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Structural and dielectric observation of Eu^{3+} doped titanium dioxide nanoparticles

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ABSTRACT

Europium (Eu^{3+}) doped TiO_2 particles have been successfully synthesized by using sol-gel technique. The prepared samples were characterized by XRD, FT-IR, UV-Vis, SEM and EDX measurements. The XRD and EDX measurements confirm the presence of Eu^{3+} and TiO_2 nanoparticles. The dielectric and electrical conductivity studies of the samples were done for a frequency range of 100Hz – 2MHz. The conductivity variation with the Eu^{3+} doped TiO_2 system has been analyzed by correlating the presence of ionic contribution to the electrical conductivity process. Also, the frequency dependence of dielectric constant and conductivity were studied.

Keywords: Titanium dioxide, Sol-gel, Nanoparticles, Europium

INTRODUCTION

Recently, lanthanide doped semiconductor has attracted more attention due to the many profitable potential application in photoelectric devices, and optical communication. This interest is mainly due to their optical properties that affect emission lifetime, structure of emission spectra, luminescence quantum efficiency and concentration quenching. TiO_2 is considered as a good host candidate for rare earth doping due to its good properties such as mechanical, thermal, and anticorrosive properties [1]. Considering the wide interest in TiO_2 nanoparticles, the synthesis on a large scale with less impurities is thus of practical importance. Various preparation methods have been developed for the synthesis of TiO_2 nanoparticles, for example, chemical vapor synthesis, ultra sonic irradiation, flame synthesis, hydrothermal methods and sol-gel [2].

Impedance spectroscopy is one of the powerful tools for the electrical characterization of solid materials. Parameters like complex impedance, AC conductivity and dielectric relaxation can be measured by the dielectric spectroscopic technique. The charge transport properties in ionically conducting glasses are a current topic of research due to their potential applications in vacuum ultraviolet optics and semiconductor [3]. Among various methods for the synthesis of Eu^{3+} Titania nanocomposites, the sol-gel process needs special mention because of the low processing temperature, high purity and homogeneity of the resultant products. To our knowledge no studies have been reported on the synthesis and characterization of Eu^{3+} nanoparticles doped TiO_2 matrix. Parameters like electrical conductivity and dielectric constant for a frequency range of 100Hz – 2MHz were studied.

MATERIALS AND METHODS

Precursor titanium isopropoxide $\text{Ti}(\text{OC}_3\text{H}_7)_4$ is added drop wise with dopant precursor Eu^{3+} dissolved in isopropyl alcohol and stirred for 30mins. The metal oxide gel was produced by increasing the pH by drop wise addition of 1 N NH_3 solution. The resultant solution was filtered after 1 day of aging in order to remove any particulates. The precipitate was washed several times with distilled water and dried in furnace for 24 h to remove the solvent. Removal of residual organics and stabilization of the materials were carried out by calcinations for 3 h at 400°C [4].

The structural characterizations were done by X-ray diffraction (PAN alyticalX'Pert PRO), Scanning Electron microscope (SEM) and Fourier transform infrared spectroscopy (Perkin E). The dielectric measurement was done by using impedance spectroscopy (HIOKI 3532-50 LCR HITESTER).

RESULTS AND DISCUSSION

X – RAY POWDER DIFFRACTION ANALYSIS

The powder XRD patterns of the rare earth doped titanium di oxide prepared by sol-gel method are shown in Figure 1 which can be indexed as a single phase of anatase. No other polymorph of titania is observed and no rare earth peaks are found except europium in XRD pattern of Figure 2.

