



Differential Scanning Calorimetric Analysis of Ni Doped Sodium Hexa-titanate

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ABSTRACT

Pure and nickel doped alkali titanates $\text{Na}_2\text{Ti}_{6-x}\text{Ni}_x\text{O}_{13}$ (where $x = 0, 0.04, 0.08, 0.12$ mol percentage) were synthesized using conventional solid-state reaction method. Phase of the synthesized samples have been confirmed with the help of X-ray diffraction (XRD) patterns recorded at room temperature (RT). Peak positions of all samples ($\text{Na}_2\text{Ti}_{6-x}\text{Ni}_x\text{O}_{13}$) exhibited the monoclinic structure. FE-SEM of these samples has been done at 10kV acceleration voltage, in secondary electron mode, at different magnifications to observe morphology (microstructure) and they have been found as rod shaped. Thermal stability of pure and nickel doped titanates was done with the help of differential scanning calorimetry (DSC) in presence of inert gas (nitrogen) from ambient temperature to 800°C, keeping heating and cooling rates 10°C/minute.

Keywords: Alkali titanates, XRD, Monoclinic, Sodium Hexa-titanate, DSC, FE-SEM.

INTRODUCTION

The common chemical formula of sodium (alkali) titanates is $\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$ (where $1 \leq n \leq 8$) [for $1 \leq n \leq 2$, they have layered structure and for $n > 2$, they have tunnel type of structure]. Titanates have been explored a lot for various technological applications such as ion exchangers in the industry, electrodes for secondary batteries, reinforcement materials, filters, catalysts, heat insulators etc. as their properties can easily be tailored¹⁻⁸. Kikkawa *et al.*, reported hydrolysis

and thermolysis of the alkali titanates, Fujishiro *et al.*, investigated cation exchange property of alkali titanates as these materials are capable in protecting the environment from radioactive wastes, the alkali titanates can also be used as capacitors, electrolyte for fuel cell, biosensors as well as dielectric sensors⁹⁻¹². Study of crystal energy and structure of various alkali titanates $\text{A}_2\text{Ti}_n\text{O}_{2n+1}$ (A=Li, Na, K) have been performed by Michele Catti *et al.*, by density functional theory, neutron diffraction, by first-principle calculations and X-ray absorption spectroscopy¹³. Kanchanawarin



et al., studied oxygen-deficiency in alkali titanates $A_2Ti_6O_{13}$ (A = Li, Na, and K) and local stoichiometric structure¹⁴.

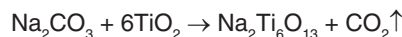
Sauvet *et al.*, reported synthesis and thermo gravimetric analysis (TGA) along with differential thermal analysis (DTA) of sodium tri-titanate ($Na_2Ti_3O_7$) and hexa-titanate ($Na_2Ti_6O_{13}$). Stengl *et al.*, investigated synthesis, microstructure characterization, photocatalytic activity, thermal analysis of sodium titanate nanorods (DTA–TG of the sample coupled with mass spectroscopy, emanation thermal analysis), Cardoso *et al.*, reported thermal characterization of lamellar titanates ($K_2Ti_4O_9$ and $Na_2Ti_3O_7$), Umek *et al.*, reported the effect of the temperature on the morphology of one dimensional sodium titanate nanostructures (Sodium Titanate Nanotubes and Nanoribbons) and their thermal stability, Razali *et al.*, reported hydrothermal synthesis, morphological and structural analysis of titanate and titania nanostructures¹⁵⁻¹⁹. Alkali titanates with tunnel and layered structure have been synthesized by various research groups including our group²⁰⁻³³.

MATERIALS

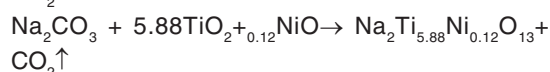
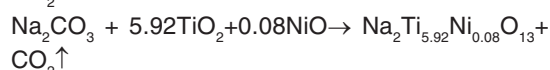
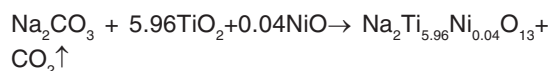
For synthesis of sodium hexa-titanate (NHT alkali titanate), titanium (IV) oxide (TiO_2) powder (<100nm, Purity 99.5%) was purchased from Sigma Aldrich. Sodium carbonate (Na_2CO_3 , Purity $\geq 99.5\%$) AR grade and nickel oxide (NiO , Purity $\geq 99.5\%$) AR grade were purchased from Thomas Baker.

