

# Structural and optical characterization of Tb<sup>3+</sup>/CdS doped Titania-Zirconia xerogels

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**Abstract**-Titania-Zirconia matrix codoped with CdS /Tb<sup>3+</sup> ions were prepared by sol-gel route. Structural properties of the matrices were characterized using TGA, DTA, FTIR and TEM studies. The incorporation of the CdS semiconductors as nanocrystallites was confirmed from the HRTEM measurements. The measurements yielded the size of the nanocrystallites to be around 8nm and the crystal inter planar spacing to be 3.533 Å. The size and optical band gap of the nanoparticles were calculated from the absorption spectrum. The fluorescence spectra reveal that the intensity of the characteristic emission of terbium increases considerably in the presence of CdS particles.

**Index Terms**-Absorption, CdS, Excitation Spectrum, Fluorescence, Nanocrystallites, Sol-gel, Terbium, Titania-Zirconia Xerogel

## 1. INTRODUCTION:

The sol-gel method is a technique which involves low temperature polymerization reactions for forming glasses and ceramic materials from liquid metallorganic precursors. It is used in the fabrication of optical glasses especially for bulk structures but also for thin films. Titania possesses various utilities in areas of coatings, catalysis, photo catalysis, energy conversion, and chemical sensors due to its nontoxic nature, unique electronic and optical properties [1]. Pure TiO<sub>2</sub> materials restrict extended applications in catalysis due to its relatively low quantum efficiency. Combination with other metal oxides is presently the most practicable approach for property tuning [2- 3]. Due to the structural and electronic modifications induced by the dopant, these combined metal oxide materials shows enhanced activity and new reactivity properties [4-5]. The increase in the surface of TiO<sub>2</sub>-ZrO<sub>2</sub> binary metal oxides exhibits higher photo catalytic activity than pure TiO<sub>2</sub>. Sol-gel-based luminescent lanthanide complexes are receiving much attention because of the higher solubility and homogeneous distribution of the complex in the matrix [6-8]. The attractive physical and chemical properties of nanosized semiconductors have opened up a special interest in the synthesis of different organo-inorganic matrices embedded with nanocrystallites [9-14].

The II-VI compound semiconductors like cadmium sulphide (CdS) has been the subject of extensive research both in fundamental studies and for potential applications in devices. Due to the unique fundamental phenomena they exhibit make them attractive for a wide range of applications such as nonlinear optical materials, blue green lasers and light emitting diodes (LEDs), magneto optical devices and radiation detectors, infrared lasers and detectors. Terbium is used as dopant for many solid-state

devices and as a stabilizer for fuel cells which operate at high temperatures. Also the terbium doped insulating materials are used as green phosphors. In view of the aforesaid special characteristics of Titania-Zirconia matrices, we have prepared TiO<sub>2</sub>-ZrO<sub>2</sub> xerogels doped with Tb<sup>3+</sup>/CdS nanocrystallites. These matrices were characterized using TGA, DTA, TEM, FTIR, UV-VIS absorption and emission studies. We also discuss the fluorescence enhancement of terbium ions in the presence of cadmium sulphide nanoparticles.

## 2. EXPERIMENTAL:

TiO<sub>2</sub>-ZrO<sub>2</sub> gels containing CdS/Tb<sup>3+</sup> were prepared by sol-gel process with titanium isopropoxide and zirconium IV propoxide as precursors in the presence of ethanol. The dopants were added in the form of cadmium acetate, thiourea, and terbium nitrate. Cadmium acetate and thiourea were used as cadmium and sulphur sources respectively. A measured volume of 1M HNO<sub>3</sub> was added as catalyst. Three samples were prepared with the following compositions