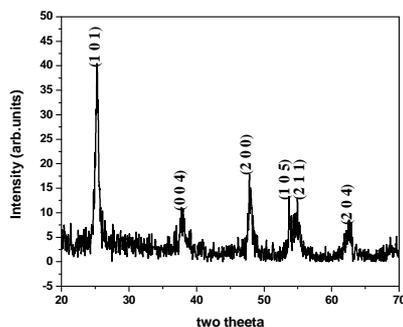


Figure 1 XRD of TiO₂

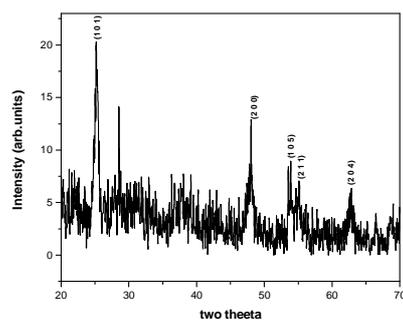


Figure 2 XRD of TiO₂:Eu³⁺

SCANNING ELECTRON MICROSCOPE AND EDX

Figure 3 and 4 depicts the Scanning electron microscopy (SEM) images, however temperature has a pronounced effect on particle morphology. The photographs of the samples showed spherical clusters of crystallized particles. These spherical particles consist of primary anatase nanocrystals interlayer by small fraction of amorphous material. The energy dispersive X-ray analysis Figure 5 and 6 confirms the presence of elements TiO₂ and Eu³⁺ present in the sample.

FT-IR

Figure 7 and 8 shows the FT-IR spectra of the obtained pure TiO₂ and Eu³⁺:TiO₂ nanoparticles after calcined at 400°C for 3h. In both the spectrum a broad absorption band between 800 and 1600cm⁻¹ is ascribed to the vibration absorption of the Ti-O-Ti linkages in TiO₂ nanoparticles. The absorption bands at 622cm⁻¹ is due to Ti-O bond of anatase phase. The absorption at 1061cm⁻¹ and peaks appeared at 1121cm⁻¹ is attributed to Ti-O-N. The vibrations band at 1710 cm⁻¹ can be associated to the asymmetric stretching mode of titanium carboxilate. The peaks in between 2253cm⁻¹ and 2326 cm⁻¹ are assigned to C-H stretching vibrations of alkane groups. The alkane and carboxilate group are attributed to titanium tetra isopropoxide and 2-propanol. The peak at 3209cm⁻¹ and 1722cm⁻¹ correspond to the surface adsorbed water and hydroxyl group. These peaks are strongly confirming the presence of hydroxyl ions in the structure of the samples [5]. When the doping concentration was increased no other peaks were formed. The obtained FT-IR is in good agreement with the XRD analysis and no alkoxy groups are present in the samples.



