ORIGINAL PAPER

PHOTOCATALYSIS OF MANGANESE DOPED SODIUM HEXATITANATE ($Na_2Ti_{6-x}Mn_xO_{13}$)

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Abstract. *Pure and Manganese doped Sodium Hexa-titanates ($Na_2Ti_{6-x}Mn_xO_{13}$ where x = 0.0, 0.04, 0.08, 0.12) were synthesized using solid state reaction method. X-ray diffraction pattern reveals single phase and exhibit monoclinic structure of pure and doped samples. Morphologies of all synthesized materials have been studied using SEM. Photocatalytic behaviour of these samples have also been studied and found that on increasing the exposure time the suspension of methlyne blue graduadually decreases under the UV-exposure and finally beacmes almost colorless after ceratin time.*

Keywords: *Sodium Hexa-titanate, Monoclinic, SEM, Photocatalysis.*

1. INTRODUCTION

The general chemical formula of titanates can be written as, $A_2Ti_nO_{2n+1}$ [where A = Lithium (Li), Sodium (Na), Potassium (K), etc. and n lies between 2 to 8] have been a subject of intensive research during the last decade due to their various technological applications. These titanates have layered or tunnel crystal structures built of TiO_6 octahedra offering edges to interlaying cations [1-3].

Pure and manganese doped Sodium Hexa-titanates were prepared using solid-state reaction method. The general chemical formula of Sodium titanates is $Na_2Ti_nO_{2n+1}$ (where $2 \leq n \leq 8$). Among the different titanates, sodium octa-titanates ($Na_2Ti_8O_{17}$) and sodium hexa-titanates ($Na_2Ti_6O_{13}$) have good applications such as ion exchange [4, 5], photocatalysis [6], and sensors [7]. Sodium hexa-titante shows a tunnel structure and has good chemical stability as compared to the open ones [8]. These hexa-titanate materials have biomedical applications [9 -11] as well.

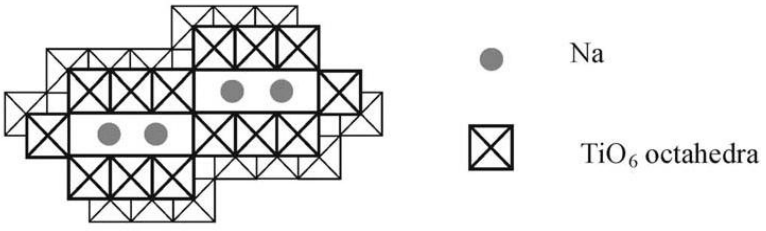

Figure 1. Layered Structure of Sodium Hexa-titanate [8].

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Sodium hexa-titanate can be synthesized using various methods. For example, sol-gel method, solid state route reaction method, hydrothermal method [12-14]. Properties of the sodium hexa-titanate material can be modified by doping transition metals.

2. MATERIALS AND METHODS

2.1. MATERIALS

For synthesis of sodium hexa-titante, titanium (IV) oxide (TiO_2) powder (<100nm, Purity 99.5%), and sodium carbonate (Na_2CO_3, Purity ≥ 99.5%) AR grade were purchased from Sigma Andrich and Thomas Baker respectively. AR grade methylene blue was also purchased from Thomas Baker.

2.2. METHODS

Sodium Hexa-titanate can be prepared by adding sodium carbonate (Na_2CO_3) and titanium dioxide (TiO_2) in a proper molar ratio.

$$Na_2CO_3 + 6TiO_2 \rightarrow Na_2Ti_6O_{13} + CO_2\uparrow$$

In the present work, various sample of pure and manganese (Mn) doped sodium hexa-titanate ($Na_2Ti_6O_{13}$) of different molar concentration (x=0.0, x=0.04, x=0.08, x=0.12) have been synthesized by solid state reaction method. For different molar concentration of manganese, chemical equations have been written below.

$$Na_2CO_3 + 5.96TiO_2 + 0.04MnO \rightarrow Na_2Ti_{5.94}Mn_{0.04}O_{13}$$

$$Na_2CO_3 + 5.92TiO_2 + 0.08MnO \rightarrow Na_2Ti_{5.92}Mn_{0.08}O_{13}$$

$$Na_2CO_3 + 5.88TiO_2 + 0.12MnO \rightarrow Na_2Ti_{5.94}Mn_{0.04}O_{13}$$

$Na_2Ti_6O_{13}$ ceramics were prepared by solid-state reaction method, taking stoichiometric amounts of Na_2CO_3 and TiO_2 powders, under acetone and calcined at 900 °C for 12 hours followed by furnace cooling. Powders were grinded properly for several hours using mortar to make it in nano/micro size. Furthermore materials were kept in a programmable furnace with controlled rate of heating and cooling. First set it to reach at 900°C with a heating rate of 4°/min then kept it constant for 12h. After that it reaches at room temperature with controlled cooling rate 4°/min. To prepare pure and magnesium doped (x = 0.0, 0.04, 0.08, 0.12 mol %) specimens, desired amount of MnO powder was added in a mixture of sodium carbonate and titanium dioxide and obtained materials was recycled through the same process as described above.

