peak was observed in other two compounds. The value of CBH model parameters (s, n, R_ω, w, $N(E_F)$) obtained from all the above equations for different compounds are compared in Table II. It is observed that the barrier height and ac activation energy (E_{ac}) of all the compounds of $ACu_3Ti_4O_{12}$ family decrease gradually with increasing atomic number of the A elements. The ac activation energy (E_{ac}) of the compounds was calculated from the slope of the $\ln\sigma_{ac}$ versus inverse of absolute temperature (i.e., $10^3/T$) plot. Similarly, the dc

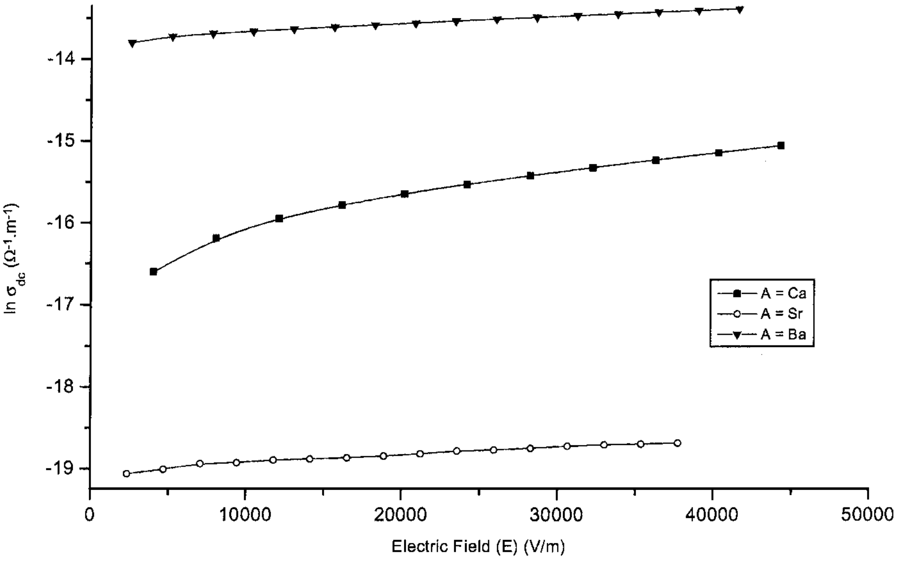


Figure 7 Variation of ln σ_{dc} with electric field of $ACu_3Ti_4O_{12}$ compounds.

activation energy (E_{dc}) was calculated from the plot of ln σ_{dc} with inverse of absolute temperature ($1/T$)(Fig. 6) at constant biasing voltage (10 V) using the relation $\sigma_{dc} = \sigma_o \exp(-E_{dc}/k_B T)$. It is also observed that the value of ln σ_{dc} is much lower for $SrCu_3Ti_4O_{12}$ compared to other two compounds. There is a wide difference in the value of ln σ_{dc} (~2.5–3) of $SrCu_3Ti_4O_{12}$ and $BaCu_3Ti_4O_{12}$ with the intermediate value of this parameter for $CaCu_3Ti_4O_{12}$. It is noted that activation energy obtained from ac and dc conductivity matches reasonably well, and has the trend of reduction with successive A-site substitution of higher atomic numbers element (i.e., Ca, Sr and Ba). The ac conductivity is contributed by hopping of both localized and free charges, whereas dc conductivity is contributed by free or delocalized charges only. Therefore, ac activation energy is slightly greater than dc activation energy (Table II). The nature of temperature dependent of dc conductivity of the compound shows the negative temperature coefficient of resistance (NTCR) effect in them.

Fig. 7 shows the variation of dc conductivity (σ_{dc}) with biasing field (E) at room temperature. With increasing field, dc conductivity slightly increases for all the compounds, which can clearly be explained from Schottky conduction mechanism.

4. Conclusion

Finally, it is concluded that though the $CaCu_3Ti_4O_{12}$ has high dielectric constant compared to that of $SrCu_3Ti_4O_{12}$ and $BaCu_3Ti_4O_{12}$ above room temperature. They do not have any ferroelectric phase transition. The electrical properties suggest that these compounds can be used as negative temperature coefficient resistors.

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