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Synthesis and Characterization of Europium Doped Hafnium Oxide Nanoparticles by Precipitation Method

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Abstract: Europium doped (0, 1, 3, 5 and 7 mol %) Hafnium oxide nanoparticles (HfO_2 NPs) have been successfully synthesized. The synthesis was carried out by the precipitation method using the precursors of $HfCl_4$ and $EuCl_3 \cdot 6H_2O$ with NaOH dissolved in Millipore water. The synthesized materials were characterized by using X-ray diffraction (XRD) analysis, UV–visible and High resolution transmission electron microscopy (HRTEM). The XRD revealed the transformation of HfO_2 NPs from monoclinic to cubic crystal structureat the addition of 7 mol% of europium and also particle size was found to be 12 nm. The HRTEM image showed that the NPs were of sphericalin shape. The EDAX spectrum clearly shows the presence of europium in HfO_2 NPs. The band gap and life time decay kinetics were also studied.
Keywords: Hafnium Oxide, Nanoparticles, Europium, Precipitation.

1. Introduction

Researchers in nanoscience and technology at present have been particularly devoted to the evolution of new synthetic methods to develop and formulate novel nanostructure with specific structural and morphological characteristics[1]. The electrical, catalytic, optical and the other physical properties of the nanoparticle are influenced by their size, morphology and surface characteristics[2,3].The excellent chemical and physical properties of HfO_2, makes it attractive for a diversity of applications.Its very high melting point (over 2700°C) and its mechanical resistance has made hafnium find application in refractory protective coatings of thermocouples in harsh conditions as in nuclear applications[4,6]. Hafnium oxide,with its high refractive index (~2.9) could be dispersed in photoresist polymers or immersion liquids to improve their refractive index and reach higher resolutions for recently developed immersion lithography techniques[7-9]. Because of its better cytocompatibility, HfO_2nanoparticle can be used for biosafety applications[10]. The ability of the densely packed HfO_2 nanoparticle to selectively absorb the high energy gamma/X-ray radiations, allows better targeting of cellular components within the tumor tissues for radiotherapy by localizing the damage of cancer cells[11].

The quantum confinement effect of nanoparticle has influenced their extensive study particularly in case of luminescent materials leading to novel optoelectronic devices. Transition metal oxides like ZrO_2 and HfO_2 being efficient luminescent materialshave recently attracted great attention for use in a broad range of applications, including fluorescent lamps, plasma displays, scintillators, lasers, etc[12]. Hafnium oxide(HfO_2) has become a material of interest for use as luminescent host lattice doped with rare earths because of its physicochemical properties, such as high melting temperature(2700°C), high chemical stability, high density(≈10g/cm^3), low optical losses, hardness close to diamond in the tetragonal phase, as well as a wide optical bandgap(5.68eV)[13,14]**.**Further, its chemical inertness, this makes HfO_2 an interesting material for optical applications, when acting as host for rare earths (RE) ions meant as luminescent activators[15-19]. The presence of

Eu^{3+} ions manifests optical features which are particularly sensitive to the local crystal field and hence the use of HfO_2 as a dopant seems to be a promising tool for the fine investigation of the host crystal structure[20-23].

Villanueva-Ibanez et al synthesized europium-doped HfO_2 by sol–gel method[24].Navarro Cerón et alsynthesizedHfO_2 doped with Eu^{3+} ions via hydrothermal route for photolumiscense applications[25]. Le Luyer et al prepared HfO_2 powders doped with Eu^{3+} or Ce^{3+} luminescent ions by sol gel process for scintillating applications[26]. To the best of our knowledge, till date, no one has reported on europium doped HfO_2 NPs by precipitation method. AnetaWiatrowska synthesized HfO_2: Eu powders with the classic Pechini method[27]. Realizing this, we designed an experiment to synthesize europium doped HfO_2 nanoparticles, using a precipitation method. In the precipitation method, the chemical reaction is comparatively simple, low cost and non-toxic compared to other synthetic methods includes solvothermal, hydrothermal, non hydrolytic synthesis[28]. In the present investigations, life time decay studies of Eu^{3+} doped HfO_2 nanoparticle are studied and also structural and optical characterization has been done.