METHOD

Addition of sodium carbonate and titanium dioxide (TiO_2) in a proper molar ratio gives sodium hexa-titanate, detailed synthesis process has already been published^{4,12}.



For the preparation of nickel (Ni) doped sodium hexa-titanate ($Na_2Ti_{6-x}Ni_xO_{13}$) for different molar concentration ($x=0.0, 0.04, 0.08, 0.12$), the equations are given below.



After adding all components, mixture was ground properly for 6 hours. After grinding, mixture was kept in a programmable muffle furnace for 12 h at 900°C, the rate of heating was fixed at 4°C per minute. After that the mixture was cooled in the furnace itself up to room temperature. The cooled material was again ground for 30 min^{12, 22-23}. It was then ready for characterization.

RESULTS AND DISCUSSIONS

X-ray Diffraction

Figure 1 represents the X-ray diffraction patterns of pure and nickel doped NHT samples recorded at room temperature, which reveals single phase with monoclinic structure. Non-existence of extra peaks in the XRD pattern confirms the single phase of the samples and successful doping of nickel in sodium hexa-titanate. Lattice parameters of the samples can also be calculated using equation (1) given below.

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

Where symbols have their usual meanings and already been explained in our previous papers^{14, 22-24}.

Table 1: Lattice parameters of pure and nickel doped

S. No.	Samples	Lattice Parametera (Å)	Lattice Parameterb (Å)	Lattice Parameterc (Å)	β (degree)	Unit Cell VolumeV (Å ³)
1	$Na_2Ti_6O_{13}$	15.5999	3.800	9.1600	99.10	543.001
2	$Na_2Ti_{5.96}Ni_{0.04}O_{13}$	15.5970	3.798	9.1560	98.89	542.377
3	$Na_2Ti_{5.92}Ni_{0.08}O_{13}$	15.5878	3.798	9.1350	98.80	541.133
4	$Na_2Ti_{5.88}Ni_{0.12}O_{13}$	15.5400	3.800	9.1110	98.71	538.023

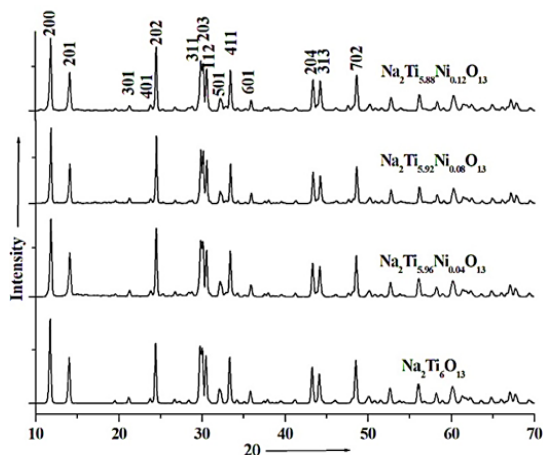


Fig. 1. XRD Analysis of pure and Ni doped NHT

It has been found that $a \neq b \neq c$, and also $\alpha = \gamma = 90^\circ \neq \beta$, as the case should be for monoclinic structure, here the value of β is decreasing on increasing the doping percentage of nickel. The unit volume cell gradually decreases on increasing the Ni in pure as shown in Table 1.

FE-SEM Analysis

Morphology of all synthesized materials have been done by field emission scanning electron microscopy (FE-SEM) at 10kV accelerating voltage. All the samples have been analyzed in secondary mode at various magnifications.

The morphological study showed that all the samples have rod shaped in micron range. It has also been confirmed that these samples have hexagonal structure.

Figures 2a, 2b, 2c and 2d show the SEM images (microstructures) of all synthesized samples as rod shaped and particle shape of all samples is hexagonal. Fig. 2a is depicting SEM image of pure NHT and edge to edge distance of the particles lies between 0.1 to 0.25 μ m and length lies between 0.8 to 1.3 μ m.

