

Dielectric and spectroscopic analysis of cobalt doped potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) ceramics

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Pure and cobalt doped ($x = 0.05, 0.10, 0.15$ mol %) polycrystalline potassium hexatitanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) ceramics were synthesized using conventional solid state reaction route. XRD result confirmed the successful doping of Co in the $\text{K}_2\text{Ti}_6\text{O}_{13}$ matrix, as no additional peak was observed in the pattern. Dielectric permittivity was found to decrease with the increase in frequency while it increased with the increase in doping. The dielectric loss decreased with small doping whereas excessive doping caused its augmentation. Ac conductivity (σ_{ac}) has also been studied as a function of frequency at room temperature for all the samples. Scanning Electron Microscope (SEM) inspection of the synthesized samples showed the formation of rod like shapes. FTIR analysis was carried out to identify the chemical bonds present in the system.

Keywords: *ceramics; X-ray diffraction; dielectric properties; infrared spectroscopy*

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1. Introduction

Titanates having chemical formula $\text{M}_2\text{O} \cdot n \text{TiO}_2$ (where $\text{M} = \text{Li}, \text{Na}, \text{K}$ etc. and $n = 2 - 8$) have been a subject of intensive research during the last few decades due to their technological applications. These titanates have tunnel or layered crystal structures constructed of TiO_6 octahedra sharing edges with interlaying cations. Among the alkali titanates, potassium titanates such as $\text{K}_2\text{Ti}_2\text{O}_5$, $\text{K}_2\text{Ti}_4\text{O}_9$, and $\text{K}_2\text{Ti}_6\text{O}_{13}$ have been attractive due to their properties such as high thermal durability, chemical resistivity, dispersibility, and various applications e.g. heavy metal ion removal, as ion exchangers and as photocatalytic materials [1–5]. The structures of $\text{K}_2\text{Ti}_2\text{O}_5$ and $\text{K}_2\text{Ti}_4\text{O}_9$ consist of layered sheets made of TiO_5 pentahedra or TiO_6 octahedra linked with the K atoms [6, 7]. This tunnel structure has also attracted additional interest in its application as photocatalytic materials. Alkali-metal hexatitanate is one of the semiconducting

photocatalyst which has the capability of invoking a photocatalytic decomposition of water to produce H_2 and O_2 [8–11]. Inoue et al. has reported that alkali-metal hexatitanate when incorporated with noble metal oxides exhibited noticeable photocatalytic activity in the decomposition of water [8].

In addition, other interesting technological applications such as ceramic capacitors, dielectric sensors, biosensors, have also been reported for the $\text{M}_2\text{Ti}_n\text{O}_{2n+1}$ ($\text{M} = \text{Na}, \text{K}$) [12, 13]. $\text{K}_2\text{Ti}_6\text{O}_{13}$ are used as reinforcements for metals, such as copper to improve their wear resistance [14], plastics to improve their mechanical and dielectric properties [15] and automotive brake lining pads as a substitute for carcinogenic asbestos [16]. Luo et al. reported the mechanical and thermal insulating properties of resin-derived carbon foams reinforced by $\text{K}_2\text{Ti}_6\text{O}_{13}$ whiskers [17]. Physicochemical properties of ambient-dried SiO_2 aerogels with $\text{K}_2\text{Ti}_6\text{O}_{13}$ whisker have been investigated by Zhang et al. [18]. In general, alkali titanates are used as metal ion absorbent [19] and in reinforced plastics [20]. Cation exchange property has been ex-

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exploited to protect environment from lethal radiation of highly radioactive liquid wastes [21]. Furthermore, nanosize titanates have plenty of important applications in the field of photocatalysis, gas-sensing, high-energy cells, photo-voltaic cells, and environment purification [22, 23]. Recently, comparative study of pure potassium hexatitanate prepared by sol-gel and solid state reaction method has been reported by our research group [24]. Properties of such materials may also be modified by doping aliovalent transition metal ions. Recently dielectric and electrical properties of Cu and Ni doped $K_2Ti_6O_{13}$ have been reported by our own research group [25–27]. It has been observed by our research group that on doping $K_2Ti_6O_{13}$ ceramics with divalent Cu^{2+} , the charge compensation process may lead to creation of oxygen vacancies (V_O), which in turn are the dominant charge carriers in ceramic oxides, modifying the ligand symmetry around the dopant and eventually improving the dielectric performance of the ceramic system. This paper reports the synthesis, dielectric and spectroscopic studies of Co doped $K_2Ti_6O_{13}$ ceramics prepared by solid state reaction route.

