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Spectral Characterization on Mn^{2+} Doped TiO_2 Thin Films.

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ABSTRACT

Thin films of semiconductor oxide materials have attracted numerous applications in electronic and optoelectronic devices such as protective coatings, heat mirrors and catalysis. Transparent conductiveing oxide based semiconductor materials play a crucial role in the development of thin film solar cells. Titanium Oxide (TiO_2) thin films have various appealing features for technical applications in solar energy conversion, flat panel displays, electrochromic devices, invisible security circuits, LEDs, etc. In the present studies, Mn^{2+} doped TiO_2 thin films were prepared by using sol-gel technique. From X-ray diffraction studies, the crystal system is indexed to be anatase crystalline state. The calculated average crystallite size of the prepared samples is 33 nm. SEM evidenced irregular shaped particle size clusters and EDS confirms the presence of constituent elements in the prepared material. The characteristic vibrational modes of constituent elements in the host lattice were confirmed by FT-IR studies.

Keywords: TiO_2, Mn^{2+} ions, Sol-gel, XRD, SEM and FT-IR.

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INTRODUCTION

Nanotechnology controls the matter on the atomic and molecular scale. It includes making products such as electronic devices, catalysts, sensors, etc. Most of the current research and development activities are in the field of functional nanotechnology. This term describes applications in which material nanostructures are used to produce optical or magnetic properties. Titanium dioxide is the naturally occurring oxide of titanium with chemical formula TiO_2. TiO_2 has attracted significant attention from researchers because of the many interesting properties that make it suitable for a variety of applications. For instance, TiO_2 has high corrosion resistance and chemical stability, excellent optical transparency in the visible and near infrared regions. It has high refractive index which makes it useful for antireflection coatings in optical devices [1]. It has been used mostly as a pigment in paints, sunscreens, ointments toothpaste etc. TiO_2 thin films have been emerged as one of the most promising oxide materials owing to their optical, electrical and photo-electrochemical properties. The synthesis of TiO_2 and its thin films formed by conventional and advanced sol-gel processes have been reported [2-6].

Titanium dioxide thin film materials act as photocatalytic effect [7, 8]. TiO_2 is regarded as the best material of potential application, because it has stable chemical property, no toxicity for organisms, no photo-corroding and higher bandgap energy (3.2 eV). It has been reported widely for its numerous applications from optoelectronics to cosmetics [9-11]. It also has excellent photocatalytic oxidative properties that depend on crystal form [12]. TiO_2 sometimes has been used in water and air pollution treatments [13]. It exhibits unique electrical and chemical properties in various technological and engineering applications like humidity sensor, gas sensor and membrane [14, 15]. TiO_2 is also proposed for solar cells and laser diodes because of its high refractive index and stability [16].

Sol-gel process is a convenient and versatile method for preparing transparent thin film at low temperature. It is involved many complex processes for both chemical and structural nature. The physical, chemical and mechanical properties are much dependant on the properties of the precursor solution [17]. Therefore, optimizing the precursor solution may produce great results of TiO_2 thin film. Sol-gel process is used to deposit transparent materials in combination with spin coating technique. Coatings are of high purity and structural homogeneity is achieved. Rao et al. have reported the results on different oxide materials in their earlier studies [18-27]. In the present investigation, TiO_2 thin films were prepared by doping Mn^{2+} ions using sol-gel method and subsequently characterized by XRD, SEM with EDS, TEM and FT-IR studies about their microstructural properties.

EXPERIMENTAL

Thin films of titanium oxide were prepared using sol–gel technique. Titanium IV isopropoxide ($Ti(OCH(CH_3)_2)_4$ as precursor and isopropyl alcohol$(CH_3)_2CHOH$ as solvent were used to synthesize the sols. Glacial acetic acid was used in order to begin hydrolysis via an esterification reaction. To prepare a stable precursor solution, first $Ti(OCH(CH_3)_2)_4$ and $(CH_3)_2CHOH$ were mixed. The molar ratio of 1.3 was maintained between $Ti(OCH(CH_3)_2)_4$ and $(CH_3)_2CHOH$. This mixture was stirred for 30 min at room temperature. Acetic acid was slowly added into the alkoxide solution under stirring for 30 min at room temperature. A molar ratio of 1:3 was utilized between acetic acid and $Ti(OCH(CH_3)_2)_4$. A white precipitate is formed. Finally Methanol (1:8) was added to get a moonstone color precipitate. Let this precipitate settle for 60 min. A soda lime glass (SLG) was dipped in this sol and remain for 30 min and one more SLG for 60 min. Both the SLG's are annealed at 500^0C after adding Manganese oxide (MnO) to the above solution.

