CHAPTER 3

Comparative Study of Potassium Hexa-titanate (K$_2$Ti$_6$O$_{13}$) Whiskers

Prepared by Sol-Gel and Solid State Reaction Routes

3.1. Introduction

Anderson–Wadsley type alkali titanates, represented by M$_2$O$_n$TiO$_2$ (M = Li, Na, K), with exclusive layered (3≤n≤5) and tunnel (6≤n≤8) crystal structures have been synthesised and characterized using different routes by many workers. Because of their excellent chemical and mechanical properties they have been used in a wide range of applications in industry as, ion–exchange materials, reinforcements, heat insulators, friction materials, catalysts, photocatalysts and a substitute of asbestos [1-5]. Till now, large numbers of not only fundamental studies on the structure, electrical, optical, mechanical, and physicochemical properties but also application-oriented research and development have been extensively carried out on such materials.

Among the alkali titanates, potassium titanates (K$_2$O$_n$TiO$_2$), the layered K$_2$Ti$_2$O$_5$ and K$_2$Ti$_4$O$_9$ have specific photoluminescence [6] and photovoltaic activities for H$_2$ evolution by the water cleavage reaction even without Pt co-catalysts [7] and have several benefits compared with other ceramic whiskers. One of the most desirable feature is the low cost of the whisker itself, which is one of the critical factor for commercial application of composites [8].

The potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$, n = 6) with tunnel structure has attracted growing interest due to its potential economic importance. This relatively cheap fibrous material has high thermal durability, chemical resistivity, and dispersibility and has found its
use as reinforcing material, heat insulating paints, automotive brake linings and photocatalytic materials [5, 9-17]. In addition to other interesting technological applications such as ceramic capacitors, dielectric sensors, biosensors, have been also reported for the A$_2$Ti$_n$O$_{2n+1}$ (A = Na, K) [22-23].

Nanotubes and nanowires have greatly attracted the attention of scientific community due to their wide applications on electronic, optical, magnetic, mechanical and catalytic properties different from the bulk materials. Titanate nanotubes and nanowires are particularly interested due to their large specific surface that may enhance the photocatalytic activity such as environmental purifications, decomposition of carbonic acid gas and generation of hydrogen gas [24, 25]. Moreover, alkali titanates have also been successfully evaluated in the degradation of chloroform [26], synthetic dyes and methyl orange, under UV light irradiation [27, 28]. Haiyan Song et al. have reported photocatalytic activity of alkali titanate nanomaterials A$_2$Ti$_n$O$_{2n+1}$ (A = Li, Na and K) [21]. Also, alkali hexa-titanates with a tunnel structure are suggested to be good photocatalysts, for the degradation of toxic substances and decomposition of pure water and for oxygen electrodes in potentiometric sensors for O$_2$ and CO$_2$ [18, 19]. Recently, sol–gel silver hexa-titanates have been reported as photocatalysts for the 4-chlorophenol decomposition [20]. Preparation and photoelectrochemical performance of potassium hexa-titanate nanofilms were also investigated by Qian Qing-hua et al. [29].

K$_2$Ti$_6$O$_{13}$ traditionally prepared by solid state reaction method has been reported by various researchers [30]. The resulting powders prepared by this method usually have serious agglomeration and inhomogeneous particle size as a result of high temperature treatment. Leticia M. et al. have reported [31] that sol–gel process has greater control over homogeneity, specific surface area, energy band gap (E$_g$), porosity, etc. compared to the solid state reaction method. This chapter deals the comparative studies of structural, dielectric, electrical, optical
and photocatalytic properties of the specimens prepared by sol-gel (PSG) and solid state reaction (PSS) methods.

3.2. Experimental

3.2.1. Synthesis

In sol-gel process, $K_2Ti_6O_{13}$ was prepared using titanium isopropoxide, potassium acetate, ethanol and distilled water. Adequate stoichiometric amount of titanium isopropoxide to produce 10 g of $K_2Ti_6O_{13}$ was placed into a 500 mL flask. Potassium acetate was dissolved in 20 ml of distilled water and ethanol, and then added drop by drop into the flask containing the titanium isopropoxide. The mixture was heated under reflux at 70°C for 72 hours under constant stirring. Basic pH of the solution was set and controlled by using small amount of ammonium hydroxide. After heating, the solution was aged at 25°C for 24 hours until the gel formation. The gel was heat treated at a temperature, 800°C for 8 hours. The obtained powder was pressed into pellets of 13 mm diameter and 1.95 mm thickness, which were further sintered at 800°C for 1 hour.