2. Experimental

$K_2Ti_6O_{13}$ (PTO) ceramics was prepared by conventional solid-state reaction route taking stoichiometric amounts of the grinded AR grade K_2CO_3 and TiO_2 powders (purity 99.9 %), under acetone and calcined at 1000 °C for 24 h followed by furnace cooling. To prepare cobalt doped ($x = 0.0, 0.05, 0.10, 0.15$) specimens, the desired amount of Co_3O_4 powder (purity 99.9 %; AR grade) was added to the mixture of potassium carbonate (K_2CO_3) and titanium dioxide (TiO_2) and the mass so obtained was recycled through the above process. The obtained powder was pressed into pellets of 13 mm diameter and 1.00 mm thickness, which were further sintered at 1000 °C for 1 hour. X-ray diffraction (XRD) spectrum on a X-ray powder diffractometer using Cu- $K\alpha$ radiation ($\lambda = 0.15406$ nm) in 2θ range from 10° to 70° with scan rate of 2°/min was recorded. Scanning electron microscopy (SEM) operating at 5 kV was performed on a NOVA NANO SEM-A to investigate

the surface structure and morphology of the materials. The dielectric measurements were carried out after applying the silver paste on the flat faces of the pellets, in the frequency range of 100 – 1000 kHz using LCR HI-Tester (HIOKI 3532-50). The loss tangent ($\tan\delta$) and parallel capacitance (C_p) of the pellet were measured directly with the impedance analyser. The value of dielectric permittivity (ϵ_r) was calculated using the formula:

$$\epsilon_r = \frac{C_p \times d}{\epsilon_0 \times A} \quad (1)$$

where ϵ_0 is the permittivity of free space, d is the pellet thickness, A is the cross-sectional area of the flat surface of the pellet and C_p is the capacitance of the specimen in Farad (F).

The ac conductivity of the samples was determined using the relation:

$$\sigma_{ac} = \epsilon_r \epsilon_0 \omega \tan \delta \quad (2)$$

where ω is the angular frequency and $\tan\delta$ denotes the dielectric loss tangent.

Fourier transform infrared spectroscopy (FTIR) spectra for all specimens were recorded on Perkin Elmer Spectrum RX1 spectrophotometer. The powder samples were pressed together with KBr to form the pellets and measurements were taken in a wavelength range of 400 – 4000 cm^{-1} with a resolution of 4 cm^{-1} .

3. Results and discussion

3.1. Structural study

Fig. 1 shows the XRD patterns recorded at room temperature (RT) for pure and cobalt doped $K_2Ti_6O_{13}$ ceramic samples. Peak positions of all samples exhibit the monoclinic structure of $K_2Ti_6O_{13}$, very well matched with peak positions by ICDS card No. 74-274. Further, no other impurity peak was observed in the XRD pattern showing the single phase sample formation and successful Co doping in $K_2Ti_6O_{13}$ matrix. Lattice parameters were calculated using the following equation:

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2hl \cos \beta}{ac \sin^2 \beta} \quad (3)$$

with the help of XRD data and found in agreement with the earlier reported data [25–27]. The ionic radius of Co^{2+} is 0.74 Å whereas that of Ti^{4+} is 0.68 Å. The Co^{2+} ions substitute the Ti^{4+} ions in the crystal due to comparable ionic radiuses. However, the increase in the lattice parameters may be due to the bigger ionic radius of Co ions. Hence, one can observe that increasing doping percentage consistently increases the unit cell volume as shown in Table 1.

