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Effect of Fe doping on Structural and Transport Properties of inverse spinel Zn_2TiO_4

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Abstract : Abstract:Undoped and Fe(II)doped Zinc titanate samples were prepared by microwave assisted solvothermal method. Structural and optical properties were carried by XRD, SEM, EDS, FTIR, UV-Vis and Raman Spectra. Transport properties were also carried on the prepared samples. Randomly oriented rodlike nanostructures were observed from SEM studies.Fe addition was evident from the EDS profiles. FTIR and Raman Studies confirmed the Fe^{2+} ions and a slight increase of absorption were observed from Uv-Vis Spectra. Dependence of Electrical conductivity and Thermopower on Fe content and Temperature were reported in this paper. The increase of conductivity from$1.8x10^{-3}$ to $2.2x10^{-3}$ $\Omega^{-1}cm^{-1}$ and thermopower from 40 to 60 μV/K with doping of Fe at room temperature was observed.
Keywords : TiO_2, EDAX, XRD, SEM, Zinc Titanate, Photocatalyst.

Introduction

Titanium oxide is one of the well-studied binary oxides for its usage as aphotocatalyst. Several authors reported that it suffers from relatively high energy bandgap, the high recombination rate of photogenerated electrons and holes and low absorption capability of visible light (1-5). Zinc titanate is the most extensively studied ternary system that used to overcome the shortcomings of TiO_2 owing to its different polymorphs. Inverse spinel cubic phase Zn_2TiO_4 is particularly important for photocatalytic studies owing to its band gap and band structure (6-10). Fe doped TiO_2 was studied by many authors and their results revealed substitution of Fe^{2+} or $Fe^{3+}$with Ti^{3+} or Ti^{4+}in TiO_2 as their radii and energy levels are very close. (11). The enhanced photocatalytic activity of Fe doped TiO_2 for phenol under visible light than that of P25 TiO_2 were found and interpreted interms of formation of shallow traps in TiO_2 lattice. (12). In the present work structural and transport properties of Fe doped Zn_2TiO_4 were carried to study and understand such mechanism that helps improve photocatalytic property Zn_2TiO_4.

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Experimental

Synthesis of Fe doped Zn_2TiO_4

The precursors used in this work were analytical Grade Zinc acetate dihydrate, Ferric acetate, titanium isopropoxide (TIP), oxalic acid, Ethanol and deionized water. All the Chemicals were purchased from S.D. Fine-chemLtd. And used without further purification. In a typical synthesis, 250ml of 0.4M zinc acetate solution in ethanol was prepared at 70°C and cooled to room temperature.250mL of the 1M Oxalic acid solution in ethanol was added slowly with stirring to give a white gel-like suspension. 12mL of TIP was then added, immediately followed by 100mL of deionized water with constant stirring for 2h. The suspension was transferred to a pyrex dish and then kept it in the domestic microwave oven (Bajaj India make) for 20 minutes operated at 500watt. The resulted powder was washed thoroughly with plenty of deionized water and then with absolute alcohol and sun-dried for 24hrs. It was annealed at 1000°C for one hour in a muffle furnace, cooled to room temperature and finely ground. This resulted in zinc titanate containing 50-50 molar ratios of zinc and titanium. By the same procedure Fe doped Zinc titanate was prepared by taking 10% (molar ratio) Ferric acetate. The resulted powders were used for characterization.

Characterization

The XRD patterns were recorded at room temperature from 10 to 80° of diffractionangle (2θ) using Philips (**PW1830)** X-ray powder diffractometer using Cu K_α radiation (λ = 1.54056Å) with Ni monochromator. SEM and EDS analysis were done using ZEISS GEMINISEM 500 with amagnification of 10k resolution. FTIR spectrum was recorded on a Jasco FT/IR 6000 spectrometer and recorded with KBr disk (1:10, sample/KBr) over a range of 4000 – 400 Cm^{-1}. HORIBA LabRAM HR was used to carry Raman analysis at room temperature. The spectra were recorded over a range of 100-1200 cm^{-1}Electrical conductivity and thermopower measurements were carried from 300-800K after making pellets of 12mm diameter using the setup supplied by Pushpa Scientifics, Hyderabad.

