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Comparison of Pure and Doped TiO_2 Thin Films Prepared by Sol-Gel Spin-Coating Method

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In this study, using spin-coating sol-gel method we fabricated TiO_2 thin films, doped with different concentrations (1, 2, and 3 mole %) of Ce, Dy, and Eu. Characterization of the prepared samples was performed by means of the X-ray diffraction, scanning electron microscopy, ultraviolet visible absorption, and differential thermal and thermo gravimetric analysis. X-ray diffraction measurements have shown that in Eu and Dy-doped samples crystal structure consists of mixed rutile and the dominant anatase phases, however the Ce doped samples consist of anatase phase only. Scanning electron microscopy images have revealed that while average thin film thickness of the Dy-doped samples decreases with increasing concentration of Dy, the average film thicknesses of samples doped with Ce and Eu increases with increasing concentrations of these dopants. Ultraviolet visible absorption spectroscopy measurements have shown that while absorbances of the samples doped by 1 and 2 mole % of the dopants have nearly similar properties, these properties differ from each other for 3 mole % of the dopants. Finally, differential thermal and thermo gravimetric analyses have shown that the chemical reactions and weight losses of the samples have occurred at the expected temperatures.

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1. Introduction

TiO_2 thin films materials with photocatalytic properties and optical permeability are preferred in many technological applications [1–3]. Titanium dioxide is one of the main materials to be used in nano-technology. Metal ions may be added to the titanium dioxide to increase its photoactivity. For this, some rare earth elements, such as Ce, Tb, Dy, Sm, Eu, La, Yb can be added as dopants. Doping with these elements alters the band gap of TiO_2.

Titanium oxide is a very cheap, handy, biodegradable and nontoxic material, widely used in industry. TiO_2 has three kinds of different crystal structures; brookite, rutile and anatase. Its structural, optical and electrical properties can be improved by using appropriate doping materials.

Nowadays, there are numerous thin film coating methods. Sol-gel is one of these methods [4–12]. Besides sol-gel method there are many different ways for producing thin films, such as electron beam evaporation, metal-organic chemical vapor deposition method, atomic layer deposition, RF magnetron sputtering, thermionic vacuum arc and pulsed laser deposition [13, 14]. However, sol-gel method is one of the most widely applied methods, since it is easy, cheap, and handy. On the other hand, sol-gel method is an appropriate method for obtaining both inorganic and hybrid inorganic-organic polymers [15–19].

In this study, we fabricated TiO_2 thin films, doped with different concentrations (1, 2, and 3 mole %) of Ce, Dy, and Eu, by spin-coating sol-gel method. We investigated the crystal structure, morphology, optical, and chemical properties of the samples by means of the data obtained from the measurements of the X-ray diffraction (XRD) scanning electron microscopy (SEM), ultraviolet visible (UV/VIS) absorption spectrometry and differential thermal analysis (DTA).

2. Experimental

In this study, undoped and Ce, Dy, Eu doped (with the ratios of 1, 2, and 3 mole %) TiO_2 thin films were fabricated using spin-coating sol-gel method.

First, to prepare TiO_2, 10.7 g tetrabutyl orthatitanate ($C_{16}H_{36}O_4Ti$, Aldrich, 97%, molecular weight 340.32) and 7.84 g diethanolamine ($HN(CH_2CH_2OH)_2$, Sigma-Aldrich, 99%, molecular weight 105.14) were slowly added into 300 ml of ethyl alcohol and left at room temperature until the mixture would become a clear sol. Then mixture was stirred in a magnetic mixer for 2 h.

During the mixing, 0.7 ml of polyethylene glycol ($HO(C_2H_4O)_nH$, Aldrich, average Mn 400) were added slowly to the mixture. After that, Ce nitrate ($Ce(NO_3)_3{\cdot}6H_2O$ (>99% pure MW=434.22 g/mol), Eu nitrate ($Eu(NO_3)_3{\cdot}5H_2O$ (Aldrich 99.9% MW=428.06 g/mol), Dy nitrate ($Dy(NO_3)_3{\cdot}H_2O$ (Aldrich, 99.9%, MW=348.51 g/mol (anhydrous basis)), were weighed in appropriate amounts, which will be used to obtain 1, 2 and 3 mole % content of Ce, Dy, and Eu in TiO_2.

