International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.4, pp 1867-1872, 2014-2015

Structural and Dielectric Observation ofGd^{3+} Doped Titanium Di Oxide

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Abstract: Gadolinium (Gd^{3+}) doped TiO_2nanoparticles are synthesized by sol – gel method and investigated through structural, optical and dielectric studies. Scanning electron microscopy technique has been performed on undoped $TiO_2$and Gd^{3+}doped TiO_2nanoparticles. Powder X-ray diffraction is carried out in order to examine the phase formation and substitution of Gd^{3+}in TiO_2matrix. Furthermore, Gd^{3+}doped TiO_2nanoparticles show a spectral shift towards lower wavelength in optical absorption spectrum as compared with undoped pure TiO_2 nanoparticles.
Keywords: Nanoparticles, Gadolinium, TiO_2, Dielectric Properties.

Introduction

Nanocrystals of transition metal oxides are a fascination class of inorganic materials, exhibiting a wide variety of structures, properties and phenomenon. Thesenanomaterials have attracted a great deal of attention from researchers of various fields due to their numerous technological applications such as, pigments, catalysts, ceramics, energy storage, magnetic data storage, ferrofluids and sensors[1]. Among them,Titania (TiO_2) has been most extensively studied owing to its versatile applications in diverse fields. TiO_2nanoparticles have found applications in solar cells, photo catalysis, photochromic devices, photovoltaic cells, gas sensors, catalysts and pigments etc. [2]. TiO_2mainly exists in three crystalline phases, namely anatase, rutile and brookite, which differ in their physical properties (refractive index, dielectric constant and photochemical reactivity). Brookitephase (band gap 3.3eV) is not often used for experimental investigations, as it is stable only at low temperatures. Rutile (band gap 3.2 eV) is thermodynamically the most stable phase and can be obtained after high temperature calcination while anatase phase (band gap 3.2 eV) is stable at comparatively low temperature. Anatase phase has gained tremendous importance and solar energy conversion due to its high photoactivity[3].

Recent experimental results have shown that the incorporation of rare earth metals (REM) such as Gd^{3+}ion in wide band gap semi conductor results in ferromagnetic property[4]. Gd^{3+} is of great interest due to its scintillation property and used in optical devices. In present work, Gd^{3+} doped anatase TiO_2nanoparticles was synthesised by sol-gel method. The possible dielectric properties were also discussed.

Material Synthesis

Pure and Gd^{3+}doped TiO_2nanopartices were made by a sol– gel method. TiO_2nanopartices were synthesized by injecting solution consisting of distilled waterand isopropanol into titanium (IV) isopropoxide. The mixture was kept under constant magnetic stirring for 12h until transparent sol was obtained. The Gd^{3+} doped nanoparicles were synthesized with the same method mentioned above. The obtained gel was calcinated at 400°C for 3h to remove residual organic compounds.

Results and Discussions

X – Ray powder diffraction analysis

Figure 1 and 2 show XRD spectra of pure and Gd^{3+} incorporated TiO_2 nanoparticles.The X-ray powder diffraction analysis was performed on the TiO_2 sample at room temperature. The diffraction pattern of the as prepared Titanianan opowder is shown in Figure 1. The pattern clearly shows that the nanoparticles are crystallized into the anatase phase of Titania with good crystalline quality though it was prepared at a relatively low temperature. The diffraction peaks corresponding to 2θ values are identified as (101), (004), (200), (105), (211) and (204) and it matches well with thediffraction pattern of bulk anatase titania (JCPDS Card No 21-1272). The peaks corresponding to other polymorphs of Titania (namely, rutile and brookite) are not detected and thus it is concluded that, the above solvothermal conditions favor the particles to crystallize in pure anatase phase. Figure 2 shows the diffraction pattern of Gd^{3+}-TiO_2nanoparticles. The diffraction peaks (1 0 0), (1 0 1), (1 0 2) and (1 0 3) are due to the presence of Gadolinium. Thus the presence of the dopant is confirmed in the X-raydiffraction pattern.