3. RESULTS AND DISCUSSION

3.1. RESULTS

Fig. 2 shows the X-ray diffraction patterns of pure, and manganese doped $Na_2TiO_6O_{13}$ samples recorded at room temperature. X-ray diffraction pattern reveals single phase and exhibit monoclinic structure. Furthermore, no extra peaks were observed in the XRD pattern showing the single phase sample formation and successful manganese doping in $Na_2Ti_6O_{13}$ matrix. Using the below equation lattice parameters were calculated for all samples.

$$\frac{1}{d^2} = \frac{h^2}{a^2 sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 sin^2\beta} - \frac{2hlcos\beta}{acsin^2\beta} \quad (1)$$

where h, k, and l are miller indices, a, b and c are lattice parameters, d is the spacing between successive miller indices (hkl) planes, α is the angle between vectors b and a, β is the angle between *a* and *c*, and γ is the angle between a and b. In case of monoclinic structure the lattice parameters cannot be equal ($a \neq b \neq c$), while $\alpha = \gamma = 90°$ and $\beta \neq 90°$.

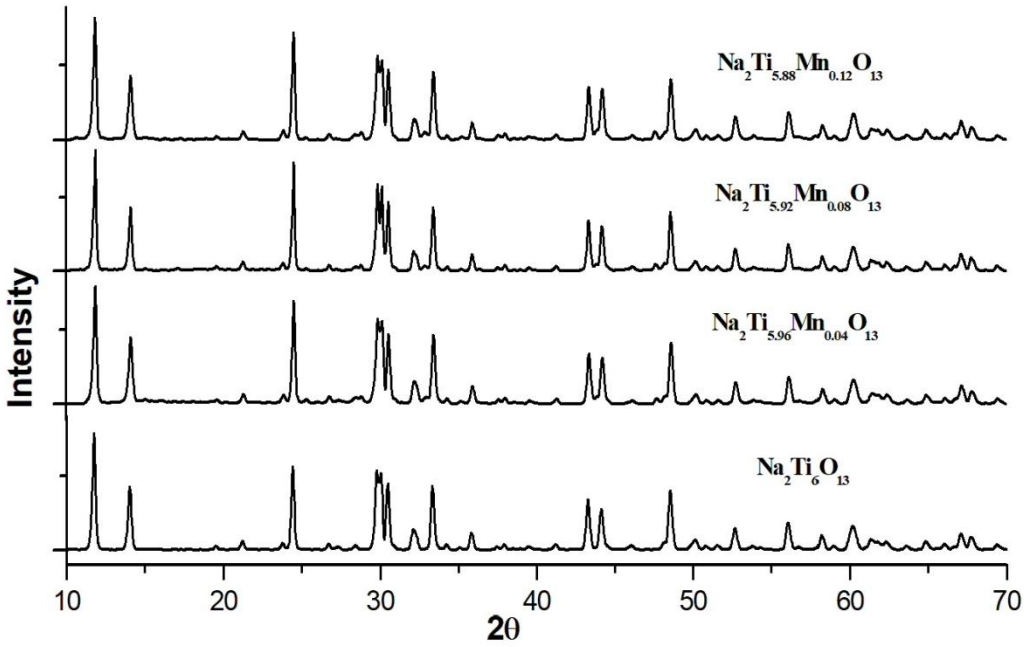

Figure 2. XRD analysis of pure and manganese doped Sodium Hexa-titanmate.

Crystalline size of all samples have also been calculated using Debye-Scherrer equation.

$$\tau = \frac{K\lambda}{\beta cos\theta} \quad (2)$$

where τ is the mean size of the crystalline, *K* is a dimensionless shape factor, λ is the X-ray wavelength, β is the full width half maxima, and θ denotes the Bragg angle. For calculating

the cryastalline size, β has been obatained from XRD, using PowderX software, value of K is 0.91, θ has also obatained from XRD pattern, λ=1.5406Å (Cu K-alpha).