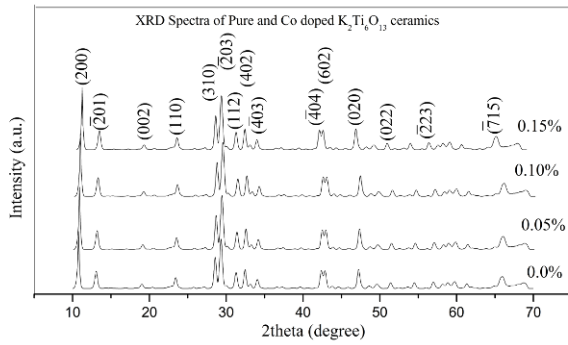


Fig. 1. XRD spectra of pure and Co doped $K_2Ti_6O_{13}$.

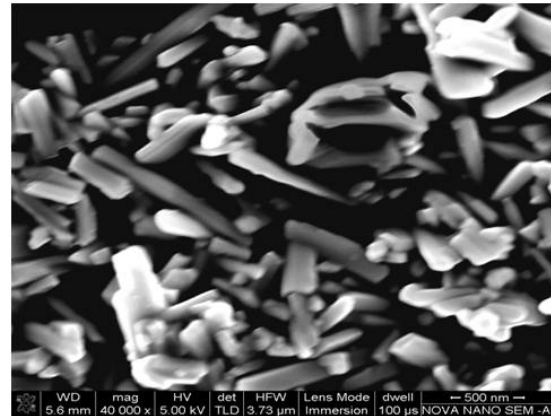
Table 1. Lattice parameters of pure and cobalt doped potassium hexatitanate.

Co-doping	Lattice Parameters				Unit cell volume(Å ³)
	a(Å)	b(Å)	c(Å)	β (degree)	
x = 0.00	15.570	3.806	9.104	99.568	531.90
x = 0.05	15.584	3.834	9.116	99.820	536.69
x = 0.10	15.625	3.834	9.128	99.832	538.74
x = 0.15	15.647	3.835	9.159	99.854	541.48

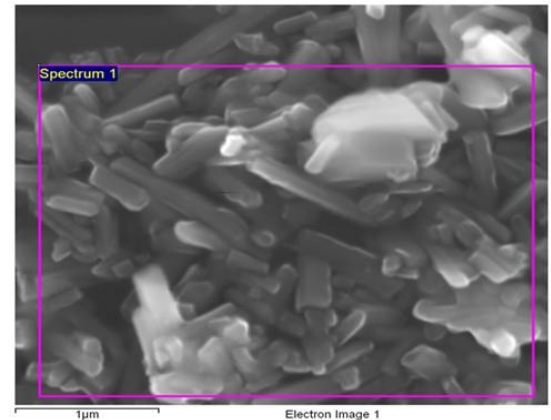
3.2. SEM analysis

The morphology of synthesised sample was observed with the help of scanning electron microscope (SEM) analysis. Fig. 2 reveals rod-shaped particles with diameter between 0.1 and 0.2 μm and length varying from 0.5 μm to several micrometers. Figs. 2(a) and 2(b) present the same sample of cobalt doped potassium hexatitanate ($x = 0.15$) but

the images were received at different SEM modes. SEM image of the pure $K_2Ti_6O_{13}$ ceramic specimen is much more uniform and fine prepared by solid state reaction, reported earlier by our own research group [26], showing microtubular particles with average cross sectional width of approximately 1 μm and length 5 μm stacked over one another. It is observed that as cobalt doping level increases, the whisker like structure starts forming agglomerates.



(a)



(b)

Fig. 2. Photographs of Co doped $K_2Ti_6O_{13}$ sample obtained at different SEM modes.

3.3. Dielectric properties

Fig. 3(a) shows the frequency response of dielectric constant, recorded at room temperature (RT) in the frequency range of 100 – 1000 kHz for $x = 0.0, 0.05, 0.10$ and 0.15 , respectively. The

large value of dielectric constant at low frequency in Fig. 3(a) is attributed to the presence of all types of polarization i.e. $P_{total} = P_e + P_i + P_d + P_{sc}$ where the subscripts indicate the electronic, ionic, dipolar and space charge contributions, respectively [28]. The figure also shows a consistent decrease in the permittivity with increasing frequency because at higher frequencies various polarisation processes are slowed down. The dielectric permittivity decreases for $x = 0.05\%$, but it shows an upsurge for $x = 0.10$ and 0.15% . The increase in permittivity with the rise in cobalt doping may be due to the growth in the number of dipoles. Almost similar behaviour for dielectric constant was also found in our previous study reported earlier [27].