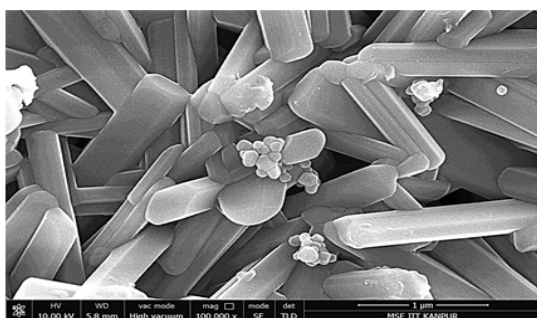


Fig. 2a. SEM image of Pure NHT

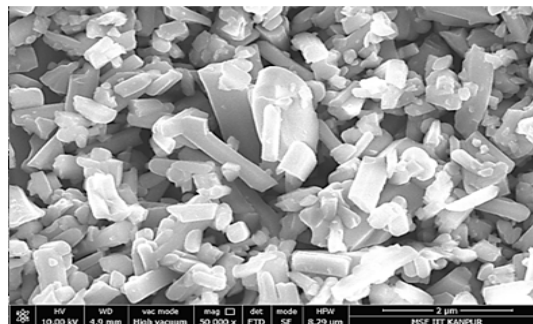


Fig. 2b. SEM image of 4% Ni doped NHT

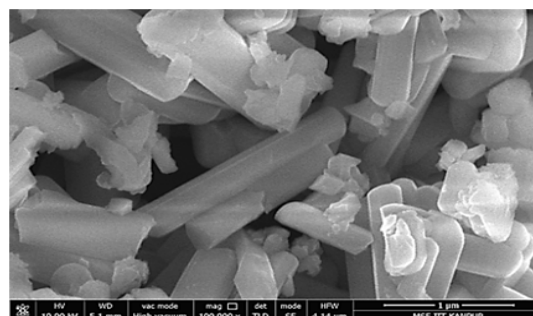


Fig. 2c. SEM image of 8% Ni doped NHT

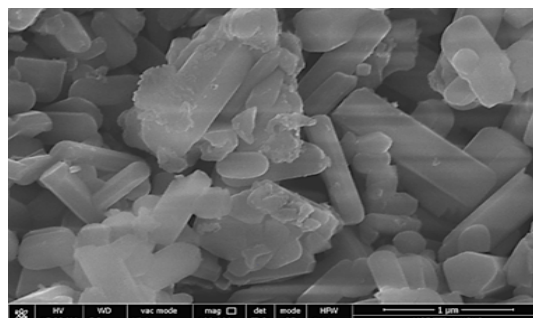


Fig. 2d. SEM image of 12% Ni doped NHT

Figures 2b, 2c, and 2d show the SEM images of transition metal nickel doped NHT ($\text{Na}_2\text{Ti}_{6-x}\text{Ni}_x\text{O}_{13}$) ($x= 4\%$, 8% , and 12%) and edge to edge distance of the particles lies between 0.1 to 0.25 μ m and length 0.7 to 1.2 μ m. Average size of the doped samples is presented in Table 2 and they are also in rod shaped. The small change in the length of the rod has been observed, only because of the doping in pure sodium hexa-titanate. The most appropriate reason behind this is atomic radius of the dopant. Atomic radius of titanium is 215 pico-meter while atomic radius of nickel is 163 pico-meter. When nickel replaces the titanium ions, size of the samples also reduces due to the smaller atomic radius of nickel.

Table 2: Particle size of pure and nickel doped Sodium hexa-titanate

S. No.	Samples	Average Length of Rod
1	$\text{Na}_2\text{Ti}_6\text{O}_{13}$	1.20 μm
2	$\text{Na}_2\text{Ti}_{5.96}\text{Ni}_{0.04}\text{O}_{13}$	1.10 μm
3	$\text{Na}_2\text{Ti}_{5.92}\text{Ni}_{0.08}\text{O}_{13}$	1.08 μm
4	$\text{Na}_2\text{Ti}_{5.88}\text{Ni}_{0.12}\text{O}_{13}$	1.00 μm

DSC Analysis

The rate of change of heat in energy has been measured using differential scanning calorimetry (DSC), with function of temperature. DSC plot gives the information that at which temperature materials release its heat, known as exothermic peak.

Thermal stability of pure and Ni doped sodium hexa-titanate was done with the help of DSC in inert gas (N_2) atmosphere from ambient temperature to 800°C, with heating rate of 10°C/minute. Fig. 3a gives the information that a transformation occurred nearly 100°C, because of the presence of some moisture or water in the samples.

After adding 4% and 8% nickel in pure sodium hexa-titanate a small exothermic peak has been obtained nearly at 100°C as shown in Fig. 3b & 3c. In 12% nickel doped sodium hexa-titanate an exothermic peak is obtained at 283 shown in Figure 3d.