Sample A TiO<sub>2</sub>-ZrO<sub>2</sub> -75:25 + Tb<sup>3+</sup> (3 Wt %)  
Sample B TiO<sub>2</sub>-ZrO<sub>2</sub> - 75:25 + CdS (3 Wt %)  
Sample C TiO<sub>2</sub>-ZrO<sub>2</sub> - 75:25 + Tb<sup>3+</sup> (3 Wt %) +  
CdS (3 Wt %)

The resulting mixture was stirred continuously using a magnetic stirrer for about an hour at room temperature till it formed a uniform clear solution. The mixture (sol) is poured into polypropylene containers, which is sealed and kept to form stiff gel for one month. The samples were clear, transparent and colourless. Finally the samples were annealed at 600°C for two days. The colour of the xerogel turned from white into yellow.

The excitation and emission spectra were taken using spectrophotofluorimeter(Shimadzu-RFPC 5301) and the absorption spectra with UV-Visible spectrophotometer (Shimadzu-UVPC 2401) for samples heated to 600C. The particle size was measured with Tecnai G2 30 S-Twin transmission electron microscope (TEM) at 300 kV. All the measurements were done at room temperature.

### 3. RESULTS AND DISCUSSION:

Figures 1(a) and 1(b) show the thermo gravimetric/differential thermal analysis (TGA/DTA) curves for a temperature range of 0-1000C for samples TiO<sub>2</sub>-ZrO<sub>2</sub> matrix and CdS doped TiO<sub>2</sub>-ZrO<sub>2</sub> matrix, respectively. The values were acquired at a heating rate of 10C/min. An endothermic peak at 1300C was observed in the DTA for TiO<sub>2</sub>-ZrO<sub>2</sub> matrix which shows a 16% weight loss around this temperature range. An endothermic peak at 1000C was observed in CdS doped TiO<sub>2</sub>-ZrO<sub>2</sub> matrix which shows a 12% weight loss around this temperature range. A broad exothermic peak at 3500C was observed in the DTA for TiO<sub>2</sub>-ZrO<sub>2</sub> matrix and peak at 2500C was observed in CdS doped TiO<sub>2</sub>-ZrO<sub>2</sub> sample. At 10000C both samples lose 36% of its weight. It could be attributed to the dissociation of various bonds due to free water, loosely held hydroxyl group, weak organic compounds, different forms of alcohol, etc. From a careful observation of both curves, we infer that both samples are equally thermally stable.