X-ray diffraction patterns were recorded on PANalytical Xpert Pro diffractometer with CuK_α radiation. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images are taken on ZEISS EVO 18. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Bruker FT-IR spectrophotometer is used for recording FT-IR spectrum of the prepared samples in the region 400-4000 cm^{-1}.

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RESULTS AND DISCUSSION

XRD Studies

TiO_2 exhibits anatase crystalline state. XRD spectra of the prepared Mn^{2+} doped TiO_2 thin films was shown in Figure-1. These prepared thin films are with a preferred orientation of (101), (004) and (211) peaks which confirms the anatase crystalline state. XRD pattern of this optimized sample is in good agreement with the reference pattern of TiO_2 with standard diffraction data of JCPDS file No.21-1272 [28]. The average crystallite size of the sample is calculated from the full width at half maximum intensity of the XRD peaks using Debye - Scherrer's formula,

$$D= (K \lambda / \beta \cos\theta)$$

where

D is the mean crystallite size,
K = 0.9 is Scherrer's constant,
λ is the wavelength of the incident beam,
θ is the diffraction angle,
and β is the full width half maximum intensity of the diffraction peak.

From the XRD pattern, the calculated value of average crystallite size is 33 nm.

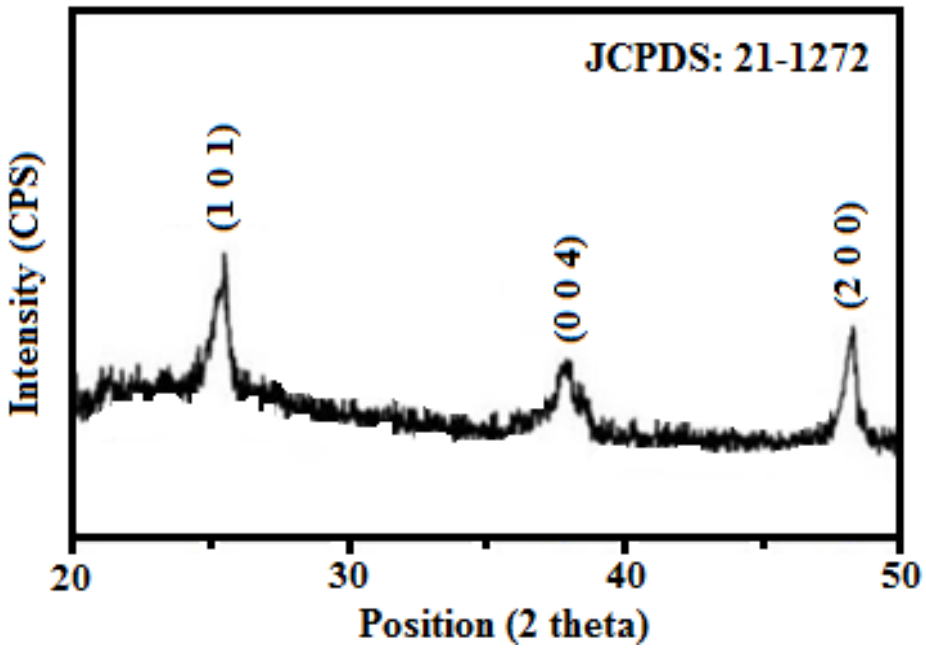

Figure-1: Powder XRD pattern of Mn^{2+} doped TiO_2 thin films

Morphological Studies

SEM and EDS analysis was used to study the morphology and chemical composition of as synthesized sample. Figure-2 shows the SEM micrographs of Mn^{2+} doped TiO_2 thin films taken at different magnifications. From low resolution SEM images, one can be clearly observe that the prepared sample shows agglomeration with an irregular morphology. The agglomeration could be induced by densification resulting from the narrow space between particles. SEM reveals that the sample consists of irregular shaped sphere like structures. EDS measurements confirm the incorporation of manganese ions into the host material. Figure-3 shows EDS pattern of Mn^{2+} doped TiO_2 thin films. The pattern showed the elemental compositions of Ti, O and manganese. From this it was confirmed that the sample contains doped manganese species. The nanocrystalline nature of the samples was confirmed by TEM measurements. The TEM image of Mn^{2+} doped TiO_2 thin films was depicted in Figure-4. The particles are more or less uniformed in size with irregular shape.

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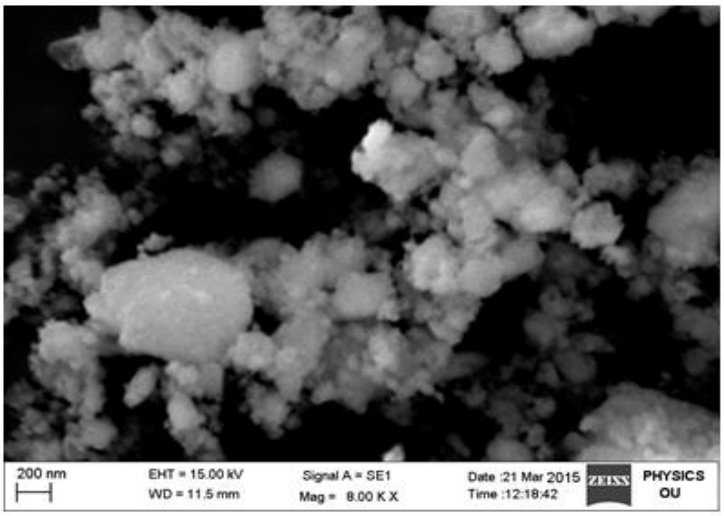