FIGURE 3 SEM image of the pure TiO₂

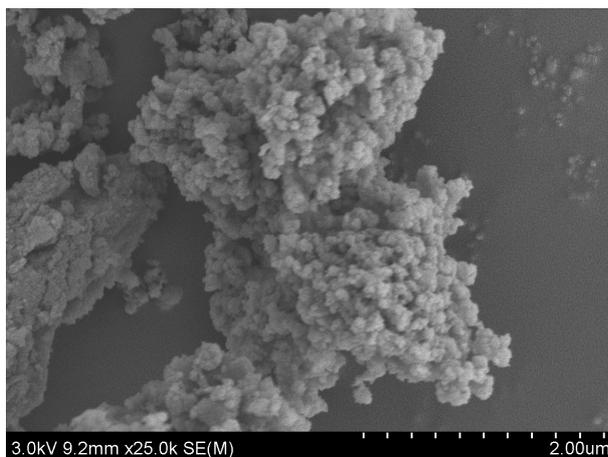


FIGURE 4 SEM image of the TiO₂:Eu³⁺ sample

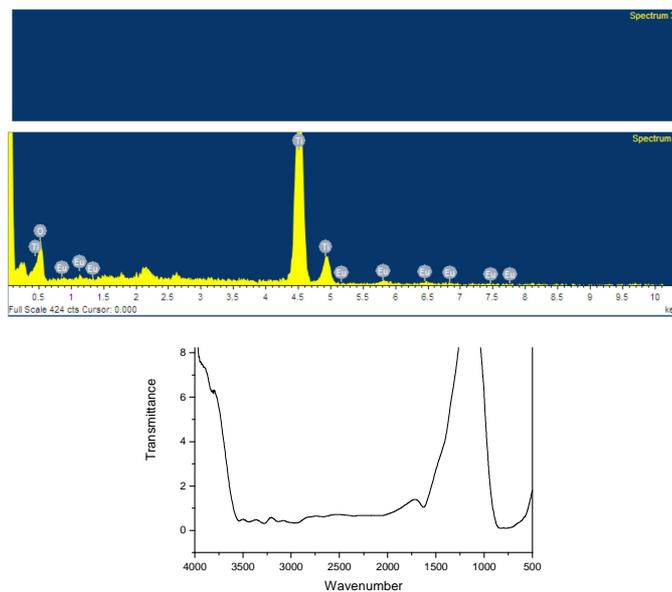


Figure 7 FT-IR Spectrum of the sample of the pure TiO₂

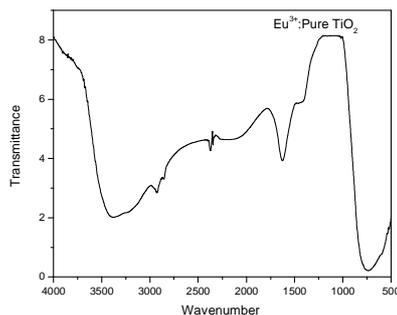


Figure 8 FT-IR Spectrum of the sample of $\text{TiO}_2:\text{Eu}^{3+}$ sample

OPTICAL PROPERTIES

UV-Visible absorption spectrum of TiO_2 nanocrystallites is shown in Figure 9. The knee edge at 360 nm in the spectrum denotes the absorption of narrow disperse nanocrystallites. The blue shift in the absorption peak compared to its bulk counterpart is nearly 50 nm, which is a significant shift due to the weak quantum effect occurred during the growth process. In UV-Vis absorption spectrum of Europium modified TiO_2 , shown in Figure 9

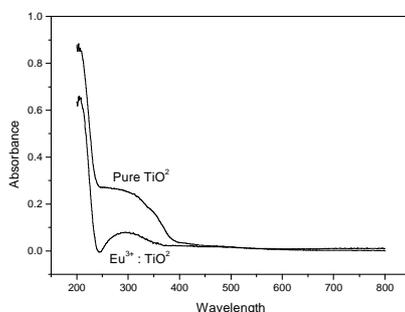


Figure 9 Absorption spectrum of the pure TiO_2 and $\text{TiO}_2:\text{Eu}^{3+}$ sample

CONDUCTIVITY STUDIES

The electrical homogeneity of the samples with frequency variation can be followed by studying the relaxation mechanism and nature of electrical conduction of the samples. These studies give the dielectric parameters of the materials. In conductivity measurements, sinusoidal voltages of various frequencies were applied across the sample of thickness d and area A . If ω is the angular frequency of the applied signal ($\omega=2\pi f$) and ϵ_0 is the permittivity of free space, then the AC conductivity is given by [3]

$$\sigma_{ac} = \omega \epsilon_0 \epsilon''$$

$$\sigma_{ac} = \omega \epsilon_0 \epsilon' \tan \delta$$

The imaginary part of dielectric constant is given by,
 $\epsilon'' = \epsilon' \tan \delta$

The real part of dielectric is given as
 $\epsilon' = C_p d / \epsilon_0 A$

And, the loss tangent or dissipation factor

$$\tan \delta = \left| \frac{1}{\tan \theta} \right|$$

Complex impedance plots can be drawn real and imaginary parts of impedance

$$Z' = Z_{\text{Real}} = Z \cos \theta$$

$$Z'' = Z_{\text{Imag}} = Z \sin \theta$$

With phase angle being
 $\theta = \tan^{-1} (Z''/Z')$

A convenient formalism to investigate the frequency dependence of conductivity in a material is based on the power-law relation proposed by [6]

Total conductivity

$$\sigma_T = \sigma_0 + A\omega^s$$

Where, σ_0 is frequency independent (dc) conductivity, and the coefficient A and exponent s are temperature and material dependent parameters. The exponent s can vary from material to material depending on temperature, etc., but is always such that, in general, $0 \leq s \leq 1$. The values of σ_0 , s and A are known as power – law parameters.

