OPTICAL PROPERTIES OF TeO₂-TiO₂ THIN FILMS DOPED WITH Eu³⁺ IONS FABRICATED BY SÓL-GEL PROCESSING

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ABSTRACT

The present study was aimed to fabricate thin films of TeO₂-based glasses by a sol-gel process. It was here demonstrated that to control the hydrolysis reaction of Te-alkoxide with a chelating agent of diethanol-amine and in low-humidity environment was important because the hydrolysis reaction was extremely rapid. As a result, transparent TeO₂-TiO₂ thin films were successfully formed by dip-coating and subsequent heat-treatment. TiO₂ component was found to be effective not only for more moderate hydrolysis reaction but also for an increase of refractive index. Photoluminescence properties of Eu³⁺ ions in TeO₂-TiO₂ thin film were also investigated.

Keywords: tellurite glass, sol-gel processing, thin film, TiO₂, Eu³⁺, photoluminescence.

INTRODUCTION

TeO₂-based glassy materials [1-6] has excellent optical properties, such as a wide optical window from visible to infrared region, high refractive index and high third-order nonlinear optical properties, and are expected to be applied to photonic devices, such as ultrafast optical switching, frequency converter, laser, amplifier, etc. Also, they have a low photon energy (600 – 700 cm⁻¹) and asymmetric structural units (TeO₄ trigonal bipyramids; tbp), TeO₂ (trigonal pyramids; tp), which is quite preferable for phosphorescent host materials doped with rare-earth ions. To develop new types of multi-functionalized phosphorescent materials with high photoluminescence performance and nonlinear refractive properties, morphology control (thin film, fiber, slab, photonic crystal (PC) etc.) of TeO₂-based glasses has increasingly been of importance. Fabrications of thin film of TeO₂-based materials were reported by several groups. Coste et al. [7] reported synthesis of stable TeO₂ sol and gel by an ester reaction with acetic acid and isopropanol and however uniform and transparent gel films were difficult to be formed because a high hydrolysis reaction of Te-alkoxide with atmospheric humidity. Subsequently, they reported thin film fabrication of TeO₂ by use of citrate acid as a chelating agent and analyzed them by small angle X-ray scattering (SAXS) [8-10]. Hodgson et al. [11] also reported a TeO₂ thin film. They added several second components of Na₂O, BaO, TiO₂ and Al₂O₃ and showed such a second component was effective to improve thermal stabilities of TeO₂ thin films [11,12]. Wei et al. [13] used non-hydrolysis sol-gel method and succeeded to fabricate TeO₂ thin films. As seen in literatures introduced above, Te-alkoxide exhibits very high hydrolysis reaction rate and so weak to atmospheric humidity. Hence, humidity level should be controlled to be lower.
On the other hand, the present authors recently investigated melt-quenched TeO$_2$-based glasses and as additional dopants, TiO$_2$ was effective to reinforce TeO$_2$ glass network due to substitutional positioning of Ti to Te site and to increase third-order optical nonlinearities [2]. In this study, a synthesis of TeO$_2$-TiO$_2$ binary thin film, in which diethanol-amine (DEA) was used as a chelating agent for Te- and Ti-alkoxides, and photoluminescence properties of europium ions doped in thin film were investigated. The heat-treatment dependency of film properties was also reported.

**EXPERIMENTAL**

The starting materials were Te(OCH(CH$_3$)$_3$)$_4$, Ti(OCH(CH$_3$)$_3$)$_4$, dehydrate isopropanol (IP), diethanol-amine (DEA) and EuCl$_3$·6H$_2$O. The metal-alkoxides, Te(OCH(CH$_3$)$_3$)$_4$ and Ti(OCH(CH$_3$)$_3$)$_4$ was firstly mixed in low humidity air (<10 %) in a glove box and added with DEA and dehydrate isopropanol to obtain a stable solution. A molar ratio of Te(OCH(CH$_3$)$_3$)$_4$ and Ti(OCH(CH$_3$)$_3$)$_4$ DEA and IP was 0.5:0.5:2:26:5. After the double-metal alkoxide isopropanol solutions were rigorously stirred for 30 min, de-ionized water with an equivalent molar of the metal-alkoxides was added to the alkoxide solution. To dope Eu$^{3+}$ ions, EuCl$_3$·6H$_2$O was dissolved to a small amount of isopropanol and subsequently added with 2 mass % Eu$_2$O$_3$ concentration. The nominal content was 50TeO$_2$-50TiO$_2$ in molar ratio. Finally a transparent, stable 50TeO$_2$-50TiO$_2$ sol was obtained and used to fabricate a corresponding thin film on a fused silica substrate by a dip-coating technique with a speed of 3 mm/s. An as-prepared thin film was dried at 200°C for 30 min and, to obtain a thicker film, the same procedure of dip-coating and drying was repeated. The gel film experienced a heat-treatment in air at 300 to 600°C. For comparison, the sol was dried to obtain the corresponding powder sample, which was heat-treated at various temperatures from 300 to 1000°C. For characterizations, X-ray diffraction (XRD; by Phillips, X’pert pro), Raman spectroscopy (by JASCO, NRS-2000), X-ray photo-electron spectroscopy (XPS; by Surface Science Instruments, SSX-100), ellipsometry (by Five Lab, Mary-102) and photoluminescence (PL; by Oriel Instruments, Instaspec V™ or EG&G, 5209), were applied. In PL measurements, two different excitation sources were used. One is a N$_2$ pulse laser (Usho, KEC-160) and the other is cw Rhodamine 6G dye laser (Coherent co., 599) excited by a green solid-state diode laser (Coherent co., Verdi V-6).