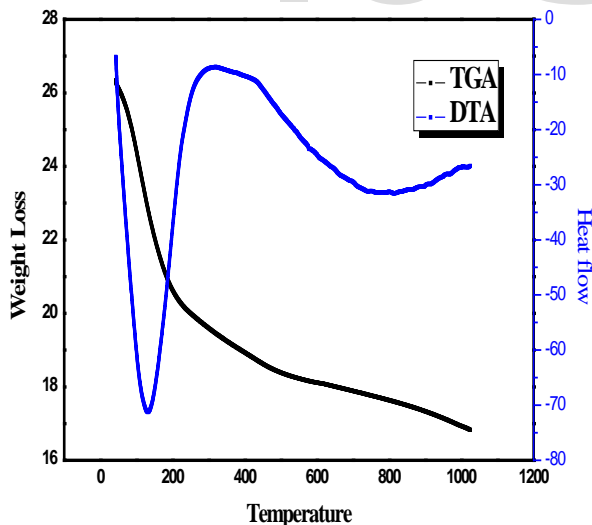


Figure 1 (a).TGA/DTA curves of the Titania-Zirconia matrix

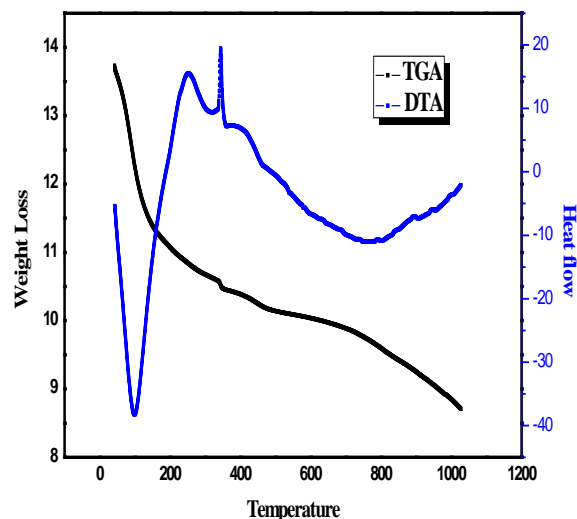


Figure 1(b).TGA/DTA curves of the CdS doped Titania-Zirconia matrix

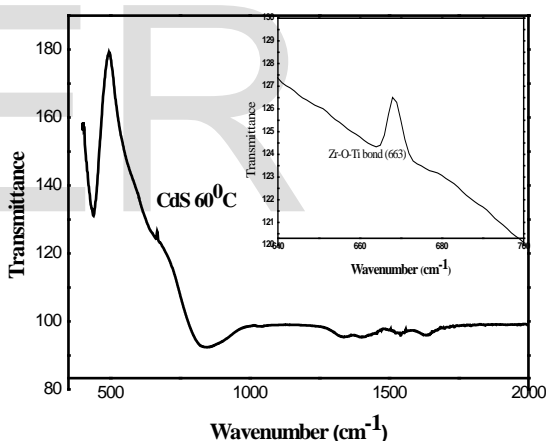
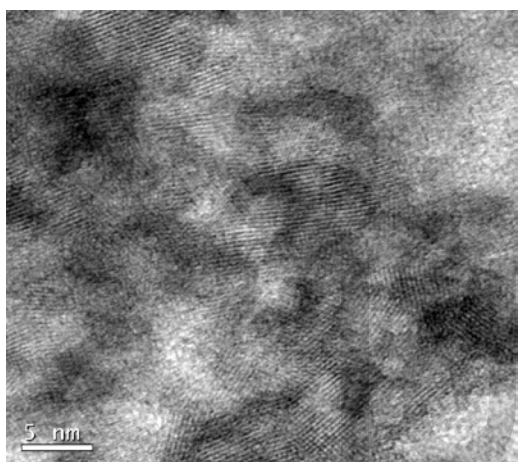


Figure2. FT-IR spectrum of CdS doped Titania-Zirconia matrix

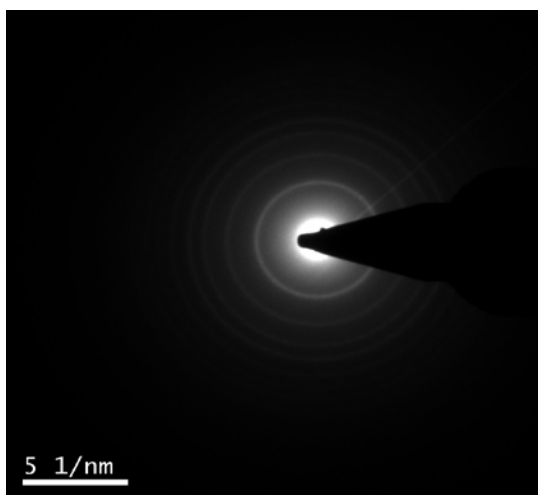
The FTIR spectra of the CdS doped TiO<sub>2</sub>-ZrO<sub>2</sub> sample is shown in Figure 2. The spectrum exhibits strong band at 440 cm<sup>-1</sup> indicating the presence of Ti-O-Ti bond. The band at 663 cm<sup>-1</sup> is related to Ti-O and Zr-O-Ti vibrations [15]. The band at 841 cm<sup>-1</sup> indicates Zr-O-Zr bond. Additional weak absorption in the 1541 cm<sup>-1</sup> indicates symmetric and asymmetric stretching modes of the acetate groups and 1338 cm<sup>-1</sup> indicates the carbonyl group. Since the bond of Cd-S is mainly electrovalent, the FTIR spectra of doped samples do not show strong bands associated with Cd-S stretching and bending vibrations. The FT-IR band assignments are shown in table 1.

