Characteristic Properties of Dy-Eu-Ce Co-Doped ZrO$_2$ Nanofibers Fabricated via Electrospinning

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Zirconium oxide (ZrO$_2$) is one of the widely studied oxide materials because of its excellent electrical, mechanical, and optical properties. In this study, undoped and Dy-Eu-Ce co-doped ZrO$_2$ nanofibers were fabricated by electrospinning method and their crystal structure, surface morphology, optical properties, electrical and electronic properties, and chemical properties have been analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM), UV/VIS spectrometer, four point probe technique (FPPT) energy dispersive X-ray (EDX) measurements, respectively.

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1. Introduction

Zirconium oxide (ZrO$_2$) is one of the most attractive oxide materials, which are used in many applications such as catalysis, luminescent materials, surface supports, laser systems, gate dielectrics, optical and electronic devices, magnetic recording disk, biomedical and prosthetic coatings [1-4], due to their desirable properties, such as high refractive index, high transparency in the visible and near-infrared region, high dielectric constants, high-energy band gap, high density, hardness, electrical conductivity, wear resistance, high fracture toughness, low thermal conductivity and extreme chemical inertness [5-8]. Researchers have used different ways for the fabrication of the ZrO$_2$ doped with different materials. Recently, most of the samples in the form of nanofibers have been developed by electrospinning method [9, 10]. The interest to nanofibers is explained by the fact that samples with nm sizes have remarkable changes in physical properties.

In the present study, we have fabricated Dy-Eu-Ce co-doped ZrO$_2$ nanofibers on aluminum foil and glass substrates using electrospinning method. Crystal structure, surface morphology and optical properties of Dy-Eu-Ce co-doped ZrO$_2$ nanofibers and their crystal structures, surface morphologies, optical properties, electrical and electronic properties, and chemical properties have been analyzed using X-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet/visible (UV/VIS) spectrometer, four point probe technique (FPPT) and EDX measurements, respectively.

2. Experimental

For the preparation of the solutions of the undoped and Eu, Dy and Ce co-doped ZrO$_2$ nanofibers, we used Zr iso-propoxide Zr(OCH(CH$_3$)$_3$)$_4$ (99.9 % pure $M_w = 383.68$ g/mol) and Dy(NO$_3$)$_3$·$x$H$_2$O (Aldrich, 99.9%, $M_w = 348.51$ g/mol (anhydrous basis)), Eu(NO$_3$)$_3$·$x$H$_2$O (Aldrich 99.9% $M_w = 428.06$ g/mol), and Ce(NO$_3$)$_3$·$x$H$_2$O (> 99% pure $M_w = 434.22$ g/mol) as the starting reagents and the absolute ethanol (CH$_3$OH, Sigma-Aldrich, 99.8%, $M_w = 46.07$ g/mol) as solvent. The preparation of the solutions of the nanofiber samples has been achieved as follows. Firstly, we poured 80 ml of propanol and 10 ml of ethanol in a beaker and this mixture was stirred for half hour. During mixing the solution, 20 drops of acetic acid were dropped slowly. Then we added 20 ml of Zr iso-propoxide into the solution and mixed it for 1 h. During this time, we added 150 ml of propanol into this solution and we continued mixing it for 2 h. This final solution was transferred equally into four separate beakers. One of these solutions was used for the fabrication of the undoped ZrO$_2$ nanofibers. The other three solutions were used to obtain 1 mole % Eu, Dy and Ce doped-ZrO$_2$ solutions. To obtain these solutions, we dissolved 0.025 g of Eu nitrate, 0.02 g of Dy nitrate, and 0.025 g of Ce nitrate, added into three separate beakers, including 2 ml of ethanol and poured each of these solutions into the ZrO$_2$ solutions which were prepared in advance, as reported above. Finally, these four solutions were mixed for 1 h until they become homogeneous. Afterwards, another solution was prepared by dissolving 1 g of polyvinylpyrrolidone (Aldrich, (C$_6$H$_9$NO)$_x$, PVP, $M_w = 1300000$ g/mol) in 10 ml of absolute ethanol. This solution was added into all four mixtures mentioned above. These solutions were stirred for 2 h at room temperature. These obtained homogeneous solutions were loaded into a plastic syringe of the pump of the electrospinning set-up constructed by us [11]. All samples have been developed at constant voltage of 25 kV, at a height of 6 cm, and with constant flow rate of 5 ml/h.

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3. Results and discussion

XRD patterns of the undoped and 1 mole % Dy, Ce, and Eu-doped ZrO$_2$ nanofibers prepared at 500°C are seen in Fig. 1a–d, respectively. Fig. 1a shows that undoped ZrO$_2$ nanofibers have a mixed phase (monoclinic + cubic) which is consistent with literature [12]. Figure 1b and c shows the XRD patterns of the 1 mole % Dy and Ce-doped-ZrO$_2$ nanofibers, respectively. As seen from these figures, doping of ZrO$_2$ with Dy and Ce does not change its crystal structure. Only, the intensities of peaks at 31°, seen in XRD patterns of both of Dy and Ce doped-ZrO$_2$ nanofibers, increase compared to that seen in the undoped ZrO$_2$ nanofibers. It is seen that there are substantial changes between the undoped and Eu-doped ZrO$_2$ nanofibers (Fig. 1a and d, respectively). While the dominant crystal structure phase is monoclinic in the first three nanofibers, the monoclinic and cubic phases in the Eu-doped ZrO$_2$ nanofibers are equally present. This suggests that during the synthesis, the Eu atoms were appropriately doped into the lattice, replacing zirconium atoms, without the formation of any europium oxide crystals [12].

