Comparative Analysis of Sodium Hexa-titanate (Na₂Ti₆O₁₃) & Sodium-Potassium Hexa-titanate (Na₁.₅K₀.₅Ti₆O₁₃)

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Abstract. The present paper discusses the synthesis and characterization of Sodium Hexa-titanate (NHT) and Sodium-Potassium Hexa-titanate (NKHT) by solid state reaction method. The phase of the synthesized material was confirmed by XRD and the particle size has been calculated using Debye-Scherrer relation. Morphology of the surface and dimensions of the crystals have been analysed using FE-SEM analysis at different magnification. EDS analysis has also been done for elemental analysis of Sodium Hexa-titanate and Sodium Potassium Hexa-titanate. IR spectra has been recorded for getting various vibration modes of the samples.

Key Words: Sodium Hexa-titanate, Sodium-Potassium Hexa-titanate, XRD, FESEM, EDS, IR

1. Introduction

Titanates are primarily materials with high dielectric constant. There are various types of titanates for different applications. Alkali titanates are also special type of titanates which have general chemical formula as, A₂TiₙO₂ₙ₊₁ [where A is any alkali metal, Lithium (Li), Sodium (Na), Potassium (K), etc. and n is between 2 to 8] have various technological importance during the last few decades due to their various technological applications. They have layered or tunnel crystal structures built of TiO₆ octahedra offering edges to interlaying cations [1-3] [Figure 1]. Among the different titanates, Sodium Octa-titanate (Na₂Ti₆O₁₃) and Sodium Hexa-titanate (Na₂Ti₆O₁₃) have potential applications as ion exchange [4, 5], photocatalysis [6], sensors [7] and biomedical applications [8]. Sodium Hexa-titanate shows a tunnel structure and have good chemical stability as compared to their layered counter parts [9]. The activity or performance for an application can be improved by making a composite material or by doping suitable dopant. In view of this, we have proposed replacement of some sodium atoms with potassium atoms that is synthesis of Sodium-Potassium Hexa-titanate. There is a greater possibility to optimize their property for specific application.

These types of mixed titanates (Na/K, Na/K/Li, Na/Li, etc.) have also been studied by various researchers including our group. Maurya et al. studied dielectric-spectroscopic and a.c. conductivity analysis of layered Na₂ₓKₓTi₃O₇ (X=0.2, 0.3, 0.4) ceramics [10]. Machida et al. have studied pillaring
and photocatalytic properties of partially substituted layered titanates: \( \text{Na}_2\text{Ti}_3\chi\text{M}_2\text{O}_7 \) and \( \text{K}_2\text{Ti}_4\chi\text{M}_2\text{O}_9 \) (\( \chi=\text{M} \equiv \text{Mn, Fe, Co, Ni, Cu} \)). [11]. Pal et al. reported effect of copper doping on structural and dielectric response on sodium lithium tri-titanate \( \text{(Na}_{1.9}\text{Li}_{0.1})\text{Ti}_3\text{O}_7\chi \text{Cu} \) \( (0.0 \leq \chi \leq 0.1) \) [12]. Singh and Shripal reported dielectric and a.c. conductivity studies of Mn-doped \( \text{Na}_{1.8}\text{Li}_{0.2}\text{K}_{0.0}\text{Ti}_3\text{O}_7 \) ceramics [13]. Pal et al. also reported dielectric-spectroscopic and ac conductivity investigations on Manganese doped layered \( \text{Na}_{1.9}\text{Li}_{0.1}\text{Ti}_3\text{O}_7 \) ceramics [14], Liao et al. studied other type of mixed titanates synthesis and properties of \( \text{Bi}_{0.3}\text{(Na}_{1-x}\text{K}_{x}\text{Ag})_{0.7}\text{Ti}_3\text{O}_7 \) lead-free piezoelectric ceramics[15]. Vikram et al. reported effect of Na-substitution on the dielectric behavior of layered \( \text{K}_{2.8}\text{Na}_{0.2}\text{Ti}_3\text{O}_7 \) \( (0.05 \leq x \leq 0.15) \) ceramics and a.c. conductivity investigations on layered \( \text{K}_{2.8}\text{Na}_{0.2}\text{Ti}_3\text{O}_7 \) \( (x=0.05,0.09,0.15) \) [16-17]. Our group has also reported synthesis and characterization of various alkali titanates [18-30].

![Figure 1. Tunnel Structure of Sodium Hexa-titanate](image)

**2. Materials and Method**

2.1 Synthesis of Sodium Hexa-titanate & Sodium-Potassium Hexa-titanate

Sodium Hexa-titanate (NHT) ceramic powder has been prepared by adding sodium carbonate \( \text{(Na}_2\text{CO}_3 \) and titanium dioxide \( \text{(TiO}_2 \) in a proper molar ratio.

\[
\text{Na}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Na}_2\text{Ti}_4\text{O}_{13} + \text{CO}_2
\]

For the preparation of Sodium Potassium Hexa-titanate (NKHT), sodium carbonate \( \text{(Na}_2\text{CO}_3 \), potassium carbonate \( \text{(K}_2\text{CO}_3 \) and titanium dioxide \( \text{(TiO}_2 \) were added in stoichiometric amount.

\[
3\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3 + 24\text{TiO}_2 \rightarrow 4\text{Na}_3\text{K}_0\text{Ti}_5\text{O}_{13} + 4\text{CO}_2
\]

Titanium dioxide \( \text{(TiO}_2 \) purity 99.5\%, sodium carbonate \( \text{(Na}_2\text{CO}_3 \) and potassium carbonate \( \text{(K}_2\text{CO}_3 \) AR-grade, purity 99.5\% were purchased from Sigma Aldrich and Thomas Baker respectively.