Field emission scanning electron microscopy gives the information of morphology of the synthesized materials. Morphology of all the samples have been observed using FE-SEM (Nova Nanosem 450) at 10kV acceleration voltage, in secondary electron mode, at different magnifications. Fig. 3 (a-d) shows the microstructure of all synthesized materials and they are rod shape particles [15-18].

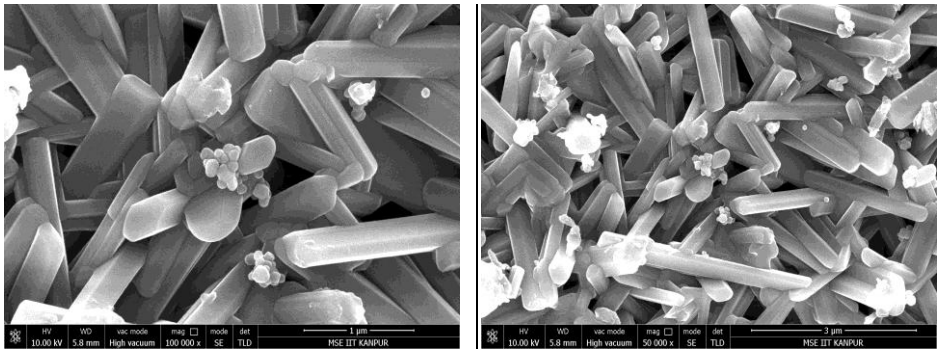

Figure 3a. SEM images of Pure Sodium Hexa-titanate.

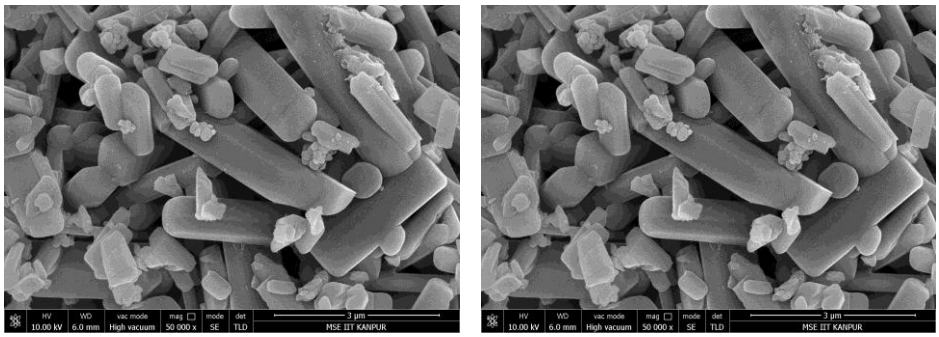

Figure 3b. SEM image of Mn doped Sodium Hexa-titanate at x=0.04.

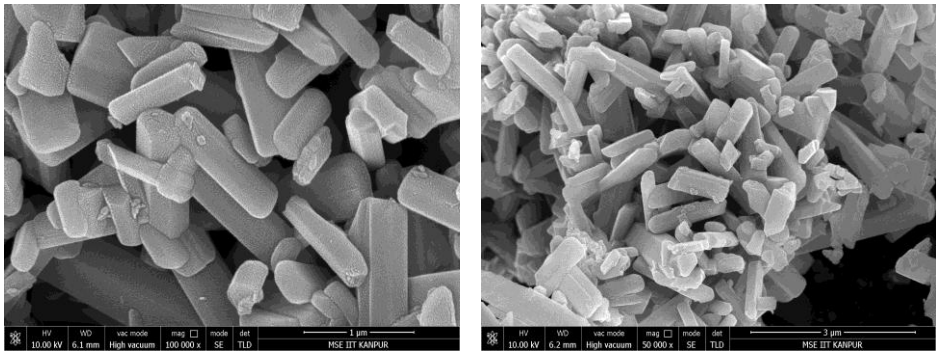

Figure 3c. SEM image of Mn doped Sodium Hexa-titanate at x=0.08.