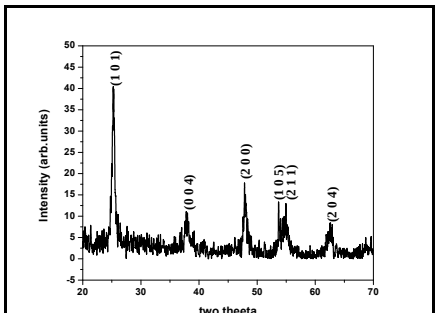

Figure 1 X-ray powder diffraction pattern of anatase TiO_2nanopowder

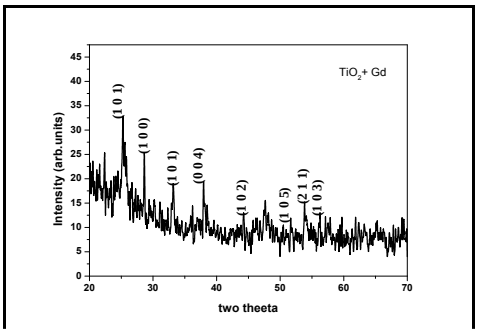

Figure 2 X-ray powder diffraction pattern of anatase Gd^{3+}-TiO_2nanopowder

Morphology Observation

Scanning electron microscope (SEM) was used for morphological study of nanocrystallites of TiO_2. Figure 3shows the SEM images of as prepared Titanianan opowder at a magnification of 100 μm. Figure 4 shows the SEM images of as prepared Gadolinium Titanianan opowder. The formation of uneven spherical grains, which is acharacteristic phenomenon of TiO_2nanoparticles, is observed. By changing the precursorand solvents or setting the annealing temperature, a material with controlled crystal structure, grain size, porosity and surface area can be prepared. The grain size can be reduced to a few or several dozen nanometers despite annealing treatment. In the SEM photograph, the individual spherical particles are not clearly observed due to the formation of nanoclusters during the growth.

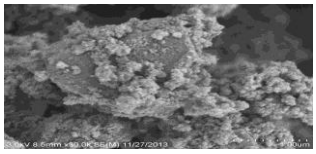

Figure 3 SEM photographs of TiO_2 nanoparticles

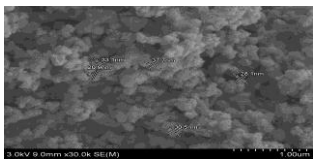

Figure 4 SEM photographs of Gd^{3+}-TiO_2 nanoparticles

EDAX is an important technique to analyze the composition of elements quantitatively and solve the chemical identity of any nanomaterials. It is inferred from the result of the EDAX spectra (Figure 5 and Figure 6) obtained for TiO_2 and Gd^{3+}-TiO_2 nanoparticles. The samples (Figure5) are composed of only Ti and O and are exactly TiO_2 and no trace of other elements is observed. From Figure 6 the presence of Gd^{3+} is confirmed. From the EDAX and XRD analyses, it is clear that the obtained products are TiO_2 and Gd^{3+}-TiO_2 respectively.

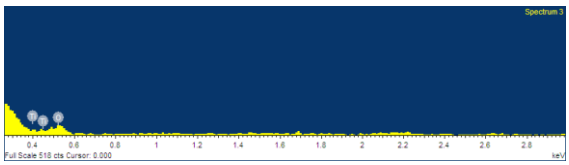

Figure 5 EDAX spectrum of pure TiO_2

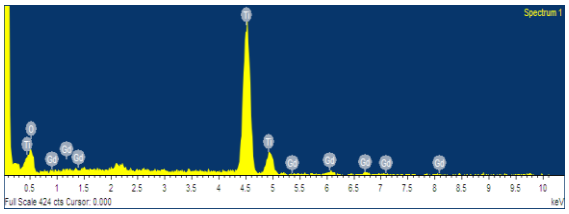

Figure 6 EDAX spectrum of Gd^{3+}-TiO_2

Optical Properties

The optical properties of the semiconductor materials are directly determined by the size and shape of the products. UV-Visible absorption spectrum of TiO_2nanocrystallites is shown in Figure 7. The knee edge at 360 nm in the spectrum denotes theabsorption 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.The UV-Vis absorption spectrum of Gadolinium modified TiO_2 is shown in Figure8. The sharp absorption edge observed at 350nm indicates the blue shift of 60 nm when compared to the absorption edge of 410 nm for bulk TiO_2. There is a tail of a more intense absorption occurring at shorter wavelength due to higher energy electronic transitions as observed in low band gap semiconductor particles. The sharp optical absorption edges and well-defined excitonic features indicate that the synthesized particles have relatively narrow size distribution. More over the presence of Gadolinium had resulted in a blue shift of 10 nm from the undoped TiO_2.