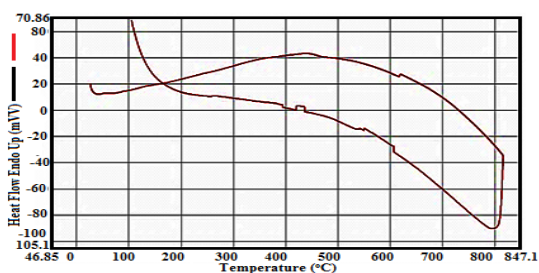


Fig. 3a. DSC analysis of pure NHT

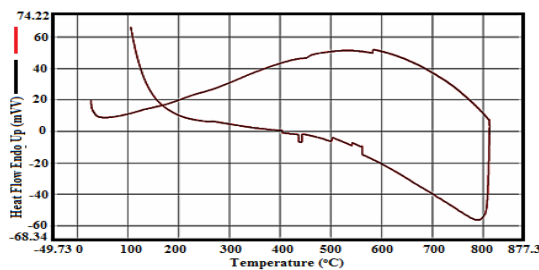
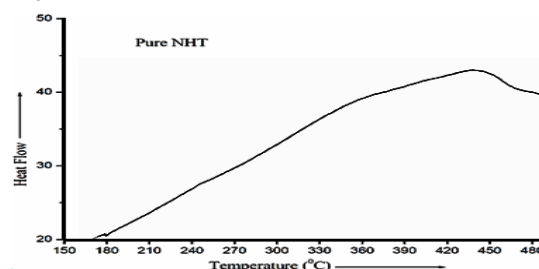


Fig. 3b. DSC analysis of 4% Ni doped NHT

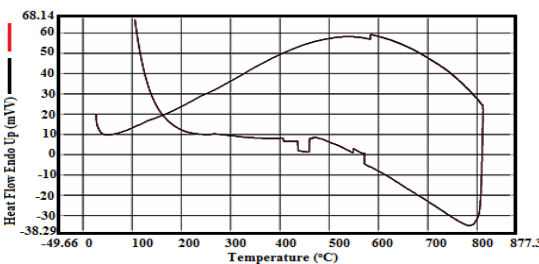
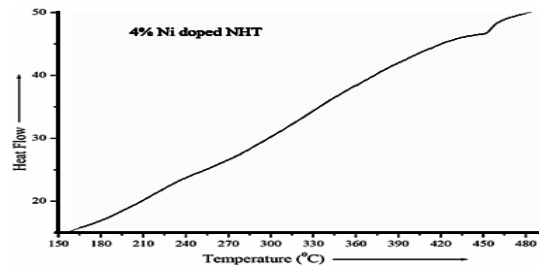


Fig. 3c. DSC analysis of 8% Ni doped NHT

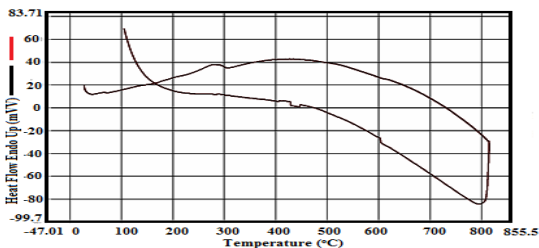
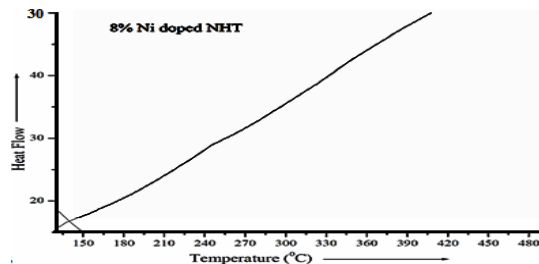
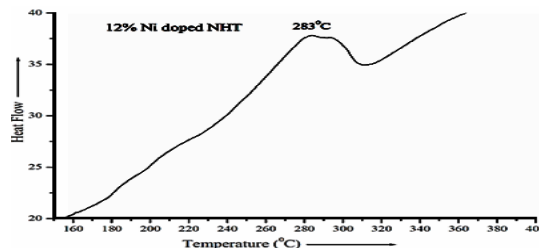


Fig. 3d. DSC analysis of 12% Ni doped NHT



CONCLUSION

The alkali titanate, sodium hexa-titanate (pure and Ni doped) were synthesized using conventional solid state reaction method and found that these materials having monoclinic structure and single-phase formation.

Morphological study of all samples shows rod shaped structure and it has been found that on increasing Ni dopant in pure sodium hexa-titanate the particle size decreases.

The most probable reason behind this is

replacement of titanium with nickel.

The thermal study of all prepared samples confirms that on increasing the doping percentage at 12% molar concentration an exothermic is obtained 283.

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Conflict of interest

There is no conflict of interest.

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