CHAPTER 6
EPR, FTIR and Thermal Analysis of Pure and Doped Potassium Hexa-
titanate ($K_2Ti_6O_{13}$) Ceramics

6.1. Introduction

A series of titanates having chemical formula $M_2O.n TiO_2$ (where $M$ = Li, Na, K etc. and $n$ = 2-8) are well known. All of them are constructed by $TiO_6$ octahedra sharing edges with interlaying cations, have been synthesised and characterized using different routes [1-2]. Alkali metal titanates have been used in ion exchange processes, for ceramic capacitors, as dielectric resonators in microwave oscillators band pass [3], as a reinforcing agent of plastic, as adiabatic materials [4] and as an oxygen electrode for potentiometric gas sensors [5-7]. Potassium di-, tetra-, and hexa-titanate have been widely used for artificial materials [8] due to their specific structure and properties. In addition to bulk material titanate nanomaterials have various important applications in the field of gas sensor, high energy cell, photovoltaic cells and as photocatalyst [9-10]. Recently in our previous report our group has investigated the comparative structural, optical and photocatalytic property of the potassium hexa-titante ($K_2Ti_6O_{13}$) prepared by sol-gel and solid state reaction route [11]. Furthermore, Inoue et al. has reported that alkali-metal hexa-titanate, when incorporated with noble metal oxides exhibited noticeable photocatalytic activity in the decomposition of water [12]. The presence of these tunnels in the structure has the advantage of being able to accommodate the active phase, which acts as a promoter [13], thus enhancing further the catalytic activity. Preparation and photoelectrochemical performance of potassium hexa-titanate nanofilms were also reported by Qian Qing-hua et al. [14].

Moreover, detailed analysis of the role of functional centres in the $K_2Ti_6O_{13}$ ceramic system is reported by our research group [15]. The 3d ions are often readily incorporated in
the perovskite structure where they act as acceptors. Electron paramagnetic resonance (EPR) spectroscopy can often determine the configuration of the incorporated impurity and yields local structure information. It has been shown by Watkins [16], that impurity ions substituting for ions of different valency attract charge compensating defects in the lattice. But, majority of EPR studies on TiO$_2$ have indicated that there is no evidence for local charge compensation when divalent or trivalent transition metal ions replace the tetravalent Ti-ion [17]. However, on doping K$_2$Ti$_6$O$_{13}$ with acceptor-type, predominantly, charge compensation process evolves oxygen vacancies ($V_o^{**}$). Detailed EPR studies have been performed on the 3d impurities, Cu [18], Mn [19] in the potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) and have shown that substitution does occur at the Ti-site.

Preparation and some properties of organically modified layered alkali titanates with alkylmethoxysilanes are studied by Yusuke et al. [20]. J. T. Luxon et al. [21] reported the effect of particle size and shape on the infrared absorption spectra of barium titanate and strontium titanate powders. The effect of temperature on thermal and spectroscopic properties of pure potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) has also been reported by Szilvia et al. [22]. The influence of temperature on the structural behaviour is of great importance since the structural properties of titanates and their derivatives can have a direct influence on their potential use and practical performance. Recently, B. C. Viana et al. [23] have reported vibrational spectroscopic analysis for alkali metal titanate nanotubes. R. Yahya et al. [24] have investigated the structural studies of potassium hexa-titanates prepared under hydrothermal and solid state methods.

The spectroscopic and thermal studies of doped (with Ni and Co dopant) potassium hexa-titanate have not been explored yet. Therefore, in this study doped potassium hexa-titanates are characterized by EPR (Electron Paramagnetic Resonance), FTIR (Fourier Transform Infra Red), and DSC (Differential Scanning Calorimetry) techniques.
6.2. Experimental Procedure

The usual first derivative of X-band (9.58 GHz) EPR absorption spectra were recorded on a Bruker EMX X-band EPR spectrometer. The high frequency modulation field amplitude ranged typically from 0.005 to 0.5mT with rectangular TE102 cavity (unloaded Q ~7000) at 100 kHz field modulation. Moreover, samples were kept in ~ 4mm quartz tube placed at the centre of resonant cavity. Fourier transform infrared spectroscopy (FTIR) spectra for all specimens were recorded on Perkin Elmer Spectrum RX1 spectrophotometer. 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\(^{-1}\). DSC measurements were performed in an MOM Q-1500 D instrument. Samples were heated from 30\(^0\)C up to 900\(^0\)C at a rate of 5\(^0\)C min\(^{-1}\).