Results and Discussion

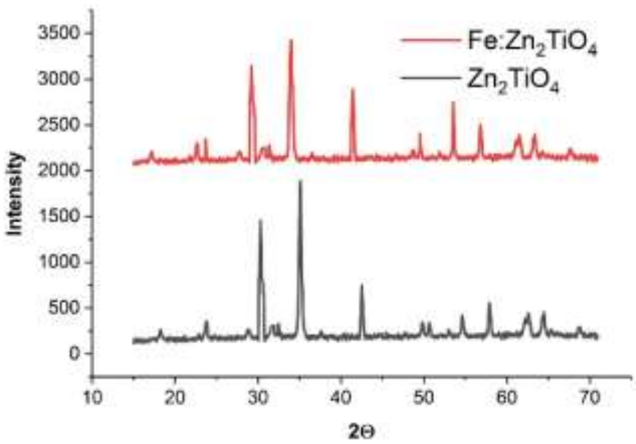

Figure 1 shows the x-ray diffractogram of Zn_2TiO_4 and Fe doped Zn_2TiO_4.

Inverse spinel cubic phase $Zn_2TiO_4$was identified using JCPDS Card no. 00-025-1164, 00-021-1276 and 00-025-1164 for ZnO, rutile TiO_2,and inverse spinel cubic Zn_2TiO_4 respectively as reference patterns. Lattice parameters and unit cell volume were obtained by Rietveld refinement using standard ICSD data as input for refinement using Full Prof suite 2017 program. Table 1 summarizes all the crystal data. The average crystallite size (T) was estimated (±5%) using the Scherrer equation

$$T = \frac{0.9\lambda}{\beta \cos\theta}$$

where T is the crystallite size, λ the X-ray wavelength, θ the Bragg angle, and β the full width at half maximum (FWHM). The crystallite size was estimated to be 80nm and 90nm respectively for undoped and doped Zn_2TiO_4.Figure 2 depicts the SEM micrographs and well-formed nanoparticles are evident from these micrographs. The average grain size was found to be 50nm and 60nm respectively for undoped and doped Zn_2TiO_4.