2. Experimental Details

2.1 Materials

All the chemicals were procured from Sigma-Aldrich and were used without further purification. Hafnium tetrachloride ($HfCl_4$, 98%)Europium (III) chloride ($EuCl_3 \cdot 6H_2O$) was purchased from Sigma-Aldrich, USA. Sodium hydroxide (NaOH, 97%) pellets were obtained from Sigma-Aldrich, Sweden.

2.2 Experimental Method

The synthesis of HfO_2 doped with Eu^{3+} ions is based on precipitation method route. An aqueous solution of 0.1M of $HfCl_4$, using double distilled water with subsequent addition of $EuCl_3 \cdot 6H_2O$ was prepared. The Eu^{3+} concentration was varied (0, 1, 3, 5 and 7 mol %). Briefly, 0.4M aqueous solution of NaOH was slowly added drop wise into 0.1M aqueous solution of ($HfCl_4$) and allowed to continuous stirring using Teflon coated magnetic bar for 12 h obtaining a white colored precipitate. The resulting precipitate was repeatedly washed with DD water, using a centrifuge (2500 rpm) to remove impurities. The precipitate was dried at 80°C for 24 hours. Finally, the obtained product was calcined at 500°C for 2 h resulting the formation of europium doped HfO_2 nanoparticle.

3. Characterization Techniques

The crystal structure and size of the HfO_2 NPs were examined using X-ray diffraction (Rigakumultiflex) using Cu kα (λ =1.5406 Å) radiation. The surface morphology of HfO_2 NPs were evaluated by high resolution transmission electron microscopy operated at maximum acceleration voltage of 120 kV (Hitachi H-7650, Singapore). The optical absorption spectra of Er^{3+} doped HfO_2 NPs were studied using UV-Vis spectrometer (Lamda35, Perkin-Elmer, Waltham, MA). The optical band gaps were calculated from the UV-Vis absorbance spectra. Lifetime measurements were made using Time Correlated Single Photon Counting System (TCSPC, Horiba JobinYuvon IBH, UK) with a fast response red sensitive photomultiplier tube (Hamamatsu Photonics, Japan) detector. Decay analysis software (DAS6V6.0, Horiba) was used to extract the lifetime components.

4. Results and Discussion

4.1.X-Ray Diffraction Analysis

The crystal structure, purity and particle size of the resultant materials were investigated by powder X-ray diffraction (XRD) measurements. Figure 1 shows the XRD patterns for HfO_2 and Europium doped HfO_2 nanoparticles. The anticipated monoclinic structure of hafnium dioxide is monitored for Eu^{3+} concentrations up to 3 mol %, as shown by XRD (Fig.1) according to reference ICDD no. 00-006-0318. For Eu^{3+} concentrations beyond 5 mol %, the crystalline nature gets converted to that of cubic HfO_2 as confirmed by its comparison with ICDD PDF no. 00-053-0560.Incidentally, the HfO_2-Eu (5 mol %) exhibit the presence of minor features of monoclinic phase and major features of cubic phase[29]. Usingthe Debye Scherer's formula, the mean particle size of HfO_2 nanoparticles was found to be 12 nm. No secondary peaks were observed, which clearly indicates the high purity of the samples.

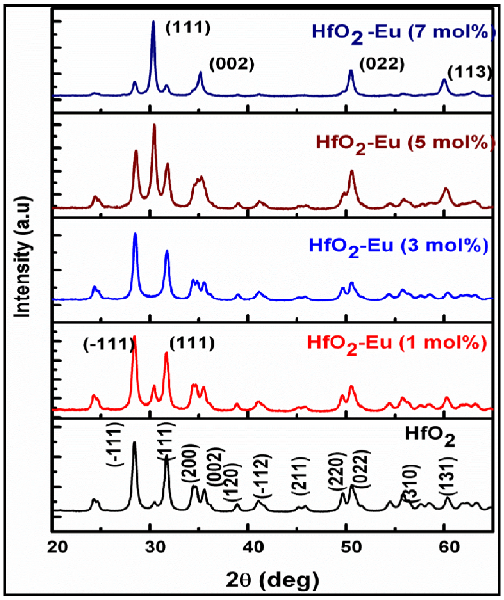

Fig.1XRDpattern of $HfO_2$and Europium (1, 3, 5 and 7 mol %) doped HfO_2nanoparticles.