6.3. Results and Discussion

6.3.1. EPR Investigation

Figure 6.1 illustrates first derivatives of X-band (9.58 GHz) EPR absorption spectra for Ni doped K\(_2\)Ti\(_6\)O\(_{13}\) samples at RT. The shape of the EPR spectra is the characteristic of axially distorted octahedral complexes. The g values (given in table 6.1) are determined by the following relation:

\[
g = \frac{h \nu}{\beta B_0}\quad [6.1]
\]

Where \(h\) is the Planck’s constant, \(\beta\) is Bohr magneton, \(\nu\) is the resonance frequency of the sample cavity and \(B_0\) is the centre of the resonance absorption signal.
Table 6.1: Spin Hamiltonian Parameters for Ni doped potassium hexa-titanates calculated from X-band EPR spectra recorded at RT

<table>
<thead>
<tr>
<th>Ni Doped K₂Ti₆O₁₃ (Fe–V⁰⁺)</th>
<th>Isolated Ni Species</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>g values</td>
</tr>
<tr>
<td>x=0.05</td>
<td>7.614 5.356 4.529</td>
</tr>
<tr>
<td>x=0.10</td>
<td>7.614 5.356 4.529</td>
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<tr>
<td>x=0.15</td>
<td>7.614 5.356 4.529</td>
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The signals at ~ 900 G (g = 7.614), ~1279 G (g = 5.356), and ~1513 G (g = 4.529) show the presence of axial components of (Fe–V⁰⁺) defect associate dipoles in the orthorhombic symmetry, formed during high temperature calcination after iron-oxygen vacancy defect association, because Fe ions present as an intrinsic impurity in the starting materials [15]. The spin Hamiltonian for this centre is given [25]

\[ H = \beta B_0 g \cdot S + D \left( S_x^2 - \frac{1}{3} S (S+1) \right) + E \left( S_x^2 - S_y^2 \right) \]  

[6.2]

Where S is the electron spin, D and E represent axial and rhombic fine structure terms respectively.

In figure 6.1, we can also observe two spectral portions at ~ 3300 G region: one above the base line attributed to g∥ spectra and the other one just ahead of it but below base line attributed to g⊥ of the absorption signal, g∥ (g⊥) is the g value parallel (perpendicular) to the symmetry axis. This signal corresponds to Ni²⁺-V⁰⁺ defect associate dipole arises due Ni doping [26].
Figure 6.1: EPR spectra of $K_2Ti_{6-x}Ni_xO_{13}$, (a): $x = 0.05\%$, (b): $x = 0.10\%$, (c): $x = 0.15\%$

Evidently, we can notice fine structure spectrum corresponding to locally distorted environment of nickel ion, substituting Ti$^{4+}$ sites. Furthermore, the hyperfine signals with $g_\parallel \sim 2.05$ (3200-3400 G) and its similar asymmetric counter part with $g_\perp \sim 1.95$ (3400-3500 G) correspond to nickel at Ti$^{4+}$ site having distorted local surrounding of Ni$^{2+}$-$V_o^{**}$.

Analysis of the calculated $g$ values ($g_\parallel$ & $g_\perp$) listed in table 6.1 indicates that, probably, the splitting occurs in the octahedral symmetry and nickel site attains at Ti$^{4+}$ host-site [27]. Moreover, nickel ion inclusion at Ti$^{4+}$ site modifies the crystal field around it into orthorhombic which finally attains axial symmetry i.e. $g_x = g_y = g_\perp$ and $g_z = g_\parallel$. Since $g_\perp < 2.0$ for the perpendicular orientation of the magnetic field illustrate the deformation occurs only in $z$-direction parallel to the field [27], this deformation may be created by one or two oxygen vacancies ($V_o^{**}$). The acceptor doping activates charge compensation mechanism consequent upon the evaluation of oxygen vacancies in the lattice producing defect associate dipoles constituted by a nickel ion (effectively negative charge) and an oxygen vacancy site
(effectively positive charge). The following equations [28] explicitly show the formation of oxygen vacancies due to doping:

\[ \text{NiO} \quad \leftrightarrow \quad \text{Ni}_{\text{Ti}} + V_0^{**} + O_o \]

Overall charge compensation is accomplished by following relations:

\[ O^{2-} \quad \leftrightarrow \quad \frac{1}{2} O_2(g) + 2 e^- + V_0^{**} \]
\[ 2O_o + \text{Ti}_{\text{Ti}} \quad \leftrightarrow \quad O_2(g) + \text{Ti}^{****} + 4e^- \]

The introduction of \( V_0^{**} \) by means of accepter doping also leads to contract the intratunnel space available for ionic conduction between adjacent Ti-Ti chains due to bigger ionic size of dopant (Ni ion) than Ti\(^{4+}\) as observed in XRD data (given in chapter 4).

**6.3.2. FTIR Analysis**

In order to study the vibrational properties of titanates we first review the Group Theory Analysis (GTA) of vibrations for \( K_2\text{Ti}_6\text{O}_{13} \) bulk structures. \( K_2\text{Ti}_6\text{O}_{13} \) at room temperature has a tunnel-like structure in a monoclinic symmetry (space group C\(_{2/m}\)) with two formulas per unit cell (\( Z = 2 \)) [29]. Group theory predicts that \( K_2\text{Ti}_6\text{O}_{13} \) should exhibit 60 vibrational modes [30] distributed as follows:

\[ 12 A_g + 18 A_u + 12 B_g + 18 B_u \]

Where \( A_g (A_u) \) and \( B_g (B_u) \) are Raman (IR) active representations.

