

The effect of paramagnetic doping on the dielectric response of $\text{K}_{1.85}\text{Na}_{0.15}\text{Ti}_4\text{O}_9$ layered ceramics

S. V. VIKRAM^{1*}, D. MAURYA², V. S. CHANDEL¹

¹Department of Physics, Integral University, Lucknow, India-226026

²Department of Materials and Metallurgical Engineering, IIT Kanpur, India-208016.

Ceramic samples of layered polycrystalline $(\text{K}_{1.85}\text{Na}_{0.15})\text{Ti}_4\text{O}_9:x\text{Cu}$ ($0 \leq x \leq 0.8$) have been prepared using high temperature solid state reaction. Room temperature X-ray diffratograms confirm the phase evolution. Room temperature electron paramagnetic resonance (EPR) data show that Cu^{2+} occupies Ti^{4+} lattice sites giving rise to electric dipoles which increases electric permittivity. The absorption peak in EPR spectra gets broadened due to increased exchange interaction in heavily doped derivatives. Dielectric data reveal that occupancy of Cu^{2+} on Ti^{4+} leads to a decrease in dielectric losses and an increase in the electric permittivity as well.

Key words: *layered ceramics; dielectric properties; electron paramagnetic resonance*

1. Introduction

The formula of alkali titanates crystallizing in a monoclinic phase is generalized by $\text{A}_2\text{O} \times n\text{TiO}_2$ ($3 \leq n \leq 8$, A is an alkali metal) [1]. Titanate nanotubes and nanowires have many important applications as photocatalysts, gas sensors, high-energy cells and in the field of environmental purification [2, 3]. Layered titanates are usually composed of slipped or corrugated host layers of edge-shared TiO_6 octahedra and inter-layer alkali metal cations (Na^+ , K^+ or $\text{H}^+/\text{H}_3\text{O}^+$ in protonic form) which are exchangeable with a variety of inorganic and organic cations [4]. Alkali metal titanates have been synthesized at nanoscale and studied on account of their robust applicability in biophysics [5]. Papp et al. [6] reported that the tendency of titanates to self-assemble makes them suitable candidates for utilization as efficient photocatalysts. Due to their TiO_2 derived structural origin, the nanotubes offer a potential in photocatalysis, solar

*Corresponding author, e-mail: svv28srf@gmail.com

energy conversion, as electrochromic materials, and self-cleaning devices [7]. The photochemical properties of Cu^{2+} doped layered hydrogen titanate have been presented elsewhere [8]. Cation exchange property has been studied for protecting environment against lethal radiation of highly radioactive liquid wastes [9].

In this array, Kikkawa et al. [10] reported that Nb^{5+} ions doped into $\text{K}_2\text{Ti}_4\text{O}_9$ naturally occupy Ti^{4+} sites and create cation vacancies leading to increased ionic conductivity. Pillaring and photo-catalytic properties of $\text{Na}_2\text{Ti}_{3-x}\text{M}_x\text{O}_7$ and $\text{K}_2\text{Ti}_{4-x}\text{M}_x\text{O}_9$ ($\text{M} = \text{Mn, Fe, Co, Ni, and Cu}$) have also been reported [11]. Recently, the influence of copper doping on mixed alkali titanates has also been reported [12]. Hence, it is interesting now, to synthesize and investigate the influence of copper doping ($0 \leq x \leq 0.8$) on the dielectric features of layered $\text{K}_{1.85}\text{Na}_{0.15}\text{Ti}_4\text{O}_9$ ceramics.

2. Experimental

The ceramic sample of $\text{K}_{1.85}\text{Na}_{0.15}\text{Ti}_4\text{O}_9$ has been prepared via conventional solid-state reaction route as reported earlier [13]. To prepare copper doped derivatives of $\text{K}_{1.85}\text{Na}_{0.15}\text{Ti}_4\text{O}_9$ ceramics, the desired molar percentages ($x = 0.0, 0.02, 0.2, 0.8$; hereafter referred to as PT, CPT-1, CPT-2, CPT-3) of CuO powder (99.9% pure, AR grade) were added to the mixture of alkali carbonates and titanium oxide. The mass so obtained was then calcined at 1200 K for 10 h. After grinding, the powder was compressed using a hydraulic press at 16 MPa to yield pellets, which were covered under the powder of the same composition and then sintered at 1200 K for 1 h, followed by furnace cooling to room temperature (RT).