Figure-2: SEM image of Mn^{2+} doped TiO_2 thin films

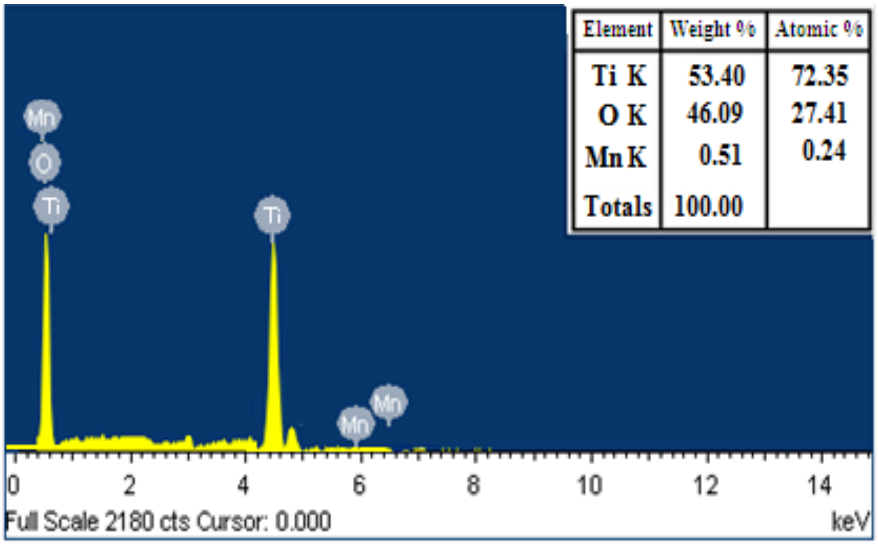

Figure-3: EDS spectrum of Mn^{2+} doped TiO_2 thin films

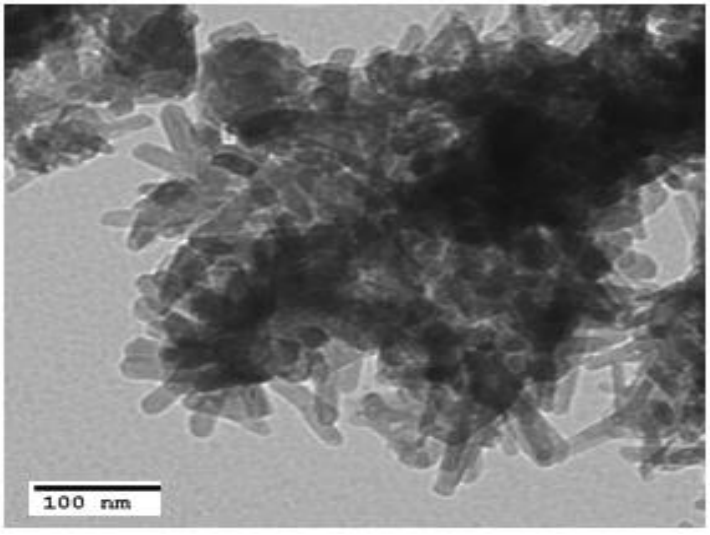

Figure-4: TEM image of Mn^{2+} doped TiO_2 thin films

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FT-IR Studies

Figure-5 shows FT-IR characteristic peaks of surface functional groups of Mn^{2+} doped TiO_2 thin films. The spectrum shows absorption peak in the spectrum at 3450 cm^{-1} possibly attributed to the OH group (molecular water). Ti-O-Ti bands appear in the range 500-900 cm^{-1}. Additionally the bands at 2956, 2836 and 1425 cm^{-1} were assigned to C-H vibrations. The C-H bond could be of NH stretching vibrations [29].