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Prepared solution was divided into ten parts. The first three solutions were used to prepare 1%, 2% and 3% Eu-doped TiO_2, for the fabrication of three thin film samples. To do this, we used 0.135 g of Eu nitrate for 1% doped TiO_2 solution, 0.269 g of Eu nitrate for 2% doped TiO_2 solution and used 0.41 g of Eu nitrate for 3% doped TiO_2 solution. These 0.135 g, 0.269 g and 0.41 g of Eu nitrate were added to the 0.2 ml of ethyl alcohol and mixed in the magnetic mixer. Then the dissolved Eu was added to TiO_2 solution and these solutions were mixed for 1 h.

The second three solutions were used for the fabrication of 1%, 2% and 3% Ce-doped TiO_2. We used 0.136 g Ce nitrate for 1% doped TiO_2 solution, 0.27 g Ce nitrate for 2% doped TiO_2 solution and 0.41 g Ce nitrate for 3% doped TiO_2 solutions. These 0.136 g, 0.27 g and 0.41 g of Ce nitrate were added to the 0.2 ml of ethyl alcohol and mixed in the magnetic mixer. Then the solutions with three different concentrations of the dissolved Ce were added into TiO_2 solutions in three different beakers and these solutions were stirred for 1 h.

The next three solutions were used for the fabrication of 1%, 2% and 3% Dy-doped TiO_2. We used 0.11 g of Dy nitrate for 1% doped TiO_2 solution, 0.22 g of Dy nitrate for 2% doped TiO_2 solution and 0.33 g of Dy nitrate for 3% doped TiO_2 solution. These 0.11 g, 0.29 g and 0.32 g of Dy nitrate were added to the 0.2 ml of ethyl alcohol and mixed in the magnetic mixer. Then the solutions with three different concentrations of Dy were added into TiO_2 solutions in three different beakers and these solutions were stirred for 1 h.

Ce, Dy, Eu-doped TiO_2 solutions, prepared as mentioned above, were used for the fabrication of the thin film samples by the spin coating method. To do this, we followed the steps described below. In the first step, we spread the solution, drop by drop, onto the entire surface of the glass substrate, which was cleaned chemically before coating. In the second step, the sol was dripped on the substrate and spun at a rate of 2000 rpm for 30 s using a G3 Spin Coater (SCS Spin Coating Systems). The TiO_2 films were prepared by spinning the glass substrates on which the sol-gel solution was prepared. In the third step, the fabricated thin films were dried at 500 °C.

Finally, the characterization of these thin films was performed. The optical properties of the TiO_2 thin films were measured using Perkin Elmer lambda 20 UV spectrometer. The microstructural features of the samples were determined by SEM (LEO 1430 VP). The determination of the crystal structure of the thin films was realized using X-ray diffractometer (X Pro Alpha). Thermal analysis of the thin films was conducted with a TG-DTA (Netzsch STA449F3) at a heating rate of 20 K/min under air atmosphere in aluminum pans, at temperatures from ambient (25 °C) to 550 °C.

3. Results and discussion

Figure 1a shows the XRD pattern of pure TiO_2 and Fig. 1b, c, and d shows the XRD patterns of 3 mole % Eu, Dy, and Ce-doped TiO_2 thin films, respectively. As seen from Fig. 1a, pure TiO_2 thin film has a mixed anatase and rutile (A+R) crystal structure. On the other hand, it is observed from Fig. 1b and c that the height of the peaks belonging to the rutile structure of the Eu and Dy-doped TiO_2 thin film samples decrease, respectively and anatase phases becomes dominant. There were similar results obtained in other studies, which are in a good agreement with our results [20]. Figure 1d shows that the Ce-doped TiO_2 thin films have only anatase phase, unlike the Eu and Dy-doped samples.

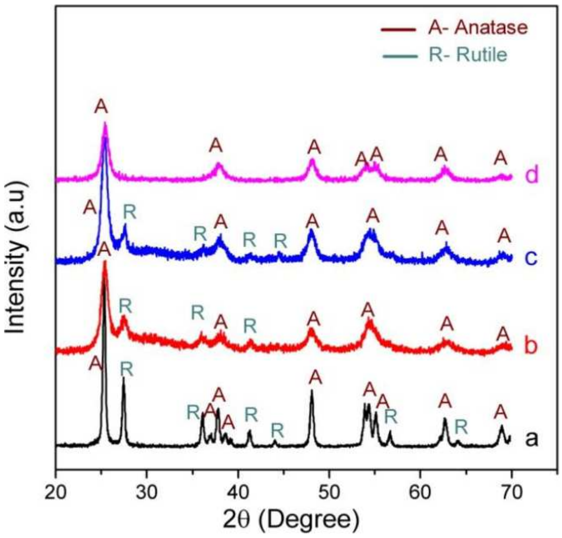

Fig. 1. XRD patterns of (a) pure TiO_2, (b) 3 mole % Eu, (c) Dy, and (d) Ce-doped TiO_2 thin films heat treated at 500 °C.

