Thermal Analysis of an Alkali Titanate: Sodium Hexa-Titanate (Na$_2$Ti$_6$O$_{13}$) in Pure and Doped (Zinc) States

Navshad Alam$^1$, Tahira Khatoon$^2$ and Vishal Singh Chandel$^3$

$^1$Department of Applied Science, BNCET, Lucknow-226201, India
$^2$Department of Physics, Integral University, Lucknow-226026, India
$^3$Department of APSH, Rajkiya Engineering College, Ambedkar Nagar-224122, India

E-mail: chandel.integral@gmail.com

Abstract: This paper deals with the synthesis of pure and Zn doped samples of Sodium Hexa-titanate (NHT, an Alkali Titanate) by solid-state reaction method and characterization by XRD, SEM and Thermal analysis. The phase of the synthesized samples has been confirmed by XRD and the particle size was estimated using the Debye-Scherrer equation. X-ray diffraction patterns of the samples reveal a single phase with monoclinic structure for both pure and doped samples. Surface morphology and the dimensions of the synthesized materials have been analysed with the help of field emission-scanning electron microscopy at different magnification. To explore the various phases of the samples under thermal conditions thermal analysis (DSC/TGA) has also been performed.

Keywords: Sodium Hexa-titanate, XRD, FE-SEM, DSC, TGA

1. INTRODUCTION

Titanium based materials such as titanates are frequently chosen for commercial applications due to their remarkable properties like thermal stability and photo-catalysis along with cost effectiveness [1, 2]. Different types of titanates have already been synthesized and consist of layered or tunnel type structures which are negatively charged, which is compensated by alkali metal ions in case of alkali titanates and thus making it more promising candidate for various applications [3]. Structure of alkali titanates depends on the metal content and due to which they possess different physical and chemical properties. Alkali titanates have a common chemical formula as $A_2Ti_nO_{2n+1}$ where n=6 correspond to hexa-titanate that possesses a tunnel like structure [4-6]. These materials have proven to be exceptionally significant in ion exchange applications, dielectric resonators, ceramic capacitors, sensors etc. [7-9], with biomedical applications [10]. Being n type semiconductors, alkali titanates have shown outstanding photocatalytic activities [11]. Due to high infrared reflectance, less thermal conductance, outstanding chemical stability and excellent mechanical properties, sodium titanates are extensively used as heat insulators [12], energy harvesters [13], refractories and frictional materials [14]. The reason for perfect chemical stability of sodium hexa-titanate is its tunnel structure with Na$^+$ ions coated inside. Sodium hexa-titanate has been synthesized using different methods such as conventional solid-state reaction method, sol-gel method and hydrothermal method [15-17]. Properties of these materials can be tailored by doping different transition metals [18-25].

In the present study, we have examined the effect of zinc doping in sodium hexa-titanate on its structural and thermal properties. A series of sodium hexa-titanate, pure and zinc doped, have been
synthesized from anhydrous anatase by conventional solid-state reaction method and the thermal properties are observed at various doping concentrations.

2. SYNTHESIS OF PURE AND Zn DOPED SODIUM HEXA-TITANATE (NHT)

Pure and zinc doped sodium hexa-titanates (NHT) have been synthesized using solid state reaction method. NHT ceramic powder can be prepared by adding Na$_2$CO$_3$ (sodium carbonate) and titanium dioxide (TiO$_2$) in a proper molar ratio.

\[ \text{Na}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Na}_2\text{Ti}_6\text{O}_{13} + \text{CO}_2 \uparrow \]

In this work, sample of zinc doped NHT (Na$_2$Ti$_6$O$_{13}$) of three different molar concentration (x = 4%, 8% and 12%) are prepared through solid-state reaction method, by utilising adequate amount of sodium carbonate (Na$_2$CO$_3$) AR grade, titanium dioxide (TiO$_2$) (Sigma Aldrich, 99.5% purity) and zinc oxide (ZnO) AR grade. The chemical formula of zinc doped NHTs are written below.

\[
\begin{align*}
\text{Na}_2\text{CO}_3 + 5.96\text{TiO}_2 + 0.04\text{ZnO} & \rightarrow \text{Na}_2\text{Ti}_{5.96}\text{Zn}_{0.04}\text{O}_{13} \\
\text{Na}_2\text{CO}_3 + 5.92\text{TiO}_2 + 0.08\text{ZnO} & \rightarrow \text{Na}_2\text{Ti}_{5.92}\text{Zn}_{0.08}\text{O}_{13} \\
\text{Na}_2\text{CO}_3 + 5.88\text{TiO}_2 + 0.12\text{ZnO} & \rightarrow \text{Na}_2\text{Ti}_{5.88}\text{Zn}_{0.12}\text{O}_{13}
\end{align*}
\]

After addition of sodium carbonate, titanium dioxide and zinc oxide, the mixture was grinded for 6 hours using A grade pestle mortar. After this, material was calcined at 900$^\circ$C for 12 hours in a programmable muffle furnace [26-30].