RT XRD for $\text{K}_{1.85}\text{Na}_{0.15}\text{Ti}_4\text{O}_9$ and for all its copper doped derivatives have been obtained on an X-ray powder diffractometer ISO-DebyeFlex 2002, Richseifert and Co. (Germany) using CuK_α radiation with the sweep of 3.0 deg/min, range (CPM) = 5 K, time constant = 10.0 s, current = 20 mA, and voltage across the cathode and target 30 kV.

The conventional first derivative of X-band (9.447 GHz) EPR absorption spectra were recorded on a Bruker EMX X-band EPR spectrometer with 100 KHz and 10.0 G modulations. The maximum calibrated power available was 0.201 mW. The high frequency modulation field amplitude ranged typically from 5×10^{-3} mT to 0.50 mT with rectangular TE_{102} cavity (unloaded $Q \approx 7000$) at 100 kHz field modulation. The samples for recording the EPR spectra were kept in a quartz tube (outer diameter ca. 5 mm) which was then placed at the centre of the resonant cavity. An incident microwave power level of 10 mW was used for most of the cases to give levels of 10^5 . The magnetic field was calibrated using a central field at 3400 G.

The dielectric-spectroscopic measurements have been performed on an HP 4194A impedance analyzer in the frequency range 100–1000 kHz at RT with an ac bias of 0.5 V superposed. To avoid the effect of moisture, the samples were heated up to 150 °C before experiments. For this, the pellets were mounted on a sample holder kept in an evacuated (10^{-3} mbar) chamber.

3. Results and discussion

Powder X-ray diffraction patterns obtained at RT for K_{1.85}Na_{0.15}Ti₄O₉ are shown in Fig. 1. The room temperature XRD patterns for all copper doped derivatives are similar to that of K_{1.85}Na_{0.15}Ti₄O₉. These patterns are in good agreement to that reported in the literature and thus confirm the formation of polycrystalline layered alkali titanates in a monoclinic phase with $P2_1/m$ symmetry [4, 13]. Layered titanates are composed of stepped or corrugated host layers of edge shared TiO₆ octahedra and interlayered alkali metal cations (K⁺, Na⁺) [13]. Two kinds of interlayer spaces exist due to shifting of neighbouring layers relative to each other in amount of b spacing [14].

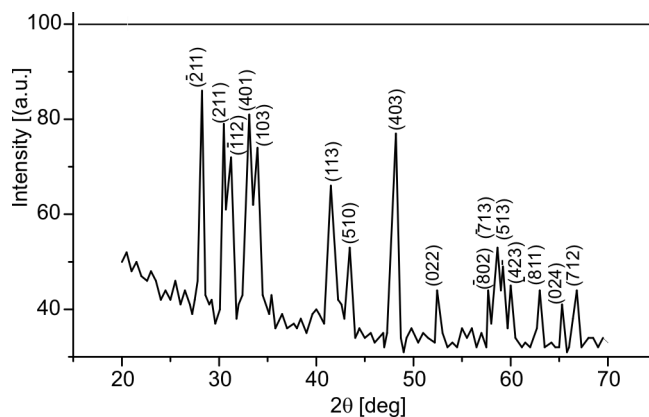


Fig. 1. Powder X-ray diffraction patterns showing indexed peaks which fairly coincide with those of a pure sample