In solid state reaction method, stoichiometric amounts of $K_2CO_3$ and $TiO_2$ powders were mixed under acetone in a mortar and grinded for 1 hour. After mixing, the powder was calcined at 1000°C for 24 hours. The grinded powder was also compacted into similar pellets as sample PSG and further sintered at 1000°C for 1 hour.

3.2.2. Characterization

Structural properties of the samples (PSG and PSS) were determined by X-ray diffraction (XRD) using Cu-Kα radiations ($\lambda = 0.15406$ nm) in 20 range from 10° to 70° with scan rate of 2°/min at room temperature (RT). Lattice parameters were calculated using relation 2.1 given in chapter 2. SEM analysis was carried out to examine the crystal morphology of the sample using HITACHI SU-70 instrument, operating at 15 kV. The high
resolution tunneling electron microscopy (HRTEM) observations were performed using instrument HITACHI 2200F, operated at 300 kV. The electrical measurements were carried out after applying the silver paste on the flat faces of the pellets, in the frequency range 75 kHz to 7 MHz using LCR HI-Tester (HIOKI 3532-50). The value of dielectric constant and ac conductivity ($\sigma_{ac}$) were calculated using relations 2.1 and 2.3 given in chapter 2.

UV–Visible absorption spectra for the samples (PSG and PSS) have been recorded using Perkin Elmer Lambda 35 UV-Visible spectrometer. The energy band gap was calculated using Tauc relationship $\alpha(h\nu) = A(h\nu-Eg)^n$. For potassium hexa-titanate, the absorption coefficient $\alpha$ is known to obey the above equation with $n=1/2$. The photocatalytic tests were carried out using 250 mL of a 30 ppm aqueous solution of methyl orange under irradiation of UV light. 200 mg K$_2$Ti$_6$O$_{13}$ (PSG and PSS) were weighed and used as photocatalysts. The photocatalyst and methyl orange were placed in the glass beaker containing distilled water and was kept in suspension by stirring continuously with a magnetic stirrer under the irradiation of UV light. The characteristic absorption of methyl orange at $\lambda = 460$ nm was chosen to monitor the photocatalytic degradation process on UV-Visible spectrometer. The change of absorbance intensity with UV irradiation time was monitored.

3.3. Results and Discussion

3.3.1. Structural Properties

X-ray powder diffraction is an important technique for characterizing bulk as well as nanomaterials. Figure 3.1 shows typical XRD patterns of potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) prepared by sol-gel (PSG) and solid state method (PSS), recorded at RT. The peak positions of each sample exhibit the monoclinic structure of K$_2$Ti$_6$O$_{13}$, which were confirmed from ICDS card no. 74-0275, no other impurity peak was observed in the XRD pattern showing the single phase formation. From XRD pattern, lattice constants were calculated using equation

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2.1 (given in chapter 2) and provided in the table 3.1. The unit cell parameters reported by other researcher [30, 32-33] fairly coincides with the calculated values. Moreover, one can see from table 3.1 that the values of lattice parameters b, c and β decrease while parameter a increases for the sample PSG. Hence, it can be inferred that sol-gel method shrinks the unit cell volume as compare to solid state reaction method; this may be due to small crystallite size in sol-gel formation.