**Table 1.** FT-IR band assignments

Wavelength	Assignment
1541	symmetric and asymmetric stretching modes of the acetate groups
1338	carbonyl group
841	Zr-O-Zr bond
663	Ti-O and Zr-O-Ti bond
440	Ti-O-Ti bond



**Figure3.(a)** HRTEM micrograph of CdS nanocrystals dried at 600C



**Figure3.(b)** selected area electron diffraction pattern

Figure 3(a) shows the planes of the CdS nanocrystallites. The plane was identified as (1 0 0) plane with a d value of 3.533Å. This is in good agreement with the value of d=3.5600 (JCPDS no: 01-0780) for bulk cadmium sulphide crystal. The average size of the nanocrystals is determined to be 8 nm. The HRTEM of CdS nanocrystals dried at 600C with selected area electron diffraction pattern is shown in Figure 3(b).

The optical absorption spectra of CdS nanocrystallites doped TiO<sub>2</sub>-ZrO<sub>2</sub> matrix heated at 600C is shown in Figure 4.

The direct absorption bandgap of the CdS nanoparticles can be determined by fitting the absorption data to the Tauc equation

$$\alpha h\nu = B(h\nu - E_g)^{1/2} \dots\dots(1)$$

in which hν is the photon energy, α is the absorption coefficient, E<sub>g</sub> is the absorption band gap and B is a constant relative to the material. The absorption coefficient can be obtained from the equation

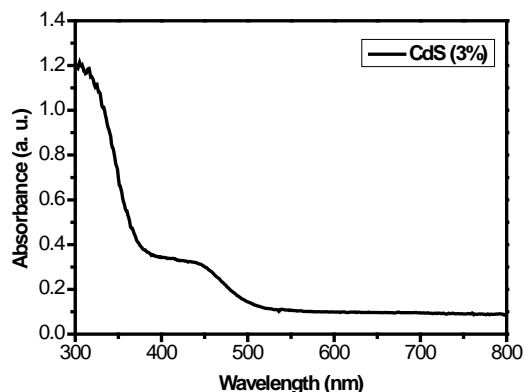
$$\alpha = \frac{2.303A}{d} \dots\dots(2)$$

where A is the absorbance and d is the thickness of the sample. The plot of α<sup>2</sup> versus hν gives the value of the bandgap as 3.18eV. This is large compared to the bulk CdS, a direct semiconductor, with bandgap energy of 2.42eV [16]. Semiconductor nanocrystals are known to have an absorption edge, which is shifted with respect to the bulk material, towards shorter wavelength [17]. The blue shift of the absorption edge can be explained by the effective mass approximation model, developed by Brus [18] and Kayanuma [19]. In the strong exciton confinement regime of nanoparticles (particle radius < ab\*), the energy E(R) for the lowest 1S excited state as a function of cluster radius (R) given by

$$E(R) = E_g + \frac{\pi e a_b^*}{8\epsilon R^2} - \frac{1.786e^2}{4\pi\epsilon R} + 2.48E_R \dots(3)$$

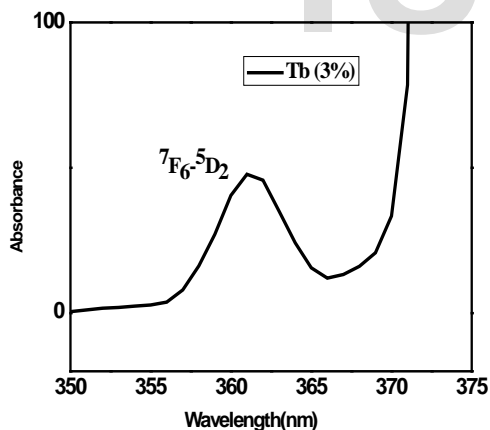
where ab\*, Bohr radius of the exciton (for CdS 2.8 nm), ε is the dielectric constant of the nanocrystallite (for CdS, 8.36) and E<sub>R</sub> is the bulk exciton Rydberg energy (for CdS 0.029eV). The first term is the band gap energy for bulk material and it is 2.42 eV for CdS. The second term is the quantum confinement localization for the electrons and holes, which leads to the blue shift. The third term is the