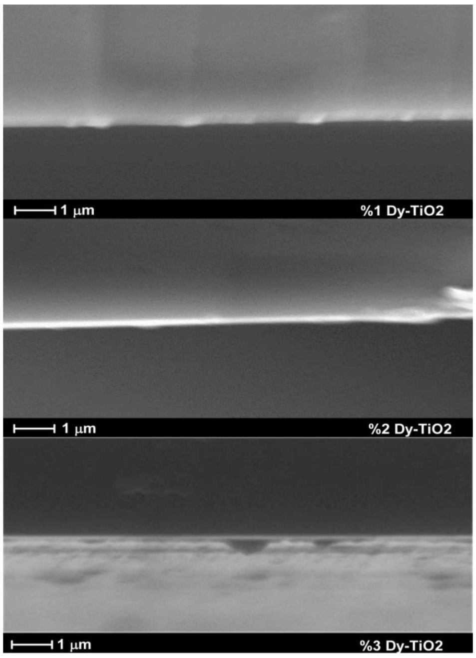

Fig. 2. SEM images of 1, 2, and 3 mole % Dy-doped TiO_2 thin films.

SEM images of 1, 2, 3 mole % Dy-doped TiO_2 thin films are given in Fig. 2. The measured average thicknesses of 1, 2, 3 mole % Dy-doped TiO_2 thin film samples are 413 nm, 232 nm and 138 nm, respectively. According to these results, we may say that increase in the concentration of Dy causes a decrease in the thickness of the Dy-doped TiO_2 thin film.

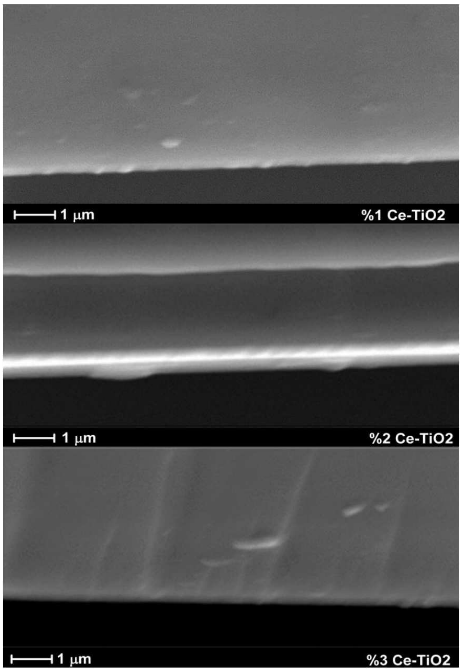

Fig. 3. SEM images of 1, 2, and 3 mole % Ce-doped TiO_2 thin films.

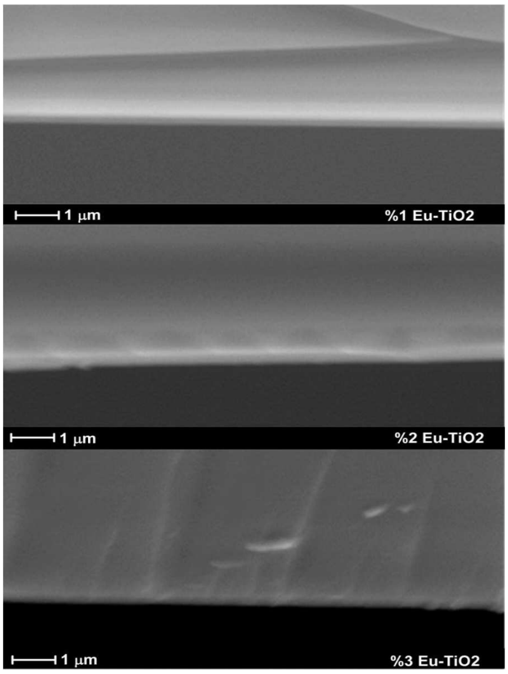

Fig. 4. SEM images of 1, 2, and 3 mole % Eu-doped TiO_2 thin films.

SEM images of 1, 2, and 3 % Ce-doped TiO_2 thin films are given in Fig. 3. The measured average thicknesses of 1, 2, 3 mole % Ce-doped TiO_2 thin films are 327 nm, 401 nm and 407 nm, respectively. If these numerical values of the thicknesses of the samples are compared with each other, we can say that increase in the concentration of Ce in Ce-doped TiO_2 thin films causes an increase in their thicknesses.