Before analysing the present vibrational study, we should mention that these materials have a tunnel-like structure and it is not appropriate to apply standard factor group analysis, because there is no radial symmetry. Therefore, the analysis will consider the atomic vibrations without specifying the mode symmetry.

FTIR spectra for pure, Ni and Co doped potassium hexa-titanate (\( K_2\text{Ti}_6\text{O}_{13} \)) have been studied in the region of 400-4000 cm\(^{-1}\) at room temperature (RT) and depicted in the figure 6.2. It has been observed from these figures that all samples (pure and doped) exhibited quite similar peaks confirming the formation of pure phase of cobalt and nickel doped potassium...
hexa-titanate ($K_2Ti_6O_{13}$) samples. All peaks obtained for prepared samples agree well with the previously reported data [31, 32]. Absorption bands around 476 cm$^{-1}$ and 721 cm$^{-1}$ for all samples are attributed to O-Ti-O bending vibrations and Ti-O stretching of TiO$_6$ octahedral groups [24]. Pure and doped potassium hexa-titanates prepared in this work using solid state reaction route contain only potassium hexa-titanate as detectable phase with no other significant impurity peak is observed (also confirmed from XRD pattern given in chapter 4 and 5). The peaks were also observed at 476 cm$^{-1}$, 502 cm$^{-1}$, 721 cm$^{-1}$, 767 cm$^{-1}$, 936 cm$^{-1}$. These peaks are quite similar to those reported by Bamberger [33] using Raman spectroscopy for potassium hexa-titanate. For both FT-IR and Raman, the most affected mode is that related to Ti–O bond whose oxygen is not shared among the TiO$_6$ units (at the corner of the TiO$_6$ octahedral slab).

![FTIR spectra of pure and doped potassium hexa-titanate](image)

**Figure 6.2:** FTIR spectra of pure and doped potassium hexa-titanate

It has been observed that potassium titanate has complex structure of Ti-O-Ti chains and sheets largely in monoclinic structure. So, a large number of Raman active frequencies are to be expected in the spectra. In most cases titanium has co-ordination number of six,
surrounded with oxygen atoms in octahedral configuration. Neither Raman nor FTIR spectra of these compounds show a Ti = O group, which would be expected to have a vibrational frequency near 980 cm$^{-1}$ [33].

6.3.3. DSC Analysis

Thermal analysis technique is widely used to study the physical changes occurring in a material when it is subjected to a varying temperature programme. So when the material is exposed to high temperature, the structure and atomic configuration will change. As a result of these changes, some exothermic (heat evolution) or endothermic (heat absorption) peaks appear in the thermogram. Thermogravimetry (TG), Differential Thermal Analysis (DTA), and Differential Scanning Calorimetry are the three major thermal analysis techniques employed nowadays. It seems that the scope of these techniques is extremely broad and includes studies of thermal stability, decomposition, solid state transition, melting, purity, crystallallinity and ageing behaviour.

Differential Scanning Calorimetry (DSC) is a thermal technique in which differences in heat flow into a substance and a reference material are measured as a function of sample temperature while the two are subjected to a controlled temperature programme. This method has application in quality control and research uses in industrial products such as polymers, pharmaceuticals, metals, dielectric materials etc.

Figure 6.3 (a) shows the DSC spectra for pure potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$), due to reaction between potassium carbonate (K$_2$CO$_3$) and titanium dioxide (TiO$_2$), a small exothermic peak is observed at T $\sim$ 300$^0$C, consistent with the previously reported data [34]. The small peaks on the DSC curve at $\sim$ 400$^0$C for cobalt doped, x = 0.15 mol % (figure 6.3-d) and at $\sim$ 250$^0$C for Ni doped, x = 0.10 mol % (figure 6.4-c) are observed, which are in close agreement with that of the permittivity versus the temperature plots (chapter 4 and 5),
though no peak in the remaining compositions, indicating that the intensities of reaction and phase change are weak.

Figure 6.3 (a-d): DSC curve for pure and Co doped potassium hexa-titanates
Figure 6.4 (a-c): DSC curves for Ni doped potassium hexa-titanates
6.4. Conclusions

EPR-spectroscopy of Ni doped potassium hexa-titanate, achieved at room temperature and at X-band frequencies ($\nu \sim 9.58$ GHz), shows partial substitutions at Ti$^{4+}$ lattice lattice sites in the TiO$_6$ octahedra with dominating Ni$^{2+}$ substitution. EPR-signals identified the presence of intrinsic (Fe-$V_0^{**}$) and extrinsic (Ni$^{2+}$-$V_0^{**}$) defect associate dipoles. FTIR spectra recorded at room temperature for pure and doped potassium hexa-titanate ceramics, revealed no significant influence on the vibrational characteristics of the chemical bonds in the prepared samples as all of them exhibited similar IR bands. DSC spectra show the small exothermic peaks.
References


