On the dielectric spectroscopy of copper doped layered $Na_{1.6}K_{0.4}Ti_3O_7$ ceramics

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Abstract

The copper doped derivatives of layered $Na_{1.6}K_{0.4}Ti_3O_7$ (SPT-3) ceramics have been investigated through dielectric spectroscopy in this work. The results indicate that the dielectric losses in these ceramics are the collective contribution of electric conduction, dipole orientation and space charge polarization. Smeared peaks in temperature dependence of permittivity plots suggest diffuse nature of high temperature ferroelectric phase transition. The light copper doping in SPT-3 enhances the relative permittivity. However, copper doping decreases dielectric loss due to inhibition of domain wall motion, enhances electron hopping conduction, and impedes the interlayer ionic conduction as well. Copper doping also gives rise to contraction of interlayer space.
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1. Introduction

In recent years, there has been much development in field of alkali titanate ceramics having layered and tunnel structures [1–26]. The physico-chemical properties including ionic and electronic conductivity have been extensively investigated due to their potential industrial applications as ion exchangers, electrodes for secondary batteries, filters, reinforcements, heat insulators, catalysts, etc. [2–16]. Investigations have been undertaken on the intercalation of alkylammonium cations into layered titanate in the presence of macrocyclic compounds [14]. Visible light induced electron transfer and long-lived charge separation have been studied in cyanine dye/layered titanate compounds [15]. The family of alkali titanates crystallizes in about 130 phases [11]. Varying grain size of layered compounds, namely $Na_2Ti_3O_7$ and $Na_2Ti_6O_{13}$ have been obtained by sol–gel process and also by solid state reaction of Na_2CO_3 and TiO_2 [17,18]. The photochemical properties of Cu^{2+} doped layered hydrogen titanates have been studied by Yanagisawa et al. [19]. Recently, Zhang et al. [20,21] have reported the preparation of $H_2Ti_3O_7$ nanotubes. Pillaring and photocatalytic properties of partially substituted layered titanates: $Na_2Ti_{3-X}M_XO_7$ and $K_2Ti_{4-X}M_XO_9$ (M = Mn, Fe, Co, Ni, Cu) have been reported [16]. $Na_2Ti_3O_7$, $K_2Ti_4O_9$ and their manganese doped derivatives have been investigated using ac conductivity and dielectricspectroscopy [22,23].

Recently, the dielectric properties of pure $Na_{1.6}K_{0.4}Ti_3O_7$ (SPT-3) [26] were reported. It is believed that metal ion M is incorporated into the host lattice at Ti^{4+} sites. Electron paramagnetic resonance (EPR) is a sensitive tool to confirm the Mn^{2+}, Fe^{3+} and Cu^{2+} oxidation sates through their characteristic EPR signals. Therefore, it is interesting to use copper as metal and investigate its oxidation state in the host lattice of $Na_{1.6}K_{0.4}Ti_3O_7$ and the resulting change in the dielectric properties of the host lattice.

2. Experimental

Polycrystalline layered ceramic samples of $Na_{1.6}K_{0.4}Ti_3O_7$ (denoted as SPT-3) have been synthesized by mixing Na_2CO_3 (Merck Germany, 99.9%), K_2CO_3 (Merck Germany, 99.9%), and TiO_2 (Merck Germany, 99.9%) powders in stoichiometric ratio and subsequently calcining the mixture at 1173 K for 16 h. Copper doped ceramic samples of $Na_{1.6}K_{0.4}Ti_3O_7$ have been prepared by adding 0.01, 0.1 and 1.0 mol% of CuO (Merck Germany, 99.9%) powder in the base matrix of $Na_{1.6}K_{0.4}Ti_3O_7$ and denoted as C_1SPT-3, C_2SPT-3 and C_3SPT-3,

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respectively. Details of the method of preparation of these ceramics are given elsewhere [26]. XRD-patterns for all the above compositions have been collected on Richseifert Iso-Debyflex 2002 diffractometer using Cu Kα radiation generated at 30 kV and 20 mA. The formation of these titanates was confirmed through the above recorded XRD-patterns. The details of ac conductivity and dielectric-spectroscopic measurements were similar to that reported earlier [26]. The EPR spectra of the copper doped samples were recorded on a Varian E-line century series spectrometer model E-109, which operates at X-band frequencies (∼9.2 GHz). The sample were in the form of fine powder filled in quartz tube of 4 mm outer diameter and were placed at the magnetic field maximum of a TE$_{104}$ rectangular cavity. First derivative absorption signals were obtained with 100 kHz magnetic field modulation. The modulation amplitude was kept 1 gauss peak to peak (p–p). The polycrystalline DPPH was used as a standard *g*-marker (*g* = 2.0036 ± 0.0002).