Coulomb term leading to red shift, while the fourth term gives the spatial correlation energy, which is small and of minor importance. For our CdS doped TiO<sub>2</sub>-ZrO<sub>2</sub> xerogel, the lowest energy of 1S transition was observed at ~ 3.18 eV (390nm), which showed the presence of CdS nanoparticles [20]. The radius was determined to be 3.5 nm using Brus formula, by considering this to be in the strong confinement region. Thus the calculated size is found to be 7 nm.



**Figure4.** Absorption spectrum of CdS doped sample

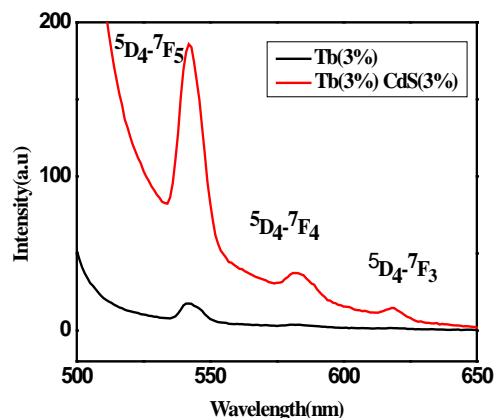
Optical absorption spectra of Tb<sup>3+</sup> doped TiO<sub>2</sub>-ZrO<sub>2</sub> matrix at room temperature is shown in Figure 5.



**Figure5.** Absorption spectrum of Tb<sup>3+</sup> doped sample

The absorption spectrum shows only one absorption band corresponding to the transition 7F<sub>6</sub>→5D<sub>2</sub> (360 nm).

Figure 6 shows the fluorescence spectra of Tb<sup>3+</sup> doped CdS nanoparticles heated at 60 °C. The doped sample was excited at 360 nm.