Figure 4 shows the SEM images of the 1, 2, 3 mole % Eu-doped TiO_2 thin films. The measured average thicknesses of 1, 2, 3 mole % Eu-doped TiO_2 thin films are 280 nm, 418 nm and 423 nm, respectively. If we take into account these numerical values, the thicknesses of the Eu-doped TiO_2 samples behave in a similar way as the Ce-doped TiO_2 thin film samples. In this case, the thickness of the Eu-doped TiO_2 samples increases with the increase of the concentration of Eu. Similar results have been observed in literature [21–23].

Optical properties of the samples have been studied using the data obtained from UV/VIS absorption spectrometer. Figure 5 shows the optical absorbance spectra of 1 mole % Eu, Ce, and Dy-doped TiO_2 thin films. As seen from these absorbance curves of the samples, there are small differences between them. Thus we can say that there is not much effect of 1 mole % of dopants on the absorbance of the samples.

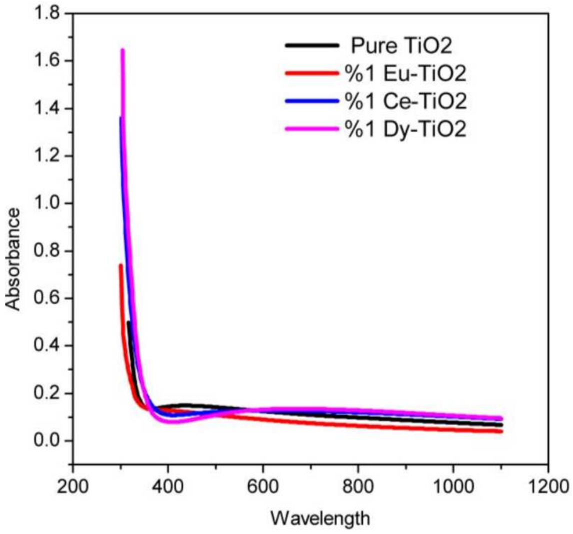

Fig. 5. Optical absorbance spectra of 1 mole % Eu, Ce, and Dy-doped TiO_2 thin films.

Figure 6 shows the optical absorbance spectra of 2 mole % Eu, Ce, and Dy doped TiO_2 thin films. As seen from these absorbance curves of the samples, there are small differences between them. Thus we can say that there is not much effect of 2 mole % of dopants on the absorbance of the samples.

Figure 7 shows the optical absorbance spectra of 3 mole % Eu, Ce, and Dy doped TiO_2 thin films. As seen from these absorbance curves of the samples, there is much more difference between them, when these

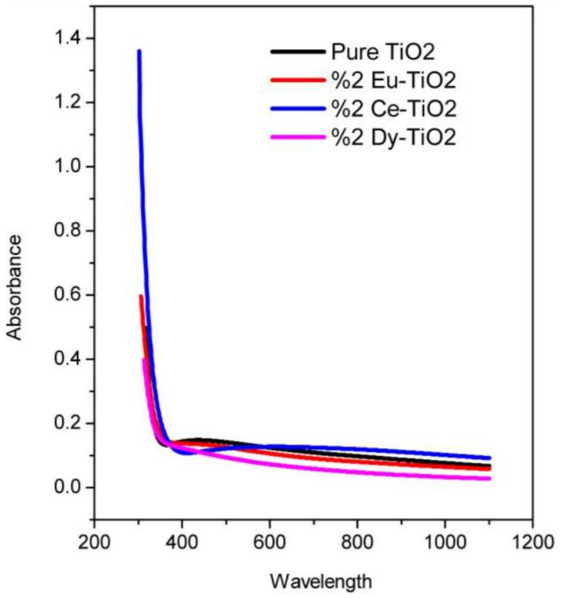

Fig. 6. Optical absorbance spectra of 2 mole % Eu, Ce, and Dy-doped TiO_2 thin films.