As an example of the fabricated nanofibers, showing their morphology, SEM images of undoped and 1 mole % Dy-Eu-Ce doped ZrO$_2$ electrospun nanofibers are given in Fig. 2a–d, respectively. These images show that all electrospun nanofibers were randomly aligned with the average diameters of 176, 131, 104, and 94 nm, respectively and overlap each other, which is characteristic for electrospun fibers.

Figure 3 shows EDX analysis of the undoped ZrO$_2$ nanofibers. Chemical composition of the fabricated nanofibers is reliable. Carbon and oxygen elements originate from polymer solvents and aluminum element originates from the aluminum collector plate which was used to collect the nanofibers.

![Fig. 1. XRD patterns of (a) undoped, (b) 1 mole % Dy-doped, (c) 1 mole % Ce-doped and (d) 1 mole % Eu-doped ZrO$_2$ nanofibers prepared at 500°C.](image1)

![Fig. 2. SEM images (a) undoped, (b) 1 mole % Dy-doped, (c) 1 mole % Ce-doped and (d) 1 mole % Eu-doped ZrO$_2$ nanofibers.](image2)

![Fig. 3. EDX analysis of undoped ZrO$_2$ nanofiber.](image3)

We have calculated the activation energy of the fabricated nanofibers with the help of the Arrhenius curves of the nanofiber samples obtained from FPPT measurements in the temperature range of 300–900°C (Fig. 4). The calculated activation energy, $E_a$, and electrical conductivity, $\sigma$, of undoped and 1 mole % Dy-Eu-Ce doped ZrO$_2$ nanofibers are given in Table I.

Figure 5 shows thermogram of the undoped ZrO$_2$ nanofibers. An intense endothermal peak is found at 175°C, followed by a 16.89 mg weight loss due to removal of organic elements from the nanofibers. Thermal decomposition of the PVP begins at 380°C in air under
TABLE I

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\sigma$ [S cm$^{-1}$]</th>
<th>$T$ [°C]</th>
<th>$E_a$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped ZrO$_2$</td>
<td>$1.88 \times 10^{-2}$</td>
<td>798</td>
<td>1.69</td>
</tr>
<tr>
<td>1 mole % Eu-doped ZrO$_2$</td>
<td>$5.19 \times 10^{-3}$</td>
<td>811</td>
<td>1.79</td>
</tr>
<tr>
<td>1 mole % Ce-doped ZrO$_2$</td>
<td>$9.9 \times 10^{-3}$</td>
<td>807</td>
<td>1.43</td>
</tr>
<tr>
<td>1 mole % Dy-doped ZrO$_2$</td>
<td>$4.83 \times 10^{-2}$</td>
<td>798</td>
<td>1.33</td>
</tr>
</tbody>
</table>

Fig. 4. The temperature dependence of electrical conductivity for undoped and 1 mole % Dy-Eu-Ce doped ZrO$_2$ nanofibers.

Fig. 5. DTA/TGA analysis of undoped ZrO$_2$ nanofibers.

Optical band gap energy of the undoped ZrO$_2$ nanofibers and nanofibers doped with metals or different lanthanides is one of the most important properties, which plays a vital role in the usage of these nanofibers in industry. To find the optical band gap energies of the samples, we have used the data obtained from UV/VIS measurements. Optical absorbance graphs $\alpha(h\nu)^2$ vs $h\nu$ of the undoped and 1 mole % Dy, Ce, Eu-doped ZrO$_2$ nanofibers are shown in Fig. 6. We have found the optical band gap energies of the samples by extrapolating the linear portions of the respective curves. The determined optical band gap energy values of the undoped and 1 mole % Eu, Ce, Dy-doped ZrO$_2$ nanofibers are 5.57, 5.16, 5.17, and 5.06 eV, respectively.

Fig. 6. UV absorbance of undoped and 1 mole % Eu, Ce, Dy-doped ZrO$_2$ nanofibers.

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4. Conclusions

In the present work, we have fabricated the undoped and 1 mole % Dy, Ce, and Eu-doped ZrO$_2$ nanofibers via electrospinning and have investigated their structural, morphological, electrical, chemical composition, and optical properties. The obtained results are as follows:

1. All samples have mixed crystal phase (monoclinic + cubic).

2. All electrospun nanofibers were randomly aligned with the average diameters of 176 nm (undoped), 131 nm (1 mole % Dy-doped), 104 nm (Ce-doped) and 94 nm (Eu-doped) and overlap each other.

3. There is a good correlation between the electrical conductivity of the samples and their activation energies.

4. Optical band gap energies of the undoped and 1 mole % Eu, Ce, and Dy-doped ZrO$_2$ nanofibers are found to be 5.57, 5.16, 5.17, and 5.06 eV, respectively. The most influencing element, causing the decrease of the optical band gap energy, is dysprosium.

Acknowledgments

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References