**RESULTS AND DISCUSSION**

Fig. 1 shows a photograph of the appearance of the resultant TeO$_2$-TiO$_2$ thin films heated at various temperatures. At lower temperatures the film was colored light- /dark-brown, while the heat-treatment at temperatures higher than 500°C resulted in transparent, clear films. This color change was also examined by XPS. Fig. 2 depicts XPS spectra of Te 3d$_{5/2}$. It was found that at temperatures lower than 450°C Te metal (573 eV) and TeO$_2$ (~ 576 eV) states [14] were both detected and that further higher temperatures led to the oxidation of metal Te and decreased the content of Te metal.

![Fig. 1. Photograph of the resultant TeO$_2$-TiO$_2$ thin films heated at various temperatures.](image)

![Fig. 2. XPS spectra of Te 3d$_{5/2}$ for 50TeO$_2$-50TiO$_2$ thin films heated at various temperatures.](image)
Fig. 3. $[\text{TeO}_2]/(\text{[Te]}+\text{[TeO}_2])$ of 50TeO$_2$-50TiO$_2$ thin films as a function of the heat-treatment temperature.

Fig. 3 shows $[\text{TeO}_2]/(\text{[Te]}+\text{[TeO}_2])$ as a function of the heat-treatment temperature. At 300°C the ratio was 0.87, indicating that 13% tellurium atom existed as a metallic state.

Correspondingly to the tendency of transparency of the thin film, the metallic phase was decreased down to 5%. The metallic Te phase was also detected in XRD data of the powder samples, as shown in Fig. 4. Thus, it was concluded that the dark-brown coloration was due to the precipitation of metallic tellurium phase and that the heat-treatment temperature higher than 500°C was enough to obtain a transparent film because of the oxidation of metallic Te to α-TeO$_2$ (see XRD data in Fig. 4) [12]. However, it should be borne in mind that further higher temperature above 600°C made the film brittle because of clacks in film and peering it off.

The precipitated crystal phases were varied with the temperature in the heat-treatment. From XRD data, α-TeO$_2$, anatase TiO$_2$ phase was observed above 450 and 500°C, respectively, the latter of which was transformed to rutile phase at 1000°C. A small amount of rutile TiO$_2$ was generated above 500°C. TiTe$_2$O$_6$ phase was also observed at temperatures above 500°C [12]. Raman spectra were measured as well and shown in Fig. 5. At lower temperatures, broad, characteristic bands of an amorphous TeO$_2$ phases were observed at 450 cm$^{-1}$ and 660 cm$^{-1}$. The former hand was attributed to Te-O-Te(Ti) bending mode and the latter stemmed from Te-O stretching vibration mode in asymmetric TeO$_4$ (tbp) units [15].

The presence of amorphous phase could be seen in XRD patterns of the powder samples, shown in Fig. 4 (a hallo peak around 20-30 degree) and still even at 600°C. At 1000°C clear XRD reflection peaks assigned
to rutile TiO₂ were observed without a TeO₂ amorphous phase. The rutile TiO₂ (280, 440 and 620 cm⁻¹) could clearly be seen in Raman spectrum. From these observations, it is found that the transparent TeO₂-TiO₂ film was a composite of amorphous TeO₂-TiO₂ crystallised phases; α-TeO₂ (450 – 600°C), anatase TiO₂ (500 – 600°C), TiTe₂O₈ (500 – 1000°C) and rutile TiO₂ (500-1000°C).

Fig. 6 shows the heat-treatment dependence of film thickness d and refractive index n. The thickness of as-prepared film was ~ 500 nm (for fourfold dip-coating) and monotonically decreased down to 100 nm at 600°C. The refractive index n, which was measured at 632.8 nm of He-Ne laser, was as high as 2.0 above 500°C of the heat-treatment temperature. With an increase in the heat-treatment temperature the refractive index was increased up to 2.2 at 600°C due to the TiO₂ incorporation and the densification of the film corresponding to the decrease in the thickness. The elementary analysis of the surface state was conducted in XPS analysis, as summarized in Table 1. On and near the surface, TiO₂ content was comparatively increased with the heat-treatment temperature, which was well correlated with the precipitation of TiTe₂O₈ and anatase/rutile TiO₂ at higher temperatures.