![XRD pattern](image.png)

**Fig. 3.1:** XRD pattern potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) prepared by sol-gel (PSG) and solid state reaction method (PSS)
Table 3.1: Lattice parameters and cell volume of K$_2$Ti$_6$O$_{13}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice Parameter a (Å)</th>
<th>Lattice Parameter b (Å)</th>
<th>Lattice Parameter c (Å)</th>
<th>β (Degree)</th>
<th>Unit Cell Volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$Ti$<em>6$O$</em>{13}$ (PSS)</td>
<td>15.534</td>
<td>3.824</td>
<td>9.167</td>
<td>99.780</td>
<td>536.624</td>
</tr>
<tr>
<td>K$_2$Ti$<em>6$O$</em>{13}$ (PSG)</td>
<td>15.570</td>
<td>3.806</td>
<td>9.104</td>
<td>99.568</td>
<td>531.992</td>
</tr>
</tbody>
</table>

3.3.2. Electron Microscopies (SEM and HRTEM)

The morphology of the potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) prepared by sol-gel method was characterized by field emission scanning electron microscope (FESEM). Figure 3.2(a) represents the low magnification image of the potassium hexa-titanate showing nanorods with cross sectional width less than 100 nm. Figure 3.2(b) shows high magnification FESEM image of the same sample. Moreover, sol-gel method allows the control of synthesis process, particularly the size, shape and homogeneity of the particles. SEM image of the same compound, prepared by solid state reaction method has been reported by our group [30(a)] showing microrods with average cross sectional width approximately 1 μm and length 5μm stacked over one another.
Figure 3.2 (a): Low magnification SEM images of $\text{K}_2\text{Ti}_6\text{O}_{13}$ (PSG)
The characteristic property of powder material is its particle size. High resolution transmission electron microscopy (HRTEM) provides the exact shape and size distribution of the crystallites. Fortunately, HRTEM can give a real space image on the distribution of particles, their surface and shape. With a finely focused electron probe, not only imaging of materials is possible, but also a single particle can be identified. Besides, electron microscopy shows the shape and state of agglomeration of particles. Figure 3.3 represents HRTEM image of an individual whisker and its selected-area electron diffraction (SAED) pattern.
Figure 3.3: HRTEM images (a-g) of K$_2$Ti$_6$O$_{13}$ (PSG), corresponding SAED pattern

3.3.3. Dielectric and Electrical Investigations

Dielectric characteristics of ceramic materials have great significance, as the field of solid-state electronics continue to expand rapidly. The principal applications for ceramic dielectrics are as capacitive elements in electronic circuits and as electrical insulation. For these applications, knowledge about the properties of dielectric constant, ac conductivity and
dielectric loss is necessary. A substance whose basic electrical property is the ability to be polarized and in which, an electrostatic field can exist is known as a dielectric material. The most important property of dielectrics is their ability to be polarized under the action of an external electric field. The amount of polarization produced is characterized by a parameter called relative permittivity or dielectric constant. When an electric field acts on any matter, a certain quantity of electric energy is transformed into heat energy. The amount of power losses in a dielectric under the action of the voltage applied to it is known as dielectric loss. Dielectric constant, ac conductivity and dielectric loss depend upon the temperature, particle size, chemical compositions and frequency of the applied ac electric field. In this chapter, it has been described that how these parameters depends upon the particle size and frequency of applied electric field.

Figure 3.4 (a) shows the comparative variation of dielectric constant with frequency at room temperature for both samples. It is clear from the figure that dielectric constant decreases with the increase in frequency for both PSG and PSS and this type of behaviour can be explained on the basis of Maxwell–Wagner model [34]. According to this model, a dielectric medium is assumed to be made of well conducting grains which are separated by poorly conducting (or resistive) grain boundaries. Under the application of external electric field, the charge carriers can easily migrate the grains but are accumulated at the grain boundaries. This process can produce large polarisation and high dielectric constant. The small conductivity of grain boundary contributes to the high value of dielectric constant at low frequency. The dielectric permittivity decreases with frequency as various polarisation processes cease at higher frequencies.

Figure 3.4 (b) shows the variation of loss tangent with frequency at room temperature for both samples. It is clear from the figure that for both specimen (PSG and PSS) loss tangent decreases with the application of ac field owing to the fact that at higher frequencies,
ceramic specimens offer low reactance to the sinusoidal signal and hence minimize the conduction losses [35]. Therefore, dielectric loss decreases at higher frequencies. These types of variations in the dielectric loss are characteristic of the dipole orientation and electrical conduction [36, 37]. Also lossy dielectric can be represented by the circuit analogue of a resistance in parallel with capacitor [38] offering low reactance to the ac signal at higher frequency and eventually minimises the conduction losses in the resistor. Hence the value of dielectric loss decreases at higher frequencies.