3. RESULTS AND DISCUSSIONS

3.1 XRD Analysis

The X-ray diffraction (XRD) patterns were recorded at room temperature for pure and zinc doped NHT. These XRD patterns confirm single phase formation and monoclinic structure as shown in figure 1. XRD patterns of doped samples have also confirmed that Zinc has replaced titanium, as no extra peaks were seen in the XRD pattern of Zinc doped sodium hexa-titanate.

Debye-Scherrer equation has been used to calculate the crystalline size of pure and zinc doped NHT and the results have been presented in table 1.

\[
\tau = \frac{K\lambda}{\beta\cos\theta}
\]

(1)

Where $\tau$ in equation 1 denotes mean crystalline size and $K$ is a constant, ($K = 0.91$), $\lambda$ is the X-ray wavelength, $\lambda$=1.5406Å (Cu K-alpha), $\beta$ is FWHM (full width half maxima) and it is obtained from X-ray diffraction of the samples, $\theta$ is the Bragg angle which is also obtained from X-ray diffraction patterns.
Figure 1: XRD patterns of pure and zinc doped sodium hexa-titanate.

Table 1: Mean crystalline size of pure and zinc doped sodium hexa-titanate.

| S. No. | Samples Name | Mean Crystalline Size (τ) |
|--------|--------------|---------------------------|
| 1      | Na₂Ti₆O₁₃    | 0.210nm                   |
| 2      | Na₂Ti₅.96Zn₀.₀₄O₁₃ | 0.202nm                   |
| 3      | Na₂Ti₅.92Zn₀.₀₈O₁₃ | 0.200nm                   |
| 4      | Na₂Ti₅.₈₈Zn₀.₁₂O₁₃ | 0.200nm                   |

From Table 1 it can be observed that on increasing zinc percentage in pure NHT, crystalline size is decreasing which may be due to smaller atomic radius of zinc than titanium. No significant change in mean crystalline size (τ) has been observed for 8% and 12% zinc doping.

3.2 FE-SEM Analysis

Field Emission Scanning Electron Microscopy of samples provides their structural information. Morphology of pure and zinc doped NHT was observed using FE-SEM (Nova Nano FE-SEM 450) at an accelerating voltage of 10kV. Figures 2, 3, 4 and 5 clearly show the microstructure of pure and zinc doped NHT materials and it has been found that these samples have rod shape.

Diameter of pure NHT lies between 0.1 micrometer to 0.25 micrometer and length of the rod shaped sample lies in the range of 0.8µm to 1.3µm as shown in figure 2. Diameter of Zn doped NHT lies in the range of 0.1 to 0.25µm, and length of the rod lies between 0.7 to 1.2µm shown in figure 3, 4 and 5. Here again it can be seen that the average length of the rod is decreasing as doping concentration is increasing. The cause of decrease in length is also due to a smaller atomic radius of zinc (139pm) than titanium (215pm).

Table 2: Average length of pure and zinc doped sodium hexa-titanate.

| S. No. | Samples Name         | Average Length of Rod |
|--------|----------------------|------------------------|
| 1      | Na₂Ti₆O₁₃            | 1.20µm                 |
| 2      | Na₂Ti₅.96Zn₀.₀₄O₁₃   | 1.10µm                 |
| 3      | Na₂Ti₅.₉₂Zn₀.₀₈O₁₃   | 1.076µm                |
| 4      | Na₂Ti₅.₈₈Zn₀.₁₂O₁₃   | 1.06µm                 |
Figure 2: FE-SEM of pure NHT

Figure 3: FE-SEM of 4% Zn doped NHT.

Figure 4: FE-SEM of 8% Zn doped NHT

Figure 5: FE-SEM of 12% Zn doped NHT
3.3 Differential Scanning Calorimetry (DSC) Analysis
The rate of change of heat in energy has been measured using Differential Scanning Calorimetry (DSC), with function of temperature. The rate of change of heat gives kinetic information of synthesized samples.

DSC analysis also gives the information of melting temperature, latent heat, heat fusion and transition temperature etc.

The phase transition study of pure and Zn doped NHT, differential scanning calorimetry (DSC) was performed in the nitrogen atmosphere. The heating rate of 10°C/min was maintained from room temperature to 900°C.

Figures 6, 7, 8 and 9 show a small exothermic peak nearly at 100°C. This peak indicates the evaporation of water and a small shrinkage process in the synthesized samples. Furthermore, no exothermic or endothermic peaks were obtained. Therefore, no shrinkage process was observed upto 900°C. Instead, this DSC analysis also shows that no melting temperature was observed from upto 900°C, while heating the samples.
4. CONCLUSIONS

- Single phase formation and monoclinic structure of pure and zinc doped sodium hexa-titanate has been confirmed using XRD analysis.
- Morphological study of pure and zinc doped sodium hexa-titanate show uniform rod shaped structure in micron size. Morphological study also confirms that increasing the doping percentage of zinc in pure NHT reduced the average length of the zinc doped samples.
- DSC analysis validates that no melting points were observed upto 900°C. Also, no shrinkage as well as exothermic peaks was found upto 900°C.

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