The first derivative of X-band EPR absorption spectra recorded at RT, shown in Figs. 2a–c has a peak (with $g \approx 2.0$) at ca. 3300 G (quartets) along with intensive asymmetric lines. Therefore the data represents a superposition of two spectra corresponding to different surroundings of the copper ions. The characteristic spectrum may be explained by an isotropic spin-Hamiltonian, given by $\mathcal{H} = g\beta(B.S.) + A(I.S.)$, where notations have their usual meaning. For the fine structure spectrum, the $g_{\parallel}$ (g_z , quartet lines or hyperfine structures) and $g_{\perp}$ ($(g_x + g_y)/2$, intensive asymmetric lines) components of the g tensor correspond to the quartet lines and intensive asymmetric lines pertaining to this peak. The hyperfine spectra have not been resolved in these materials. Also on heavy doping, the characteristic peak in the higher field side gets broadened due to increased exchange interaction (dipole–dipole). As anticipated, analysis of the calculated g values ($g_{\parallel}$ and $g_{\perp}$) listed in Table 1 indicates that the splitting occurs in the octahedral symmetry, and the copper site attains Cu²⁺ (3d⁹, $S = 1/2$, and $I = 3/2$) state at the host site of Ti⁴⁺ ion [15, 16]. Furthermore, Cu²⁺ inclusion at the Ti⁴⁺ site modifies the crystal field around it into an orthorhombic one, which eventually attains axial symmetry on heavy doping [17]. Moreover, this acceptor doping activates a

charge compensation mechanism, dependent upon the evolution of oxygen vacancies in the lattice, producing electric dipoles consisting of a Cu^{2+} ion (effectively negative charge) and an oxygen vacancy site (effectively positive charge).

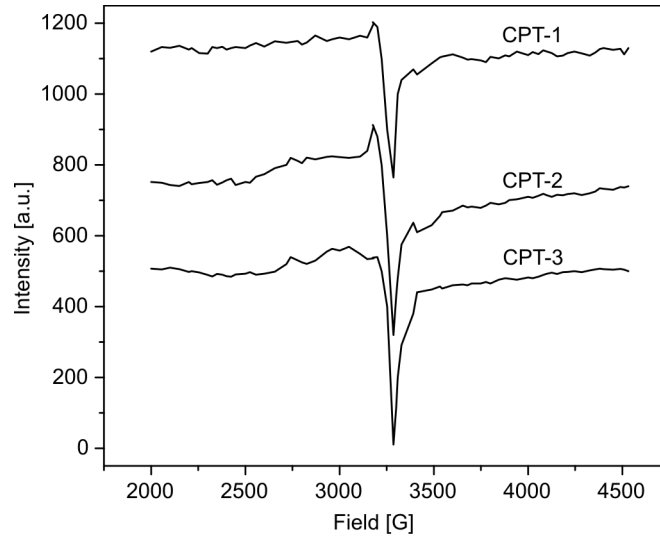


Fig. 2. First order derivative of EPR absorption spectra recorded at RT showing the characteristic Cu^{2+} peak (ca. 3300 G)

Table 1. Spin Hamiltonian parameters calculated for peak B using centre field at ca. 3400 G showing the presence of Cu^{2+} ions at Ti^{4+} sites

Sample	$g_{\parallel}$	$g_{\perp}$
CPT-1	2.3151	2.0278
CPT-2	2.3072	2.0165
CPT-3	2.3472	2.0929

The loss tangent ($\tan\delta$) and parallel capacitance (C_p) have been measured directly from the impedance analyzer. However, the relative permittivity (ϵ_r) has been calculated using relation $\epsilon_r = C_p / (\epsilon_0(a/t))$, where t is the thickness and a is the area of cross-section of the pellet. In Figure 3, room temperature $\tan\delta(\omega)$ plots are shown in the frequency range of 100–1000 kHz. These plots reveal that on copper doping ($x = 0.02, 0.2$), dielectric losses decrease primarily due to inhibition of domain wall motion [18] and then slightly increase for heavy doping ($x = 0.8$) of copper, due to a higher leakage current. Moreover, it can be seen from these plots that the loss tangents have very low frequency dispersion. The low value of dielectric loss at high frequency is the outcome of the low reactance offered by ceramic samples [19]. The trend of variation of dielec-

tric losses with frequency is a feature of dielectric losses due to dipole orientation and space charge polarization [20–22].