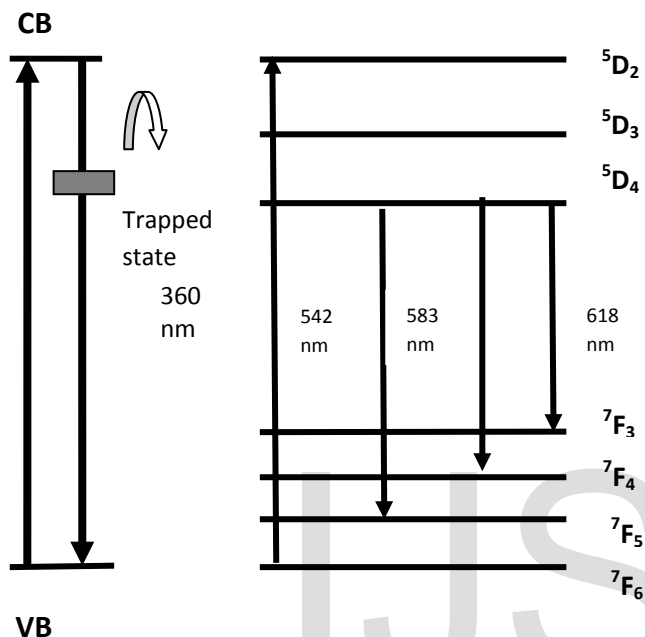


**Figure6.** Emission spectrum of Tb<sup>3+</sup> and Tb<sup>3+</sup>/CdS doped sample

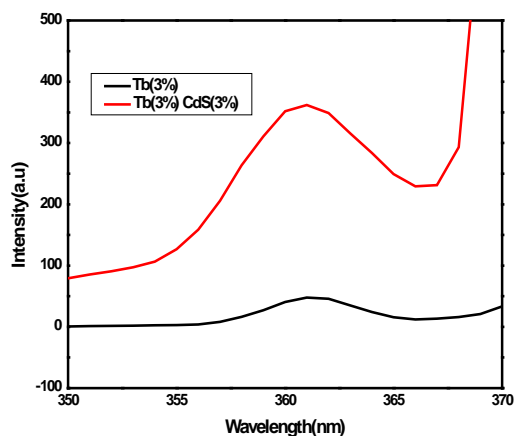
In Tb<sup>3+</sup> doped glasses, the 4f-5d transition would play an important role for the emission of Tb<sup>3+</sup>. The emission spectrum of Tb<sup>3+</sup> consists of several bands located at 542 (green), 583 (yellow) and 618 (red) nm, corresponding to transitions 5D<sub>4</sub>→7F<sub>5</sub> (542 nm), 5D<sub>4</sub>→7F<sub>4</sub> (583 nm) and 5D<sub>4</sub>→7F<sub>3</sub> (618 nm). Among them, the green emission at 542 nm associated with the transition 5D<sub>4</sub>→7F<sub>5</sub> is the strongest. The typical luminescence of Tb<sup>3+</sup> appears to be green to the human eye, because the emission due to the 5D<sub>4</sub>→7F<sub>5</sub> transition (542 nm) usually dominates overall emissions. The fluorescence intensity is considered to be dependent on the host lattice through the crystal field [21].

From the fluorescence spectra we observe that the fluorescence intensity of Tb<sup>3+</sup> increased due to the presence of CdS nanoparticles. As the particle size decreases, there is the possibility of the existence of the electron or hole trapped surface levels on CdS particles [22, 23]. These surface levels can transfer energy to the Tb<sup>3+</sup> ions in an efficient way. The plausible explanation of the Tb<sup>3+</sup> emission in the following way. The photo generated electron is first trapped in the surface levels of CdS particles and then interacts with Tb<sup>3+</sup> ions located close to the surface CdS. Secondly, the electron in the surface trap recombines with a valence band free hole and the energy is nonradiatively transferred to the Tb<sup>3+</sup> ions [24]. The fluorescence intensity of CdS/Tb<sup>3+</sup> doped sample is 10 times stronger than that of Tb<sup>3+</sup> alone doped sample. The energy transfer mechanism from trapped surface level on CdS particle to the Tb<sup>3+</sup> ions is shown in Figure 7. The fluorescence excitation spectrum confirms the energy

transfer from CdS nanoparticles to the Tb<sup>3+</sup> ions. The excitation spectrum is shown in Figure 8 taken with an emission wavelength of 542 nm shows strong excitation bands with the codoping of CdS nanocrystallites



**Figure 7.**Energy transfer mechanism from trapped surface level on CdS particle to Tb<sup>3+</sup> ions



**Figure8.**Excitation spectrum of Tb<sup>3+</sup> and Tb<sup>3+</sup>/CdS doped sample

**CONCLUSION:**

Nanometer sized CdS crystallites along with Tb<sup>3+</sup> ions were incorporated in to Titania-Zirconia matrix by Sol-Gel process. Thermal stability of the sample was analysed using TGA-DTA measurements. The structure is explained using the FT-IR spectral assignments. The electron diffraction and TEM measurements have yielded the values of crystal plane spacing and the crystallite size. The absorption spectrum and band gap energy also confirmed the formation of CdS nanocrystallites. The emission spectrum shows ten fold enhancement of green emission from terbium ions in the presence of CdS nanocrystals. This clearly suggests that there is an efficient energy

transfer from the surface level on CdS nanocrystallites to the Tb<sup>3+</sup> ions.

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