4.2 Morphology Study

The morphology of the europium doped (1 and 7 mol %) HfO_2 nanoparticles were characterized by High resolution transmission electron microscopy. It can be observed from the HRTEM images that the particles are found to be spherical in shape and a small agglomeration was observed. This is due to the high surface interaction between nanoparticles which have large specific area and high surface energy[28]. The crystalline nature of the NPs can also be proved by the selected area electron diffraction pattern. The SAED pattern in Fig. 2(c & f)shows several diffraction rings consisting of some spots. It reveals that the NPs are polycrystalline in nature.

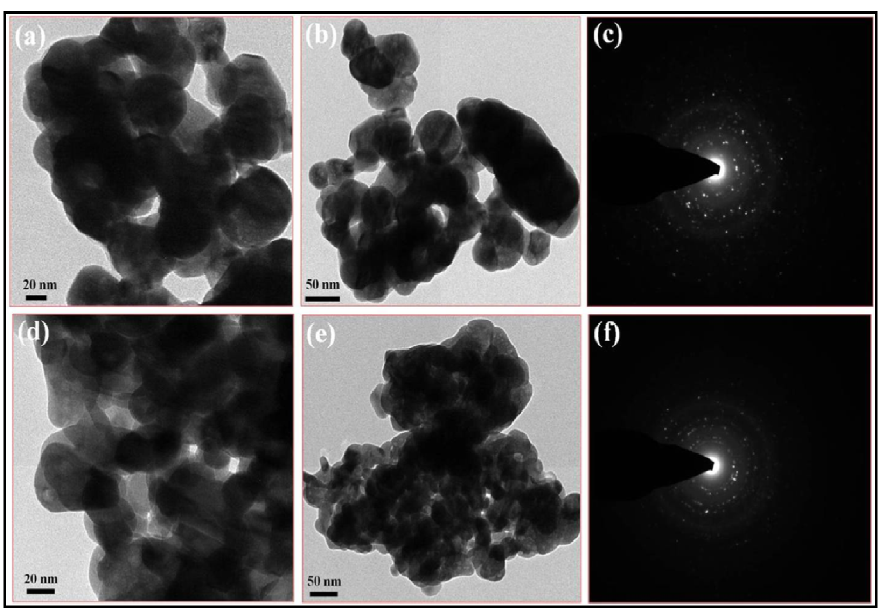

Fig.2. HRTEM images of (a - c) HfO_2-Eu (1 mol%) nanoparticles and its SAED pattern (d - f) HfO_2-Eu (7 mol%) nanoparticles and its SAED pattern

4.3 Elemental Analysis

In order to prove the nature of the final compounds the EDAX spectroscopy has been performed. The EDAX spectra of the europium doped HfO_2 nanoparticle were shown in Fig. 3. According to EDAX measurements presence of europium in HfO_2 nanoparticle was detected. The lines of C, Cu, O, Eu and Hf (C and Cu from the carbon coated copper TEM grid) can be observed from Fig. 3. The spectrum clearly shows the presence of europium (Eu), hafnium (Hf), and oxygen (O) elements in the europium doped HfO_2 NPs. The Hf and O elements originated from the HfO_2 nanoparticles, and the Eu was contributed by the europium.