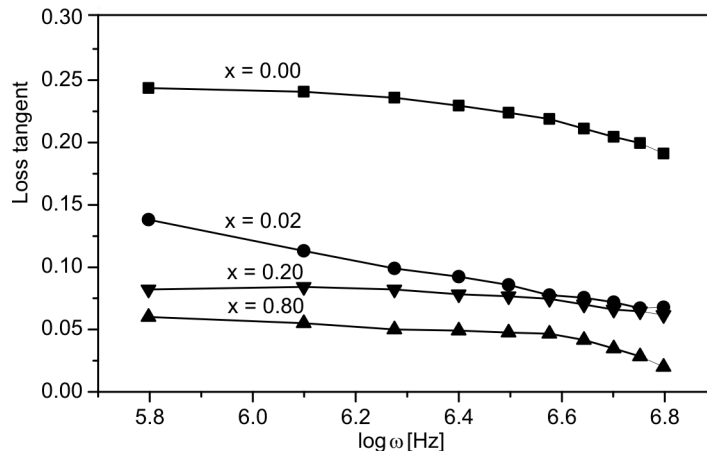


Fig. 3. Loss tangent in function of frequency for pure and doped derivatives of $(K_{1.85}Na_{0.15})Ti_4O_9$ ceramics

Figure 4 shows $\epsilon(\omega)$ plots at room temperature for various pure and copper doped derivatives. These plots show almost frequency-independent behaviour of the electric permittivity. On copper doping, relative permittivity first increases for $x = 0.02$ but decreases for heavy doping ($x = 0.2$ and 0.8).

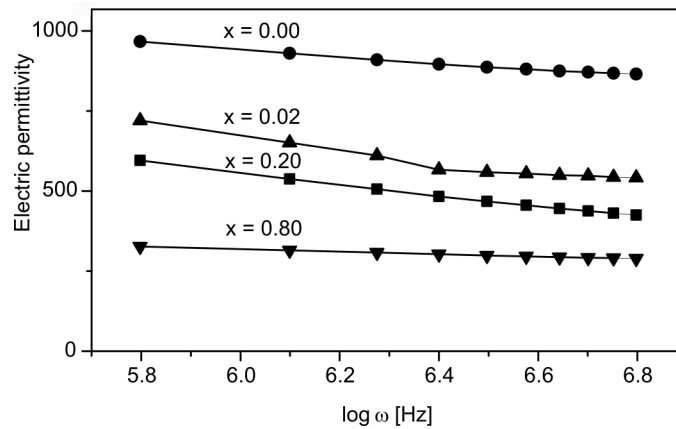


Fig. 4. Electric permittivity in function of frequency for pure and doped derivatives of $(K_{1.85}Na_{0.15})Ti_4O_9$ ceramics

Thus, for slight copper doping ($x = 0.02$), the increase in the values of the electric permittivity is accompanied by a simultaneous rapid decrease in $\tan\delta$ values, which may be ascribed to the pinning of domain wall motion due to oxygen vacancies. The

acceptor doping activates a charge compensation mechanism dependent upon the evolution of oxygen vacancies in the lattice, producing electric dipoles constituted by a Cu^{2+} ion (effectively negative charge) and an oxygen vacancy site (effectively positive charge). However, heavy doping increases leakage current due to the orientation of dipoles created by the acceptor doping.

4. Conclusions

Polycrystalline layered ceramics $(\text{K}_{1.85}\text{Na}_{0.15})\text{Ti}_4\text{O}_9\text{:}x\text{Cu}$ ($0 \leq x \leq 0.8$) have been synthesized via solid state reaction and characterized using electron paramagnetic resonance and dielectric spectroscopy. The EPR spectra show the characteristics of Cu^{2+} and confirm the occupancy of the Ti^{4+} sites by Cu^{2+} . Moreover, these peaks broaden due to increased exchange interaction for increased dopant densities. Copper doping is found to increase the electric permittivity along with a decrease in loss tangent in lightly doped compositions.

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