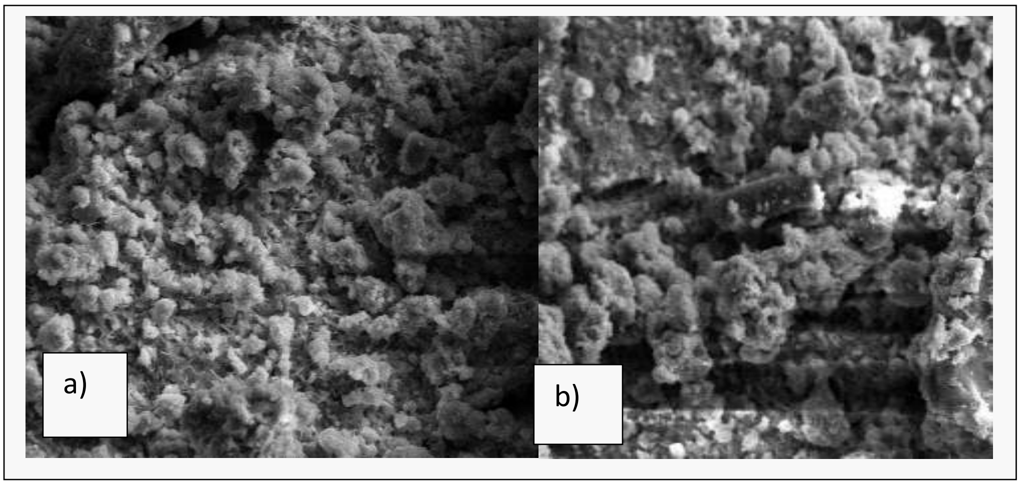

Figure 2. SEM micrograph a) Zn_2TiO_4 and b) $Fe:Zn_2TiO_4$

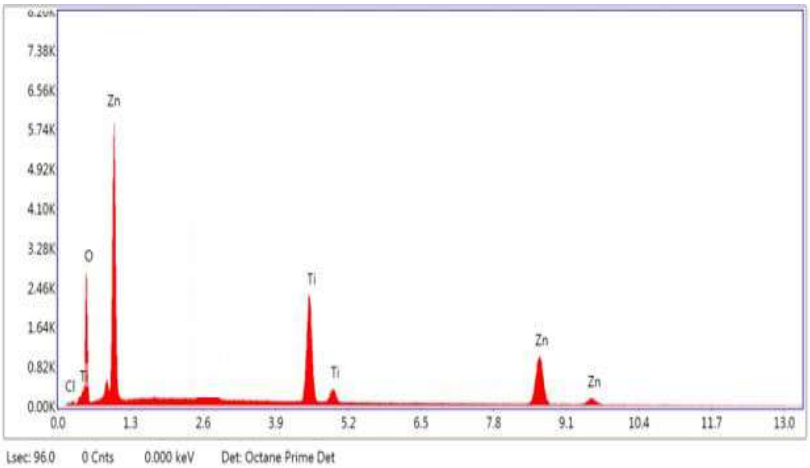

Figure 3. EDAX profile of Zn_2TiO_4*-

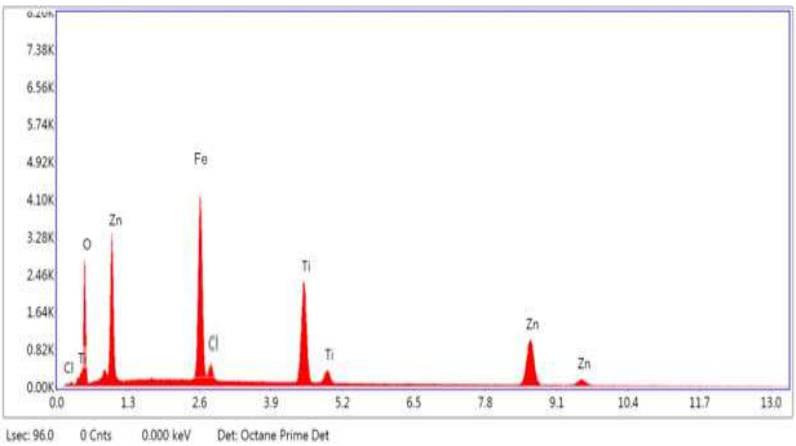

Figure 4. Fe doped Zn_2TiO_4.

Zn and Fe addition was evident from EDAX profilesshown in figures 3 and 4.This was also confirmed from FTIR and Raman spectra shown in figure 5 and figure 6 respectively. Addition of Fe^{2+} ion brought no change in the crystal structure that was evident from XRD. This may be due to the substitution of Ti^{2+}at $Fe^{2+}$and absence of ZnO and Zn^{2+}, Ti^{3+}or Ti^{4+} that were evident from FTIR and Raman spectra.From Raman spectrum, it is also evident that the Fe-O bond exists corresponding peaks are found at 611, 446 and 143 cm^{-1}. The results were in good agreement with the values reported in literature (12-14).