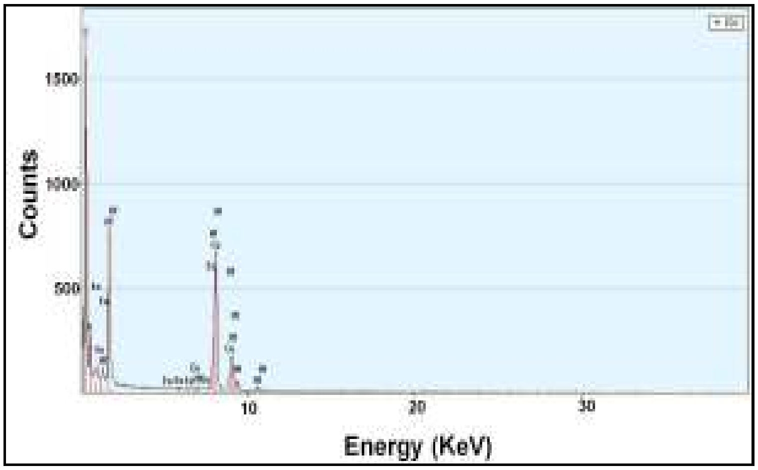

Fig.3.EDAX spectrum ofEu doped HfO_2 nanoparticles

4.4. Optical Properties

UV-Vis absorption spectra of HfO_2, europium doped HfO_2 nanoparticles (1, 3, 5 and 7 mol %) is shown in Fig. 4. The absorption peak at 208 nm can be assigned to the absorption of HfO_2 NPs[30]. The absorption wavelength increases gradually up to (5 mol %), then starts to decrease at (7 mol%). The optical band gap energy was calculated from the absorption spectra by the method proposed by Wood and Tauc[31].

$$\alpha h\nu = B\,(h\nu - E_g)^{n} \qquad (1)$$

Where α is the absorption coefficient, h is the Planck's constant, ν is the frequency, B is a constant, E_g is optical band gap and n is the constant associated to the different electronic transitions (n=1/2,2,3/2 or 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden respectively). Previously Park et al. reported structures that the monoclinic HfO_2 belong to indirect band gap[32]. Figure 5 shows the plot of $(\alpha h\nu)^2$ versus hν.

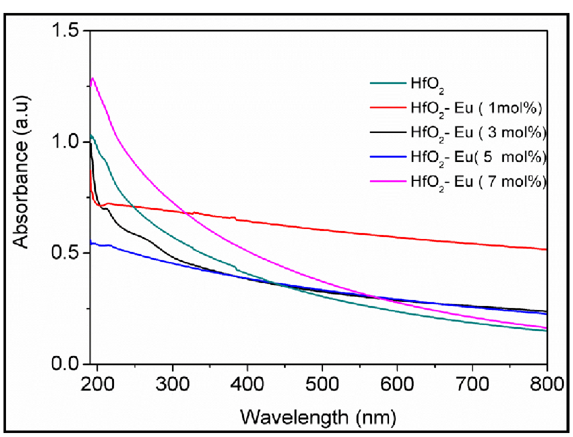

Fig.4. UV-Visible absorption spectra of$HfO_2$and Europium (1, 3, 5 and 7 mol %) doped HfO_2 nanoparticles

The band gap values of HfO_2 were measured by the intercept on the x (hν) axis. The estimated band gaps are 4.71, 3.30, 3.90, 4.28 and 3.77 eV corresponding to HfO_2, HfO_2-Eu (1 mol %),HfO_2-Eu (3 mol %), and HfO_2-Eu (5 mol %) and and HfO_2-Eu (7 mol%) and respectively.

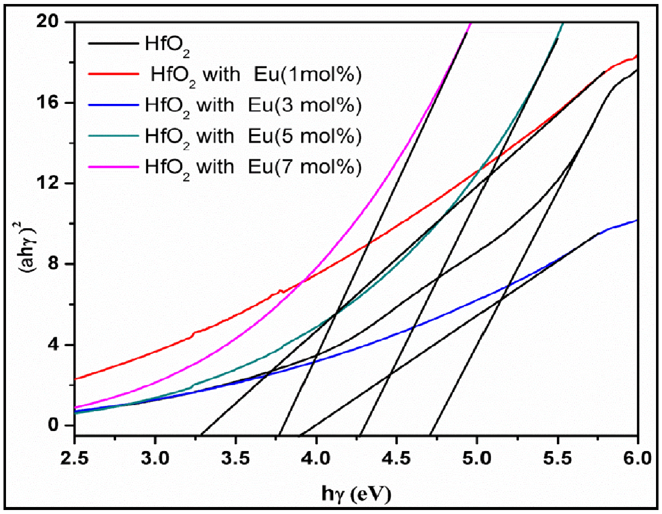

Fig.5. Band gap values of$HfO_2$and Europium (1, 3, 5 and 7 mol %) doped HfO_2nanoparticles

4.5 Lifetime Measurements Analysis

Mean fluorescence lifetimes <τ> for two-exponential iterative fittings were calculated from the decay times and the pre-exponential factors using the following relation [33].

$$<\tau> = \frac{\sum \alpha_i \tau^2}{\sum \alpha_i \tau} \quad (2)$$

Where α_i represents pre-exponential factors, χ^2 indicates goodness of fit.Fluorescence lifetime decay profile of Europium doped HfO_2 nanoparticles at 280 nm emission is shown in Fig.6 and their corresponding average lifetime values are presented in Table 1.