In addition it has also been observed from the figures 3.4 (a) and 3.4 (b), that the dielectric constant and loss tangent for the sample PSG is higher than PSS, which is due to particle size effect as reported by M. Aparna et al. [39]. As the particle size is reduced, volume percentage of interface boundaries and therefore the amount of defects that causes the various types of polarizations increases. Jiang et al. [40] observed a similar variation for BaTiO$_3$ and PbTiO$_3$. They explained this variation based on a number of factors such as method of preparation, amorphousness of surface, high surface energy, micro mechanical stress, surface domain polarisation and domain wall effect. A similar variation is also observed in TiO$_2$ reported by Mei et al. [41].

![Figure 3.4 (a): Variation of Dielectric Constant with frequency at RT](image)
Figure 3.4 (b): Variation of loss tangent with frequency at RT

Figure 3.4 (c) shows the variation of ac conductivity with frequency at room temperature for both specimens. Total conductivity of the system is given by

\[
\sigma = \sigma_0(T) + \sigma(\omega, T) \tag{3.4}
\]

where \(\sigma_0(T)\) represents dc conductivity due to excitation of electrons from the localised states to the conduction bands, independent of frequency, while second term \(\sigma(\omega, T)\) represents pure ac conductivity due to the electron hopping between the ions and depends upon the frequency of external field and temperature. It has been observed that ac conductivity gradually increases with the increase in frequency of applied ac field because the increase in frequency enhances the electron hopping frequency.

Figure 3.4 (c) also reveals that ac conductivity is higher for the sample (PSS) than the sample PSG. This may be due to increase of vacancies, dislocations and grain boundary scattering with reducing particle size which increases the resistivity and therefore corresponding conductivity decreases. This type of behaviour i.e. decrease in conductivity
with reduction in particle size has already been reported in literature [42, 43]. According to Bakonyi [44], besides the crystallite boundaries, the presence of a large number of other types of lattice imperfections has also some effects on the electrical resistivity.

![Graph](image)

**Figure 3.4 (c):** Variation of ac conductivity with frequency at room temperature (RT)

### 3.3.4. Optical Properties

UV–Visible absorption spectroscopy is a powerful technique to explore the optical properties of semiconducting materials. It is well known that the properties of optical absorption (UV–Vis) by semiconductors are relevant to the electronic structure features and hence are the key factors in determining their band gaps [45]. The value of $n$ is respectively 1/2, 2, 3/2, and 3 for allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions. The value of $n = 1/2$ allows for direct transition, thereby giving direct band gap. Optical measurements in the UV-Visible range have been made in order to obtain clues regrading the electronic structure of the potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) shown in figure 3.5 (a). The absorbance is expected to depend on several factors, such as band gap, surface roughness and impurity centers. The spectrum obtained for sol-gel sample is seen to have been enhanced towards the shorter wavelength region. This effect might result due to quantum size effect [46].
In order to calculate the direct band gap we used the Tauc relationship [47]:

\[ \alpha(h\nu) = A(h\nu - E_g)^n \]

Where \( \alpha \) is the absorption coefficient given by \( \alpha = 2.303(A/t) \), \( A \) is absorbance and \( t \) is the thickness of cuvette, \( n=1/2 \) for potassium hexa-titanate (direct band gap semiconductor) [48]. The plots of \((\alpha h\nu)^2\) versus \( h\nu \) for both the specimens are shown in figure 3.5 (b). Extrapolation of linear region of these plots to \((\alpha h\nu)^2 = 0\) gives corresponding direct energy band gap. The measured band gap was found to be 3.48 eV for the sample PSG, which is higher than the value 3.06 eV found for the sample PSS. This can be attributed due to the quantum confinement effect of the nanoparticles [49]. This result agrees with the previously reported values [50]. The present observations indicate that the band gap increases as the particle size approaches to nano regime.