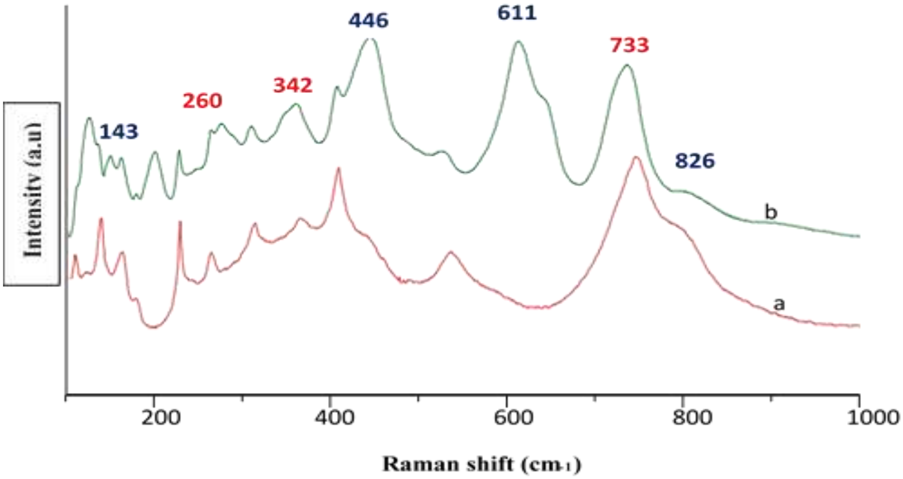

Figure 5. Raman Spectra of Zn_2TiO_4 and Fe doped Zn_2TiO_4

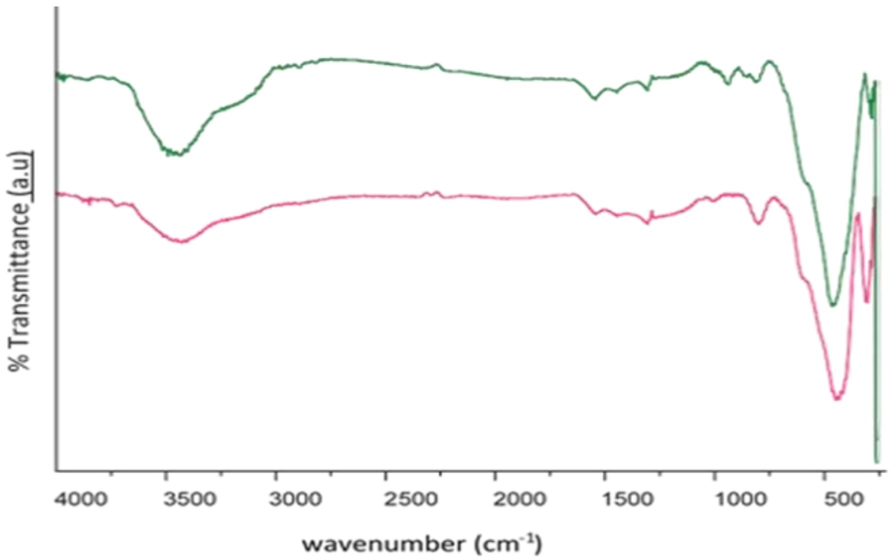

Figure 6. FTIR Spectra of Zn_2TiO_4 and Fe doped Zn_2TiO_4

Figures 7 and 8 depict the temperature variation of electrical conductivity and thermopower of undoped and Fe doped zinc titanate. Electrical conductivity measurements showed an increase in conductivity from 10^{-3} to $6x10^{-3}\ \Omega^{-1}cm^{-1}$ with the increase of temperature from 300-800K confirming its semiconducting nature. The p-type conductivity of the sample was confirmed by thermopower measurements. Thermopower was found to be 50µV/K at room temperature. The increase of conductivity and thermopower indicate thermal excitations that may be the result of the addition of Fe^{2+} increasing the phonon interaction (15). The increase of both conductivity and thermopower with Fe addition were observed from figures 7 and 8. The increase of electrical conductivity may be due to the decrease of bandgap energy that was observed from optical absorption study shown in figure 9.

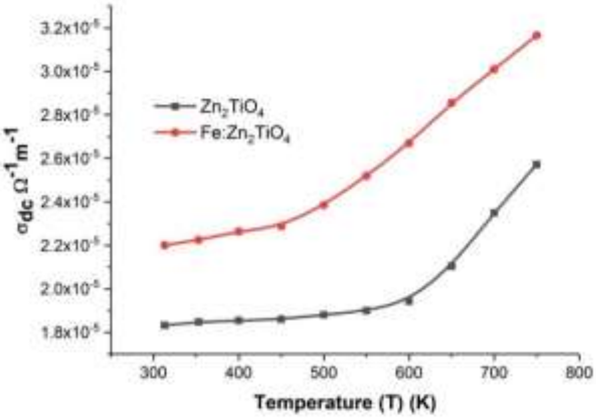

Figure 7. Temperature variation of the conductivityof Zn_2TiO_4 and Fe doped Zn_2TiO_4