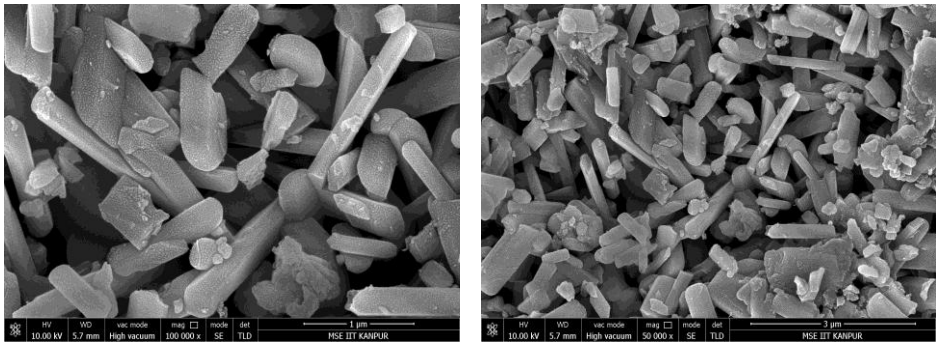

Fig. 3d. SEM images of Mn doped sodium hexa-titanate at x=0.12.

Pure sodium hexa-titanate prepared in this work was tested as photocatalyst [19-24] on the degradation reaction of methylene blue under UV irradiation and evaluated by measuring the photodegradation of a solution of methylene blue (5 mg of methylene blue was added in a 100 mL in a quartz vessel) in the presence of 100mg $Na_2Ti_6O_{13}$ under exposure to UV light at room temperature.

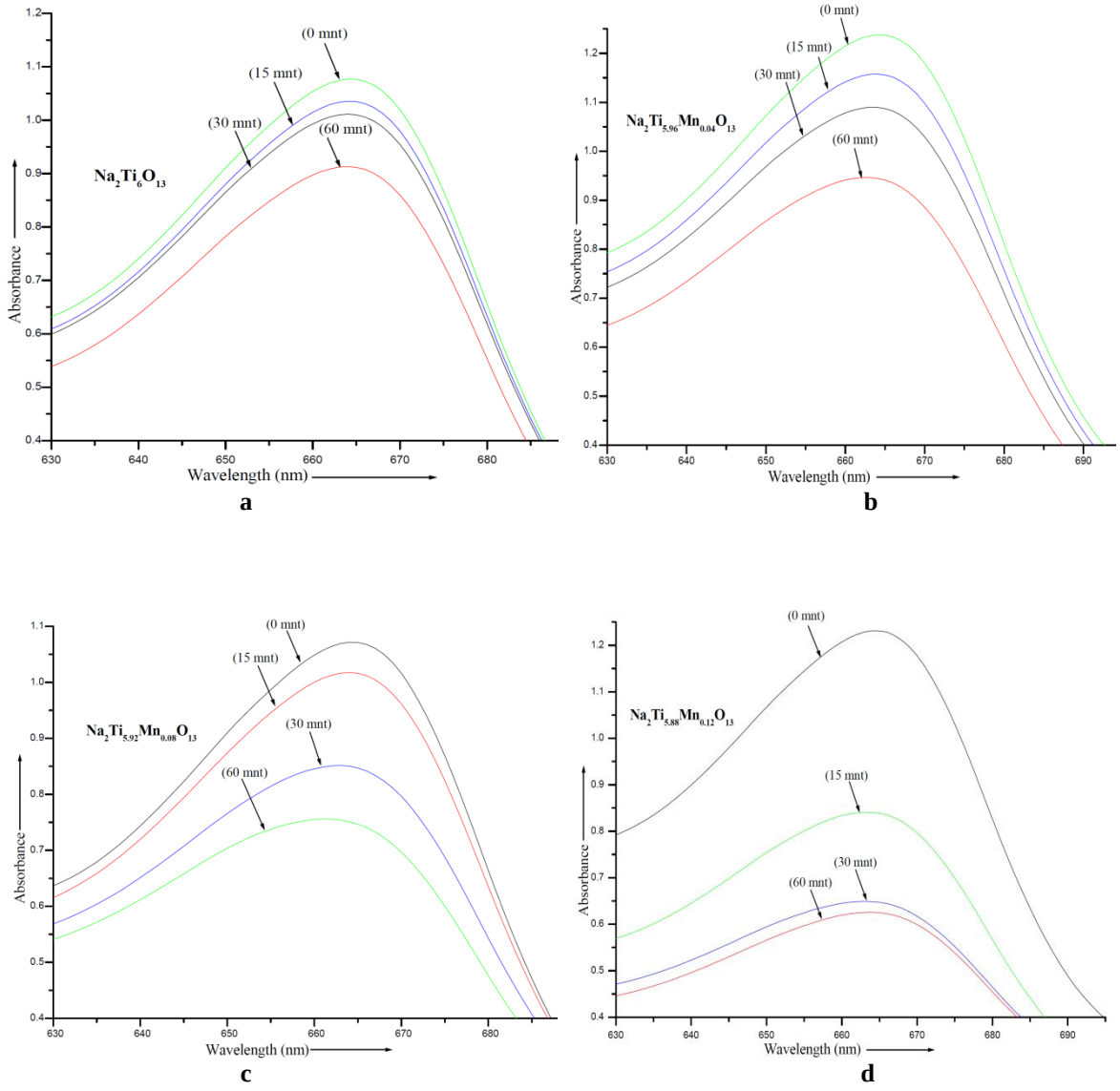

Figure 4. Absorbance of methylene blue solution in the presence of pure and Mn doped sodium hexa-titanate.