**Figure 3.5 (a):** UV–Vis absorption spectrum for potassium hexa-titanate (\( \text{K}_2\text{Ti}_6\text{O}_{13} \))
Figure 3.5 (b): Plots of $(\alpha h \nu)^2$ versus $h \nu$ for both specimen

3.3.5. Photocatalytic Test

The term photocatalysis is always used to describe the process undergoing in a semiconducting material, when it is irradiated by light of a certain wavelength. Semiconductors like titanium dioxide and alkali titanates etc. have attracted great interest in the past decade due to its environmental applications such as air purification and water remediation [24, 51]. In photocatalysis, light of energy greater than the band gap of the semiconductor, excites an electron from the valence band to the conduction band. Upon photo-activation, an electron-hole pair is produced that reacts with adsorbed species to produce hydroxyl radicals (OH•). These radicals are powerful oxidising agents and will oxidise organic contaminants to CO$_2$ and H$_2$O. Properties such as crystal size, structure, pore size/volume, surface charge, number and nature of trap sites and absorption/desorption characteristics, all play an important factor in the photocatalytic activity of semiconducting material [52, 53]. Smaller crystal sizes result in larger surface area which increases the
number of active degradation sites available for degradation reactions, and therefore enhances the photocatalytic activity.

Potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) prepared in this work was tested as photocatalyst on the degradation reaction of methyl orange under UV irradiation and evaluated by measuring the photodegradation of a solution of methyl orange (30 ppm, 250 mL in a quartz vessel) in the presence of 200 mg K$_2$Ti$_6$O$_{13}$ under exposure to UV light at room temperature. Figure 3.6 shows the decay of absorbance with time (0–1 h) during the progress of the reaction upon stirring the suspension. The absorption spectra corresponded to the UV-light irradiation times. The colour of the suspension faded gradually with an increase in irradiation time. Finally, the suspension changed from orange to approximately colorless. While colour of the methyl orange solution remained unchanged when no K$_2$Ti$_6$O$_{13}$ was added even under UV irradiation. The potassium hexa-titanate (K$_2$Ti$_6$O$_{13}$) therefore, act efficiently as a photocatalyst and break methyl orange molecules into several different smaller molecules.

![Absorbance of methyl orange solution before and after photocatalytic reaction](image)

**Figure 3.6:** Absorbance of methyl orange solution before and after photocatalytic reaction in the presence of 200 mg K$_2$Ti$_6$O$_{13}$ prepared by PSG and PSS.
In this experiment $\text{K}_2\text{Ti}_6\text{O}_{13}$ with a rectangular tunnel structure has high efficiency to produce photoexcited charges (electrons and holes) [19], which are thought to be associated with its high photocatalytic activity. Furthermore, it can be inferred from figure 3.6 that the photocatalytic capabilities were found to be better for the $\text{K}_2\text{Ti}_6\text{O}_{13}$ prepared by sol-gel method as compare to the same, prepared by solid sate method. This is attributed due to larger surface area or smaller particle size obtained in sol-gel formation.

### 3.4. Conclusions

Potassium hexa-titanate ($\text{K}_2\text{Ti}_6\text{O}_{13}$) has been prepared as a single phase through sol-gel as well as by solid state reaction method. Its crystal structure corresponds to a monoclinic as confirmed by XRD pattern. Surface morphology was studied by field emission scanning electron microscope (FESEM) of single phase, $\text{K}_2\text{Ti}_6\text{O}_{13}$ (PSG), exposing nanorods. The data revealed that the dielectric constant and loss tangent exhibit the normal dielectric behaviour and decreases with increase in frequency while the same parameters having higher values for the sample, prepared by sol-gel method. The ac conductivity shows the frequency and particle size dependent behaviour. It increases with the increase in frequency and decreases with particle size. The optical studies have been carried out using optical absorbance. The band gap of the samples were measured from the Tauc relation and found that energy band gap increases with the reduction in particle size. Additionally, $\text{K}_2\text{Ti}_6\text{O}_{13}$ was tested as photocatalyst on the degradation of methyl orange (MO) under UV light and better results were found for the sample PSG.
References


    (c) ICDS Card No. 74-0275.
    (b) ICDS Card No. 40-0403.