3. Results and discussion

The EPR spectra recorded at room temperature (RT) for all the three copper doped compositions C$_1$SPT-3, C$_2$SPT-3 and C$_3$SPT-3 are shown in Fig. 1. The shape of the EPR spectra is the characteristic of axially distorted octahedral copper(II) (3d^9, $S = 1/2$, $I = 3/2$) complexes. The EPR spectra comprise two signals one is called ‖-spectrum and other is ⊥-spectrum. The *g*-values (listed in Table 1) are calculated by the following relation: $g = 2.0036 (B_{DPPH}/B_o)$, where B_{DPPH} is the resonance magnetic field of DPPH standard *g*-marker and B_o is the observed resonance magnetic field of the sample. The observation of EPR signal at RT confirms the Cu^{2+} (3d^9) oxidation state of copper. Since copper has two isotopes Cu^{63} and Cu^{65} and both of them possess closely similar magnetic moment and a nuclear spin $I = 3/2$, due to electronic spin $S = 1/2$ and a nuclear spin $I = 3/2$ one expects a quartet (a set of four hyperfine lines) for Cu^{2+} ion [27] in its EPR signal. But, the observed EPR spectra do not show any hyperfine splitting and isotopic splitting. This is due to the exchange narrowing of the EPR signal, which smears out the

hyperfine splitting. Hence the observed EPR signals are the characteristic EPR spectra of an exchange narrowed system. Since in a powder sample, we observe only an averaged EPR spectrum due to random orientation of crystallites, spectra for the so-called parallel and perpendicular orientations are observed [27]. By nature parallel part of the spectrum remains much weaker than the perpendicular part of the EPR spectrum in powder and hence the observed EPR spectra conform to axial symmetry of the copper complex i.e. $g_x = g_y = g_\perp$ and $g_z = g_\parallel$. The observation that $g_\parallel > g_\perp > 2$ indicates that the ground state of the Cu^{2+} ion in the distorted octahedral (tetragonal) complex is $d_{x^2-y^2}$ [28]. The observed distorted octahedral symmetry of copper complexes suggests that copper occupies Ti^{4+} site with divalent oxidation state (Cu^{2+}) giving rise to oxygen vacancy in the lattice required for charge neutrality of the lattice, thereby generating electric dipoles [29–32]. For the samples having higher concentration of dopants, it can be seen that the peaks get broadened due to dipolar broadening and the exchange interaction of neighboring copper atoms.

Fig. 2a–d show the temperature dependence of loss tangent (tan δ) at several frequencies for SPT-3, C$_1$SPT-3, C$_2$SPT-3 and C$_3$SPT-3, respectively. From Fig. 2a, it can be seen that the values of tan δ for SPT-3 remain invariant with the rise in temperature up to 498 K and then increases to give symptoms of a relaxation loss peak around 623 K. Fig. 2b shows that values of tan δ for C$_1$SPT-3 remains invariant up to 423 K and then with the rise in temperature the variation in the values of tan δ shape three small peaks around 448, 498 and 573 K and then increase above 598 K. Fig. 2c shows that values of tan δ for C$_2$SPT-3 remain almost invariant with the rise in temperature up to 523 K and above 523 K, it rises rapidly with the rise in temperature. While, from Fig. 2d, it can be seen that the values of tan δ for C$_3$SPT-3 rise slightly with the rise in temperature and indicate a small relaxation loss peak around 448 and 548 K. The higher rate of increase of tan δ at lower frequency and higher temperature may be ascribed to the space charge polarization [33]. The usual increase in tan δ at higher temperature may be ascribed to an increase in number of ions taking part in relaxation polarization and an increase in leakage current [34]. It is observed that tan δ decreases appreciably with increasing frequency at higher temperatures, which may be attributed to the increased space charge polarization. The trend of variations for all the copper doped compositions is similar and showing the features of dielectric losses due to dipole reorientation and electric conduction [34,35].

Fig. 3a–d depict the frequency dependence of tan δ at various temperatures for SPT-3, C$_1$SPT-3, C$_2$SPT-3 and C$_3$SPT-3, respectively. These plots show that the tan δ decreases with the increasing frequency giving resonant type small peaks around 600 kHz for C$_2$SPT-3 and C$_3$SPT-3, while it is found around 700 kHz for C$_1$SPT-3. The origin of these resonant peaks may be attributed to the presence of dipoles arisen due to doping as these types of peaks are not resolved for undoped SPT-3. Moreover, the decreased resonant frequency (600 kHz) for the heavily doped C$_2$SPT-3 and C$_3$SPT-3 may be attributed to the increased relaxation time due to collective relaxation of increased number of dipoles in heavily doped ceramics. The low value of dielectric
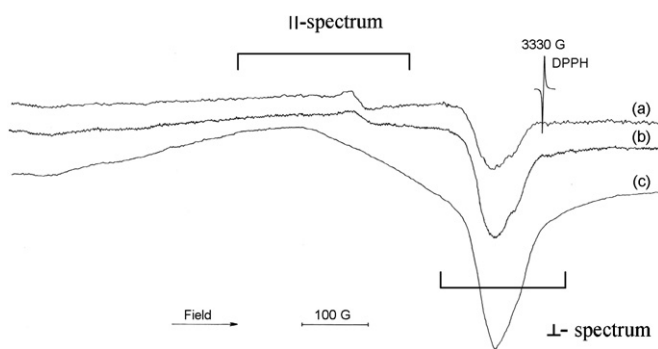

Fig. 1. EPR spectra of copper doped SPT-3 recorded at RT for (a) C$_1$SPT-3, (b) C$_2$SPT-3 and (c) C$_3$SPT-3.

Table 1
g-Values calculated from the EPR spectra of different doped derivatives of SPT-3

Sample	$g_\parallel$	$g_\perp$
C$_1$SPT-3	2.197 ± 0.002	2.049 ± 0.002
C$_2$SPT-3	2.202 ± 0.002	2.055 ± 0.002
C$_3$SPT-3	2.260 ± 0.002	2.056 ± 0.002