Photoluminescence (PL) spectra were measured under an excitation of ultraviolet (UV) pulses of N₂ gas laser (337.1 nm), as shown in Fig.7. Eu³⁺-doped TeO₂-TiO₂ films heated at 500 and 550°C exhibited a red PL assigned to ¹D₀→F₁ (~ 590 nm) and ¹D₀→F₂ (~ 610 nm), while undoped films had no PL lines. Fig. 8 is a low-temperature PL spectrum (9 K) of Eu³⁺-doped TeO₂-TiO₂ film heated at 550°C, which was detected by a direct excitation of ¹D₀ level of doped Eu³⁺ ions excited by a cw Rhodamine 6G dye laser pumped with a green solid-state diode laser. Clear PL peaks due to ¹D₀→F₁,2,3 of Eu³⁺ could be observed. The broad PL bands indicate that Eu³⁺ ions are at most in glass phase. From the figure an asymmetry ratio of Λ= I(¹D₀→F₂)/I(¹D₀→F₁) was estimated to be 2.98. Higher Λ values indicate enhanced red radiative probability of ¹D₀→F₂ transition (electric dipole character) because ¹D₀→F₁ is

![Graph showing film thickness and refractive index as a function of temperature](Image)

**Fig. 6. Film thickness d and refractive index n as a function of the heat-treatment temperature.**

![Graph showing photoluminescence spectra](Image)

**Fig. 7. Photoluminescence spectra of non-doped and Eu³⁺-doped 50TeO₂-50TiO₂ thin films (d ~ 100 nm), heated at 500 and 550°C (λₑₓ = 337.1 nm).**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>300°C</th>
<th>350°C</th>
<th>400°C</th>
<th>450°C</th>
<th>500°C</th>
<th>550°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Te:Ti</td>
<td>48.7:51.4</td>
<td>48.4:51.6</td>
<td>50.1:49.9</td>
<td>39.4:60.0</td>
<td>38.3:61.7</td>
<td>43.8:56.2</td>
<td>37.2:62.8</td>
</tr>
</tbody>
</table>

Table 1. Results of elementary analysis of 50TeO₂-50TiO₂ thin films by XPS as a function of the heat-treatment temperature.
a magnetic dipole transition in nature and almost independent of mother matrix [16]. From literatures, A was reported to be 0.98 (LaF₃:Eu³⁺) [17], 1.89 (Na₂O-Al₂O₃-TeO₂) [18] and 0.87 (SnO₂-SiO₂) [19]. By comparison, it is found that Eu⁺⁺-doped TeO₂-TiO₂ film has a potential as a red phosphor. The excellent optical properties might come from an asymmetric structure of TeO₂-based glasses. The main constituent of TeO₂ unit (tbp) consists of fourfold-coordinated Te atom with oxygen anions and has a non-bonded electron lone pair in an equatorial position. The central Te atom has two equatorial positioned oxygens with shorter bonding length of 1.85 Å and two axial positioned oxygens with longer bonding length above 2 Å [20]. In TeO₂ glass-network, titanium atoms are substitutionally positioned with Te atoms and oxygen-coordination number is increased to sixfold. However, TeO₂-TiO₂ glasses have similar Raman spectra with a TeO₂ glass and it is thus believed that TiO₂ can reinforce TeO₂ network structure without a coordination transformation from TeO₂ (tbp) to TeO₃ (tp), which was observed in alkali- and alkaline-earth-tellurite glasses and produced via cleavage of three-dimensional network of Te-O-Te. In such a reinforced TeO₂-TiO₂ glass networks, Te-O₉ can coordinate the luminescent center of Eu⁺⁺ ions with an asymmetric ligand structure. Further analysis of ligand field structure around Eu⁺⁺ ions is in progress and will be reported elsewhere.

CONCLUSIONS

By a sol-gel technique a transparent and uniform TeO₂-TiO₂ thin film could be fabricated and photoluminescence of Eu⁺⁺ ions doped was examined. For the purpose to obtain the transparent film, it was demonstrated that the use of chelating agent (DEA) and the humidity-controlled environment in dry grove box were essential. Furthermore, it should be kept in mind that the heat-treatment below 450°C brought about light-/dark-brown coloration due to the precipitation of metallic Te phase. When as-prepared TeO₂-TiO₂ thin film was heated between 500°C and 550°C, the aimed transparent TeO₂-TiO₂ thin film was obtained and Eu⁺⁺ PL was clearly observed even with a thickness of ~ 100 nm. Low-temperature PL of Eu⁺⁺-doped TeO₂-TiO₂ film revealed strong ⁵D₀→⁷F₃ PL in comparison with ⁵D₀→⁷F₁ PL, indicating that Eu⁺⁺ ions could be positioned in an asymmetric ligand field structure. The incorporation of TiO₂ was found to reinforce TiO₂ 3D-network. However at higher temperatures α-TeO₂ (450 – 600°C), TiTe₂O₈ (500 – 1000°C), anatase/rutile TiO₂ (500 - 1000°C) were precipitated and thus the film became brittle with titanate rich surface. High refractive index and high third-order optical non-linear properties of TeO₂ based sol-gel thin film would open further applications to such as high-performance optical waveguides, filters, photonic-crystal (PC) multi-structures and so on.

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