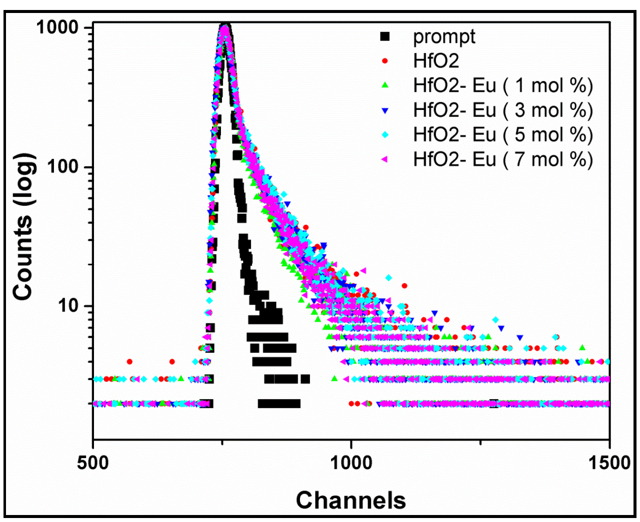

Fig. 6.Lifetime decay studies of$HfO_2$and Europium(1, 3, 5 and 7 mol %) doped HfO_2 nanoparticles

Table 1. Fluorescence Lifetime Analysis

Material	α_1	α_2	τ_1 (ns)	τ_2 (ns)	$\langle\tau\rangle = \frac{\sum \alpha_i \tau^2}{\sum \alpha_i \tau}$ (ns)
HfO_2	66.19	33.81	0.36277	3.9927	3.4440
HfO_2- Eu (1 mol %)	70.68	29.32	0.31538	3.7114	3.1100
HfO_2- Eu (3 mol %)	63.49	36.51	0.36146	3.7375	3.2409
HfO_2- Eu(5 mol %)	63.36	36.64	0.34780	3.8080	3.2480
HfO_2- Eu (7 mol %)	66.92	33.08	0.33609	3.7143	3.3360

As it can be seen, the emission lifetime value increases with gradual addition of europium with HfO_2 NPs. Finally, from our studies it was found that HfO_2NPs showslower decay time (3.44 ns) while HfO_2 – Eu^{3+} (1 mol %) show faster decay time (3.11 ns).Cherepy et al predicted that the generally accepted decay time for scintillator applications was < 3 μs[34]. This is lesser than the generally accepted decay time of < 3 μs and provides high count rate capability. The essential requirements of scintillating materials are high density and high effective atomic number linked to high atomic numbers of its constituents in addition to high count rate capability[35]. As per the investigation, the requirements are satisfy by 1 mol% europium (Z = 63) doped hafnium oxide nanomaterial (density 10g/cm^3, Z=72).

5. Conclusion

In this work, we performed Eu^{3+} doped HfO_2 nanoparticles by precipitation method. The XRD analysis revealed that the size of the synthesized NPs was found to be of 12 nm. The HRTEM images show that the particles are found to be spherical in shape. From Wood and Tauc plot, the band gaps were found to be 4.71, 3.30, 3.90, 4.28 and 3.77 eV corresponding to HfO_2, HfO_2-Eu (1 mol %),HfO_2-Eu (3 mol %), and HfO_2-Eu (5 mol %) and and HfO_2-Eu (7 mol %).The EDAX spectrum confirms the presence of europium in HfO_2 NPs. Based on its life time decay properties, HfO_2-Eu-1 mol %) with its faster decay time of 3.11 ns and can be an excellent candidate for scintillator applications.

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