The mixture of sodium carbonate and titanium dioxide were grinded approximately for 6 hours using pestle mortar to make it smaller in size. Material was kept in a programmable muffle furnace followed by grinding. Temperature was set to reach up to 900\°C with controlled heating rate of 4\°C/min, where it was kept for 12 hours, and then allowed to cool up to room temperature. To prepare Sodium Potassium Hexa-titanate, required amount of potassium carbonate powder were added in a mixture of \( \text{TiO}_2 \) and \( \text{Na}_2\text{CO}_3 \) and obtained ceramic material was processed by the same method as described for NHT.

**3. Results and Analysis**

3.1 XRD Analysis

Phase formation and structural information have been analyzed using X-ray Diffraction and found that pure Sodium Hexa-titanate and Sodium Potassium Hexa-titanate have monoclinic structure (figure 2). Furthermore, XRD confirms that sodium has been replaced by potassium, as peaks in NKHT are similar to peaks in pure NHT. It confirms that NKHT does not have any impure peaks, which clearly indicates that potassium has replaced sodium and doping was successful.

Crystalline size of pure and potassium doped NHT have been calculated by Debye-Scherrer equation.

\[
\tau = \frac{K\lambda}{\beta\cos\theta}
\]
Where $\tau$ denotes mean size of the crystalline, and $K$ is a dimensionless shape factor having a constant value of 0.91, $\lambda$ is the X-ray wavelength, and $\lambda=1.5406\text{Å}$ (Cu K-alpha), $\beta$ denotes full width half maxima and obtained from X-ray diffraction, and $\theta$ is Bragg angle which is also obtained from X-ray diffraction.

The mean crystalline size of NHT and NKHT are obtained 0.210nm and 0.215nm respectively. From the calculation, for crystalline size, it was found that, on doping potassium in pure NHT, there is a fractional decrease in the surface area of prepared samples. The reduction in surface area may be due to the increase in the particle size of the doped Sodium Hexa-titanate, which have also been confirmed by morphological study.

![XRD analysis of NHT and NKHT](image1.png)

Figure 2. XRD analysis of NHT and NKHT

### 3.2 FE-SEM Analysis

Morphology of the samples, any defect in the crystal as well as dimensions of the crystals have been analysed using FE-SEM analysis at different magnification. Figure 3 and 4 show that NHT and NKHT have hexagonal crystal structure, and rod shaped. Since potassium has large atomic radius than sodium, it may cause increase in length of the rod. Morphological study confirms that, NKHT have 0.05µm larger average rod shaped crystal than NHT. Length of the rod of NHT lies in the range of 0.8 to 1.3µm, while average length is 1.2µm. The NKHT also have rod shaped crystal with average length 1.25µm, and diameter of the NKHT lies between 0.12µm to 0.3µm, where pure NHT have diameter between 0.1µm to 0.25µm.

![FE-SEM image of Sodium Hexa-titanate](image2.png)

Figure 3. FE-SEM image of Sodium Hexa-titanate
3.3 EDS Analysis
Figures 5 and 6 show elemental analysis of Sodium Hexa-titanate and Sodium Potassium Hexa-titanate. Figure 5 confirms that in NHT element presents are Na, Ti, O and C. while figure 6 shows that elements present in NKHT are Na, Ti, K, O and C which clearly indicate that replacement of Na with K was successful, as well it was already confirmed from XRD that no impurity was present in NKHT. The presence of carbon is due to carbon tape used in analysis.

3.4 FTIR Analysis
Vibrational properties of titanate ceramic materials can be studied with the help of Group Theory Analysis (GTA). Sodium Hexa-titanate ceramic has tunnel like structure and symmetric formation is monoclinic (space group C2/m) with two formulas per unit cell (Z = 2) [31]. As per prediction of Group theory, Na$_2$Ti$_6$O$_{13}$ exhibit nearly 60 vibrational modes [32] and they can be distributed as follows:

\[12 \text{Ag} + 18 \text{Au} + 12 \text{Bg} + 18 \text{Bu}\]

Where Ag (Au) and Bg (Bu) are Raman (IR) active representations.

FTIR spectra for NHT and NKHT have been analysed at room temperature within region of 400-4000 cm$^{-1}$ and shown in the figure 7 and 8.
Figure 7. FTIR spectra for Sodium Hexa-titanate

Figure 8. FTIR spectra for Sodium-Potassium Hexa-titanate.

It has been analyzed with the above figures that Sodium Hexa-titanate and Sodium Potassium Hexa-titanate prepared by solid state reaction method have same peaks, which is shown in figure 7 & 8. The peaks obtained of synthesized samples matched with previous reported data [33-34]. Absorption bands are obtained around at 515cm\(^{-1}\) and 714cm\(^{-1}\) and are attributed to O-Ti-O bending vibrations and Ti-O stretching of TiO\(_6\) octahedral groups [35, 36].

4. Conclusions
In the present study of NHT and NKHT, it has been found that both samples have monoclinic structure. The atomic radius of sodium is 227pm and atomic weight is 23u, while atomic radius of potassium is 280pm and atomic weight is 39u, which is cause of increase in the crystalline size of NKHT. NHT and NKHT are rod shaped in longitudinal nature, and hexagonal in diameter. The length as well as diameter of NKHT is greater than NHT because of the atomic radius of potassium. The presence of Na, K, O and Ti were also confirmed using EDS analysis, and successful replacement of Na with K was also confirmed with EDS analysis. FTIR spectroscopy gives absorption band and also confirms that there is no impurity in the samples. There were no impure peaks obtained in X-ray analysis, which also confirm that doping of K in NHT was successful.

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