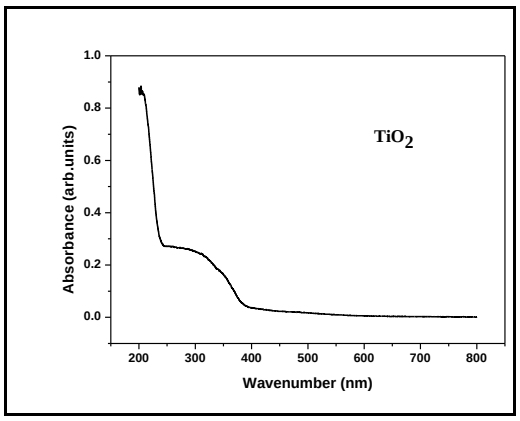

Figure 7 UV-Vis absorption spectrum of pure TiO_2 nanoparticles

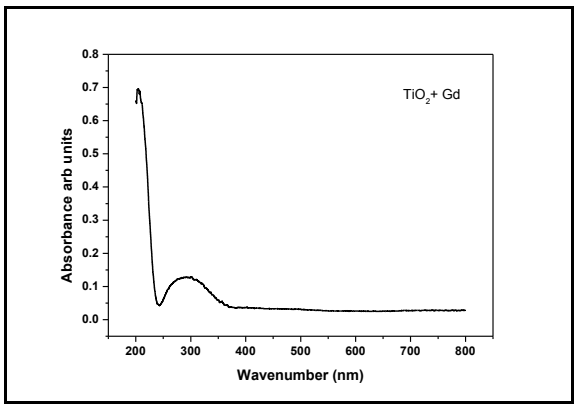

Figure 8 UV-Vis absorption spectrum of Gd^{3+}-TiO_2 nanoparticles

3.4. Dielectric Studies

The electric properties of dielectric substances are usually described in terms of the dielectric constant. For most materials, this quantity is independent of the strength of the electric field over a wide range of the latter, but in the case of alternating fields, it depends on the frequency.

Figure 9 shows the plots of dielectric constant against log frequency for TiO_2 nanoparticles. The dielectric constants ε_r at low frequencies depend on the excitation of bound electrons, lattice vibrations, dipole orientations and space-charge polarization. At very low frequencies all four contributions may be active. It is observed that the dielectric constant $\varepsilon_r$decreases with increase in frequency. The large value of dielectric constant at low frequency is due to the presence of space charge polarization.

The space charge contribution depends on the purity and perfection of the material. Its influence is mainly noticeable in the low frequency region. Figure 10 corresponds to Gd^{3+}-TiO_2 which also show a similar pattern.

Figure 11 shows the variation of dielectric loss with log frequency for TiO_2 nanoparticles. It is observed that the dielectric loss decreases with increase in frequency in the case of all samples. The low values of dielectric loss suggest that the grown crystals are of good quality. In the lower frequency region, dielectric loss shows larger values due to the loss associated with ionic mobility. Figure 12 represents the variation of dielectric loss with frequency of Gd^{3+}-TiO_2 nanoparticles.

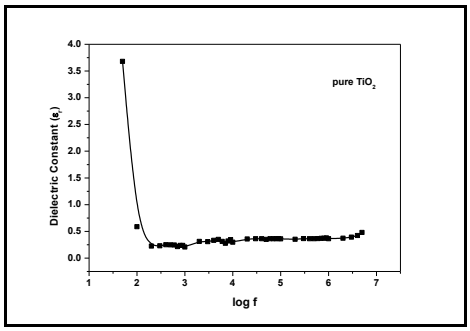

Figure 9 Variation of dielectric constant of TiO_2 nanoparticles

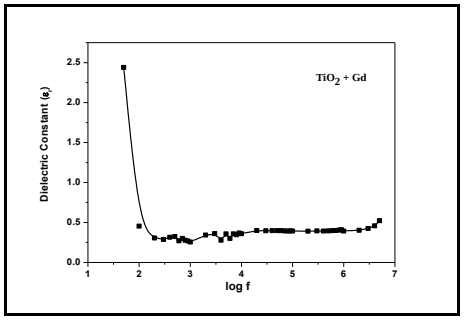

Figure 10 Variation of dielectric constant of Gd^{3+}-TiO_2 nanoparticles

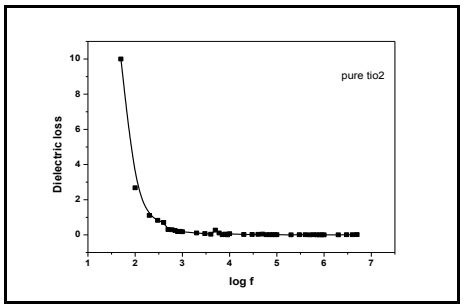

Figure11 Variation of dielectric loss of TiO_2 nanoparticles

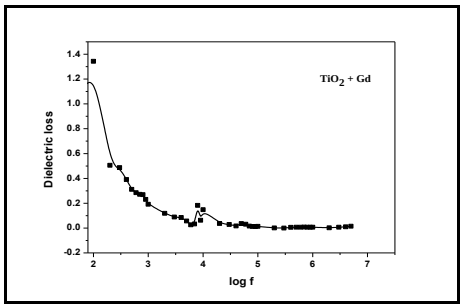

Figure12 Variation of dielectric loss of Gd^{3+}-TiO_2 nanoparticles

Conclusion

Nanoparticles of pure and doped TiO_2 are successfully prepared. The prepared nanoparticles exhibit well defined morphology, high crytstallinity and narrow size distribution. X-ray powder diffraction confirms that the particles crystallize purely in anatase phase and the broadening of Bragg's peaks ascertains smaller particles size. The formation of uneven spherical grains composed of small primary Titania particles are observed from SEM. From the optical absorption spectrum, a spectral shift towards lower wavelength is observed as compared to bulk TiO_2 crystal.

References

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