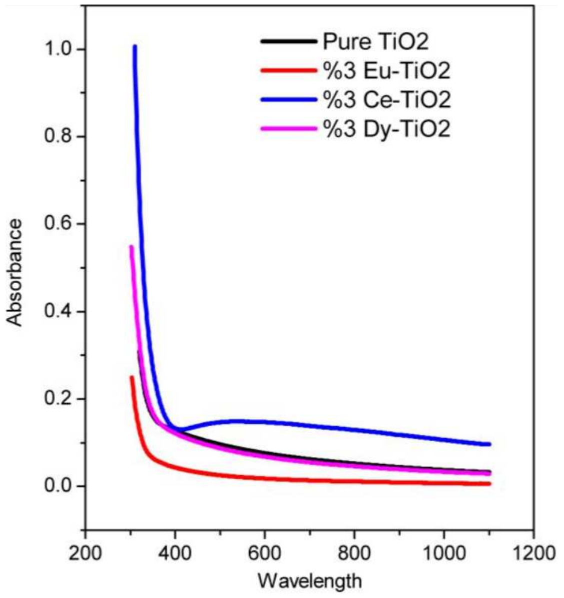

Fig. 7. Optical absorbance spectra of 3 mole % Eu, Ce, and Dy-doped TiO_2 thin films.

results are compared with the results obtained for 1 and 2 mole % Eu, Dy, and Ce-doped TiO_2 thin film samples.

Chemical properties of the samples have been determined by DTA/TGA measurements. Figure 8a and b shows results of DTA and TG analysis of 3 mole % Ce, Dy, and Eu-doped TiO_2 thin films. As seen from Fig. 8a, the peak at 200 °C on the DTA curve corresponds to an endothermic reaction which occurs due to the removal of water, trapped in the network, and of organic solvents.

The thermogravimetric analysis (TGA) shows that weight loss is observed for every sample and confirms the results obtained from DTA measurements. Weight loss in the range between 25 °C and 500 °C is ascribed to the removal of absorbed water molecules from every sample. Total weight loss of pure TiO_2 thin film was 75.50% in the temperature range between 50 °C and 500 °C (Fig. 8a).

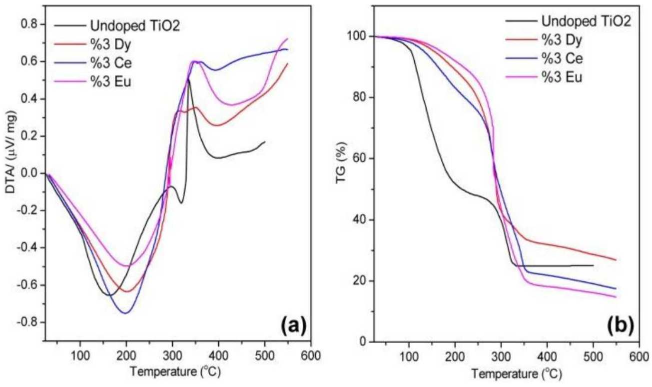

Fig. 8. (a) DTA and (b) TG analysis of 3 mole % Ce, Dy, and Eu-doped TiO_2 thin films.

The process also resulted in the synthesis of doped TiO_2 in the temperature range between 50 °C and 500 °C (Fig. 1b). Total weight losses of 1 mole % Ce, Dy and Eu-doped TiO_2 (Fig. 8b) were 82.57%, 73.17%, 85.25%, respectively. Weight loss terminates at 400 °C (Fig. 8b), where Dy nitrate was completely converted into Dy_2O_3 after a gradual loss of crystalline water. The chemical conversion reactions, the decomposition of Ce and Eu nitrates into CeO_2 and Eu_2O_3, has occurred at 360 °C (Fig. 8a). Figure 8a also shows that second exothermic peak at 375 °C indicates transformation temperature for doped TiO_2. The second one is ascribed to the transformation of the amorphous phase into the anatase phase. It is observed that 3% Ce, Dy and Eu-doped TiO_2 materials have transformation temperatures at 360 °C. Similar results have been obtained for similarly doped TiO_2 [24]. There is no significant weight loss at and above 500 °C.

4. Conclusions

Using the sol-gel method pure and Ce, Dy and Eu-doped TiO_2 thin films were deposited by spin coating technique. The results obtained from the characterization measurements of the samples are as follows;

XRD measurements have shown that crystal structure in Eu and Dy-doped samples consists of mixed rutile and dominant anatase (A+R) phases, however the Ce-doped samples have only anatase phase.

SEM images have revealed that while average thin film thickness of the Dy-doped samples decreases with increasing concentration of Dy, the average film thicknesses of Ce and Eu-doped samples increase with increasing concentrations of these dopants.

Optical measurements have shown that while the absorbances of the 1 and 2 mole % Eu, Dy, and Ce-doped TiO_2 thin film samples have not been affected by the dopants, the absorbances of the samples doped with 3 mole % dopants have been affected.

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