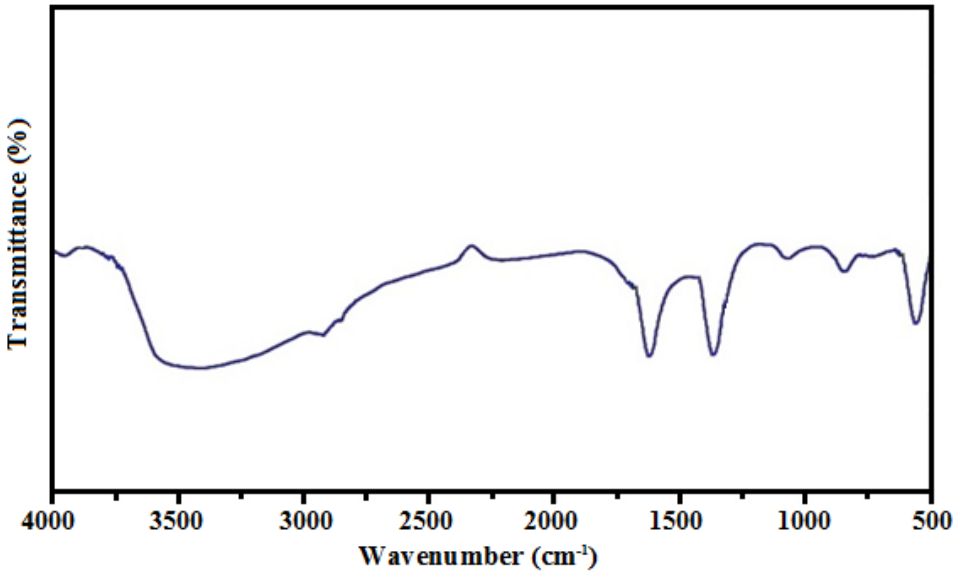

Figure-5: FT-IR spectrum of Mn^{2+} doped TiO_2 thin films

CONCLUSIONS

TiO_2 thin films were prepared successfully by sol-gel method by doping Mn^{2+} ions. X-ray diffraction studies revealed the crystal system is indexed to be anatase crystalline state with JCPDS file No. 21-1272. The calculated average crystallite size of Mn^{2+} doped TiO_2 thin films is around 33 nm. SEM revealed irregular shaped sphere like structures and EDS confirms the presence of constituent elements in the host material. The formation of nanorods is confirmed by TEM analysis. The characteristic vibrational modes of host lattice are evidenced by FT-IR spectrum.

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