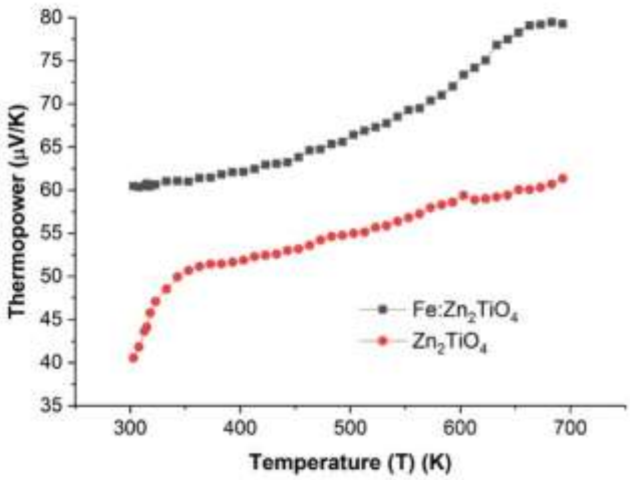

Figure 8. Temperature variation of the thermopowerof Zn_2TiO_4 and Fe doped Zn_2TiO_4

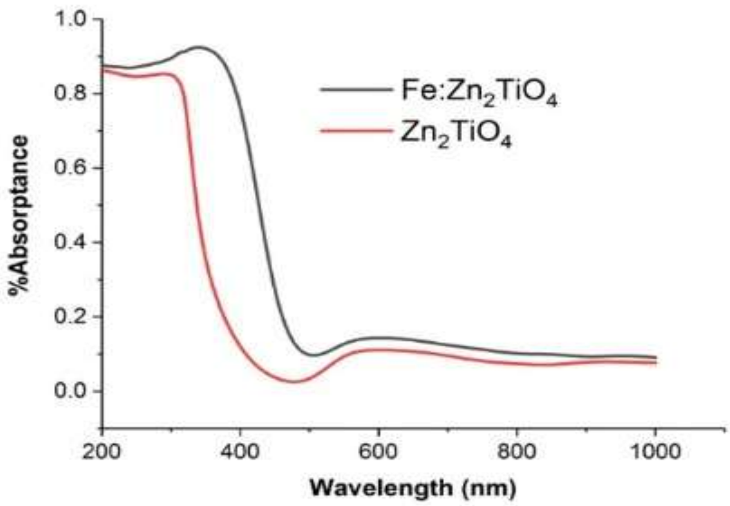

Figure 9.Uv-Vis Spectra of Zn_2TiO_4 and Fe doped Zn_2TiO_4

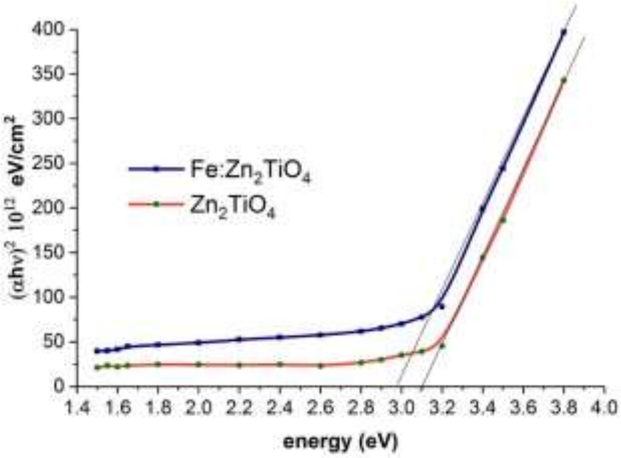

Figure 10. Energy gap of Zn_2TiO_4 and Fe doped Zn_2TiO_4

The energy band gap was determined to be 3.1 eV and 3 eV for undoped and Fe doped zinc titante for Zn_2TiO_4 the reported value is in good agreement with the literature.

Conclusion

Undoped Zn_2TiO_4 and Fe doped Zn_2TiO_4 powders were successfully prepared by microwave assisted solvothermal method. Pure crystalline phase Zn_2TiO_4 was identified and with the inclusion of Fe^{2+} into it no change in crystal structure was observed. Cell parameter cell volume and bandgap were found to be decreased with Fe addition.XRD, FTIR and transport properties confirmed the same. Further investigation of effect of compositional changes and calcination temperatureis needed to interpret the results.

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