Fig. 3(b) shows the room temperature frequency response of $\tan\delta$ in the frequency range of 100 – 1000 kHz for all specimens. The loss tangent initially decreases for $x = 0.05\%$, but afterwards increases for moderate and heavy doping concentrations due to inhibition of domain wall motion [29]. The increasing trend of $\tan\delta$ is due to space charges produced after all doping [30]. Also $\tan\delta$ decreases with a rise in frequency, proving that at higher frequency, ceramic specimens offer low reactance to the ac signal and hence minimise the conduction losses [31]. Therefore the magnitude of $\tan\delta$ decreases at higher frequency. These types of variations in the dielectric losses are characteristic of the dipole mechanism and electric conduction [31, 32]. Oxygen vacancies produced due to the substitution of Co ions at the host Ti sites, as a result of charge compensating mechanism, cause deformation of the surrounding area and modification of the local fields.

3.4. Electrical investigations

Fig. 3(c) shows variation of ac conductivity with frequency in the range of 100 – 1000 kHz at room temperature for all specimens. It shows a consistent increase with frequency for all samples due to enhancement of electron hopping frequency. It can also be observed in Fig. 3(c) that ac conductivity increases up to $x = 0.10\%$ due to the fact that the increase in dopant concentration raises the number of the oxygen vacancies pro-