The variation of real and imaginary part of dielectric constant of sample as a function of frequency is shown in Figure 10 and 11, respectively. From the figure it is evident that at lower frequencies there is variation in real and imaginary part of dielectric constant values and above 100 KHz the dielectric values remain constant. The higher values of dielectric constant at lower frequency are due to simultaneous presence of space charge, dipolar and ionic electronic polarizations. The Eu^{3+} doped sample shows low dielectric values in the log f versus real and imaginary part of dielectric constant plot; it may be due to the interfacial charge transfer. The Eu^{3+} nanoparticles behave like induced dipoles in the low frequency region are one of the possible reasons for low dielectric values at lower frequency [7].

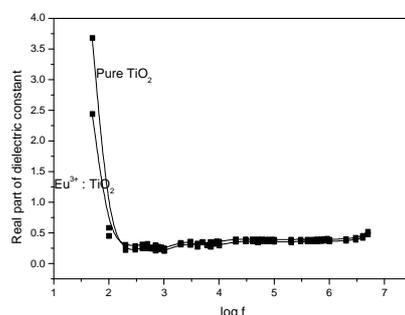


Figure 10 Variation of real part of dielectric constant with frequency of the pure TiO_2 : Eu^{3+} sample

Nanomaterials can be polarized mainly due to space charge polarization, hopping exchange of charge carriers between the localized states and the resultant displacement of dipoles with respect to the applied field. The decrease in the dielectric constant values with Eu^{3+} substitution in the low frequency region observed due to the effects of grain boundaries is prominent at lower frequencies. The doping of Eu^{3+} nanoparticles thickens the grain boundary and can cause a decrease in the polarization value and hence the dielectric constant decreases. Figure 12 shows the conductivity versus frequency plot for both samples. It shows that value of conductivity is the same for both samples at lower frequencies but at higher frequencies the value of conductivity goes on increasing. The value of conductivity is less for Eu^{3+} doped sample as compared to undoped sample at higher frequencies. This could be due to large surface scattering which results in a decrease in conductivity and also the short range intra-well hopping of charge carriers between localized states. But with the addition of Eu^{3+} the effective number of charge carriers involved decrease and thus the conductivity was found to decrease [7, 8].

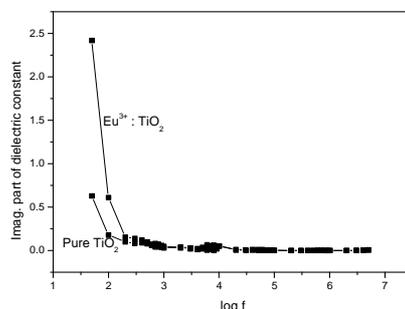


Figure 11 Variation of imaginary part of dielectric constant with frequency of the pure TiO_2 and TiO_2 : Eu^{3+} sample

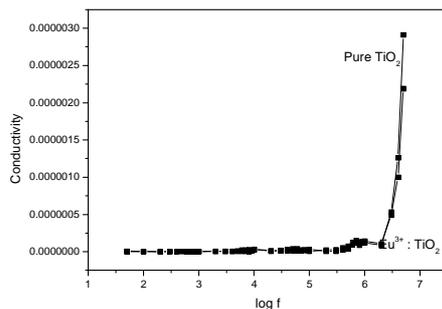


Figure 12 Variation of conductivity with frequency of the pure TiO_2 and $\text{TiO}_2:\text{Eu}^{3+}$ sample

CONCLUSION

Pure TiO_2 and Eu^{3+} nanocrystallites along with titanium dioxide are prepared by sol-gel route. The dielectric response and the AC electrical conductivity studies of the samples with the Eu^{3+} content are performed for a frequency range of 100Hz-2MHz. The presence of Eu^{3+} reduced the dielectric constant and AC Conductivity and shifted the dielectric constant and AC conductivity to a higher frequency region. At higher frequencies, the dielectric constant was found to be a constant and low but AC conductivity increased rapidly. This property of the materials can, therefore, be used for dielectric and electronic applications.

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