3.2. DISCUSSION

It has been found that as increasing the dopant percentage of manganese, unit volume of the synthesized materials decreases. The possible reason behind this is that particle size of the samples decreases on increasing doping percentage of manganese in pure sodium hexa-titanate which is revealed in FE-SEM analysis.

Table 1. Crystalline size of pure and Mn doped sodium hexa-titanate.

S. No.	Samples	Mean crstalline size (τ)
1	$Na_2Ti_6O_{13}$	0.211
2	$Na_2Ti_{5.96}Mn_{0.04}O_{13}$	0.203
3	$Na_2Ti_{5.92}Mn_{0.08}O_{13}$	0.20
4	$Na_2Ti_{5.88}Mn_{0.12}O_{13}$	0.20

Fig. 3a shows SEM image of pure Sodium Hexa-titanates and the diameter lies between 0.1μm to 0.25μm (edge to edge) and length lies between 0.8μm to 1.3μm. Fig. 3b, 3c, and 3d shows the SEM image of Mn doped sodium hexa-titanates with 4%, 8%, and 12% concentration and the diameter lies between 0.10μm to 0.25μm and length 0.70μm to 1.2μm. Average size of the synthesized materials having rod shape is shown in table 2.

Table 2. Particle size of pure and manganese doped Sodium Hexa-titanate.

S. No.	Samples	Average Length of Rod
1	$Na_2Ti_6O_{13}$	1.20 μm
2	$Na_2Ti_{5.96}Mn_{0.04}O_{13}$	1.16 μm
3	$Na_2Ti_{5.92}Mn_{0.08}O_{13}$	1.10 μm
4	$Na_2Ti_{5.88}Mn_{0.12}O_{13}$	1.06 μm

Figs. 4a-d shows the decay of absorbance of pure and manganese doped sodium hexa-titnate ($Na_2Ti_{6-x}Mn_xO_{13}$ where x = 0.0, 0.04, 0.08, 0.12) at different time interval (0, 15, 30 & 60 minutes). The absorbance of the samples have been recorded during reaction and solutions were under continuous stirring. The absorption spectra corresponded to the UV-Vis light irradiation. The colour of the solution faded regularly with increase in irradiation time. Finally, the solution changed from blue to approximately colorless. When no sodium hexa-titanate was added in methylene blue solution then color of the materials remained unchanged under the UV irradiation. Pure and manganese doped sodium hexa-titanate, act efficiently as a photocatalyst and break methylene blue molecules into several different smaller molecules.

Table 3. Decay of absorbance of pure and manganese doped Sodium Hexa-titnate at different time interval with methylene blue.

S. No.	Samples	Percentage of degradation with irradiation time		
		15 min	30 min	60 min
1	$Na_2Ti_6O_{13}$	03.85	05.890	29.74
2	$Na_2Ti_{5.96}Mn_{0.04}O_{13}$	06.51	12.030	23.57
3	$Na_2Ti_{5.92}Mn_{0.08}O_{13}$	05.09	20.470	29.29
4	$Na_2Ti_{5.88}Mn_{0.12}O_{13}$	31.70	47.303	49.63

4. CONCLUSIONS

Manganese doped Sodium Hexa-titanates were prepared using solid-state reaction method and calcined at high temperature. XRD peaks give the information of phase and structure of the synthesized materials. Crystalline size has been calculated using Scherrer formula.

Morphologies of pure and doped hexa-titanate were studied by scanning electron microscopy which reveals that particle size slightly decreases on increasing the concentration of manganese in sodium hexa-titanate. Photocatlytic degradation of the several materials has

been tested with methylene blue under the UV-exposure at different time intervals. Percentage of degradation has increased on increasing the concentration of manganese. Photocatalytic capabilities have found better in $Na_2Ti_{6-x}Mn_xO_{13}$ (at x=0.12) because of the smaller particle size.

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