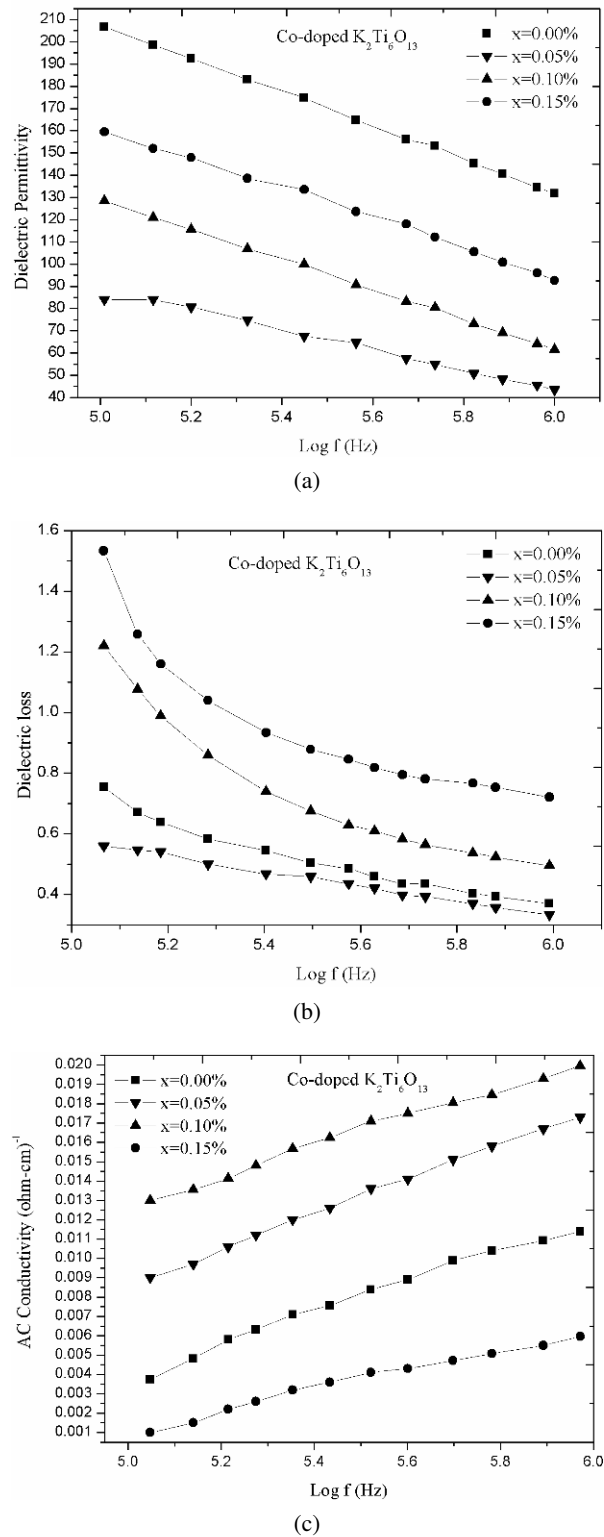


Fig. 3. (a): Variation of dielectric permittivity with frequency at RT; (b): Variation of dielectric loss with frequency at RT; (c): Variation of a.c. conductivity with frequency at RT.

duced due to charge compensation, which results in an increase of free electron density and conductivity. The ac conductivity decreases for heavy doping ($x = 0.15\%$) due to shrinkage of the tunnel space on dopant entry in the lattice, resulting in the hindrance suppressing ionic conduction and also due to the trapping of conduction electrons by Co^{2+} from nearby oxygen ions.

3.5. FTIR analysis

FTIR spectra for pure and Co doped potassium hexatitanate have been studied in the region of $400 - 4000\text{ cm}^{-1}$ at room temperature (RT) and depicted in Fig. 4. It can be observed from the figure that all samples (pure and doped) exhibit quite similar peaks. All peaks obtained for potassium hexatitanate samples agree well with the previously reported data [33, 34]. Absorption bands around $470 - 510\text{ cm}^{-1}$ and $720 - 770\text{ cm}^{-1}$ for all samples are attributed to O–Ti–O bending vibrations and Ti–O stretching of TiO_6 octahedral groups [35]. Moreover, FTIR spectra show a peak near about 940 cm^{-1} for all the prepared samples, which is expected for Ti=O group [36]. Pure and doped potassium hexatitanates prepared in this work using solid state reaction route contain only potassium hexatitanate as detectable phase and the peaks observed at 476 cm^{-1} , 502 cm^{-1} , 721 cm^{-1} , 767 cm^{-1} , 940 cm^{-1} . These peaks are quite similar to the ones reported by Bamberger [36] using Raman spectroscopy for potassium hexatitanate.

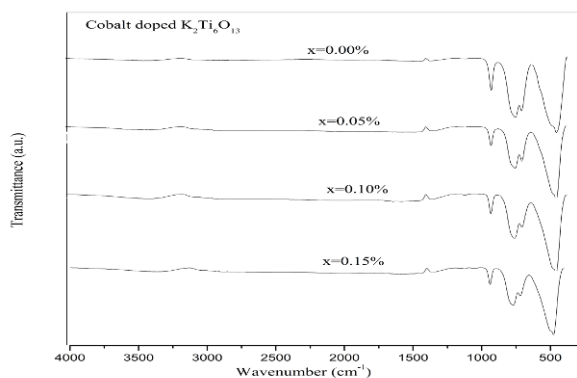


Fig. 4. FTIR spectra of pure and Co doped $K_2Ti_6O_{13}$.

4. Conclusions

Cobalt doped $K_2Ti_6O_{13}$ ceramics were prepared by high temperature solid state reaction route. Room temperature XRD pattern revealed the confirmation of single phase formation in the sample. Morphology of the potassium hexatitanate, investigated by SEM, revealed microrods. On cobalt doping, the losses primarily decreased due to inhibition of domain wall motion and thereafter increased due to space charge polarisation. Dielectric permittivity decreased with frequency followed by an increase for enhanced doping, attributed to growing number of dipoles. Ac conductivity initially increased with dopant concentration but for heavy doping it decreased due to shrinkage of tunnel space on the dopant entry. Through FTIR analysis it was observed that doping concentration of cobalt did not have significant influence on the vibrational characteristics of the chemical bonds in these samples as all of the four potassium hexatitanate samples exhibited similar IR bands.

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