SnO_2 BASED GLASSES: A VIABLE PHOTONIC SYSTEM

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Abstract

The present work focuses on sol-gel derived SnO_2-based thin glass-ceramic films doped with Er^{3+} ions, fabricated by dip-coating technique. Our goal is to find a viable fabrication protocol to obtain them. Thin films with a variety of composition were synthesized and their structural, optical and spectroscopic properties were investigated. The FTIR spectra and X-ray diffraction patterns were used to characterize the structure of the thin films. The transparency of the thin film was tested by UV-Vis transmittance measurements. The energy transfer dynamic was investigated by time-resolved spectroscopy and photoluminescence measurements.

1. Introduction

Silica-based materials doped with rare earth ions are widely employed in photonics. However, in pure silica, doping ions easily form clusters which lead to quenching effect due to the ion-ion energy transfer. As a result, the concentration of these active ions is limited. A possible strategy to reduce this problem is to use transparent glass-ceramics. The incorporation of rare earth ions in nanocrystals prevents the aggregation of these ions and allows nanocrystal-ion energy transfer [1]. This phenomenon increases the luminescence quantum yield because SnO_2 has a higher absorption cross section than that one of rare earth ions. Moreover, these glass-ceramic materials merge the unique optical properties of both crystals and glasses [2]. Among the various materials that could be used as nanocrystals embedded in silica matrix, tin dioxide presents some interesting characteristics. SnO_2 is a wide-band gap semiconductor (Eg = 3.6 eV at 300 K) with very low cut-off phonon energy of 630 cm^{-1} [3]. Increasing as much as possible the concentration of SnO_2 nanocrystals in amorphous SiO_2 is one of the crucial problems. In [4], un-doped thin films were fabricated with different molar percentages of SnO_2: from 12 mol% to 60 mol% in order to focus on the compositional effects. In this case, the limit of SnO_2 concentration embedded in host material reached 30 mol% instead of 25 mol% like in earlier approaches [5][6]. Van et al [7] recently suggested that Er^{3+} inhibits the growth of SnO_2 crystals on the surface of SiO_2-SnO_2 films, so the effect of rare earth on the SnO_2 crystallization deserves careful investigation.

In this study we synthesize glass-ceramics $xSnO_2$-$(100-x)SiO_2$ thin films doped with Er^{3+} ions. Optical, spectroscopic and structural assessment of the samples has been investigated by several characterization techniques.

2. Experimental procedure

2.1. Fabrication of $xSnO_2$-$(100-x)SiO_2$ doped with Er^{3+} thin films

The $xSnO_2$-$(100-x)SiO_2$ (x = 10, 20 and 30 mol%) glass-ceramic thin films doped with different concentrations of Er^{3+} (1, 2 and 3 mol%) were fabricated by sol-gel route and dip-coating technique. Precursors $SnCl_2{\cdot}2H_2O$ and $Er(NO_3)_3{\cdot}5H_2O$ were dissolved into ethanol before being added to the starting solution that had been prepared by mixing tetraethyl orthosilicate (TEOS), ethanol, de-ionized water, and hydrochloric acid as a catalyst. The final mixture was stirred for 16 hours. Then, thin films activated by Er^{3+} were deposited on the high purity silica and silicon substrates by dip-coating technique with the dipping rate of 8 cm/min. After each dip-coating step the film was annealed in air at 150ºC for 3 min. After three steps, final thin films were transparent and crack-free after heat-treatment for 1 hour in air at various temperatures ranging from 600ºC to 1200ºC. Figure 1 shows the diagram illustrating whole fabrication procedure of thin films.

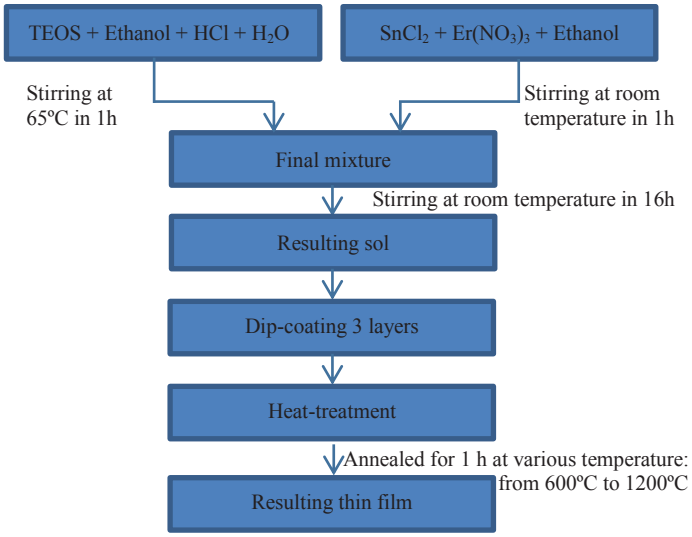

Fig. 1 Flowchart of the fabrication protocol of sol-gel derived SnO_2-SiO_2-Er^{3+} glass-ceramic thin films.

2.2. Characterization of resulting thin films

As mentioned before, the structure, transparency and photoluminescence features of all resulting thin films were characterized. FTIR transmission measurements were performed to get information about structure and residual water and solvent content. The crystallization of tin-dioxide component was studied with X-ray diffraction. In addition, the transparency of the thin films was investigated by UV-Vis transmittance spectra. The photoluminescence of the Er^{3+} ions in the surrounding glass-ceramics environment was employed to investigate the role of SnO_2 nanocrystals as sensitizer of Er^{3+}ions.

3. Results and discussion

3.1. Structure

3.1.1 FTIR

The infrared absorption spectra of the $30SnO_2$-$70SiO_2$ thin film doped with 1 mol% Er^{3+} heat-treated in air at temperature ranging from 600ºC to 1200ºC for 1 hour is shown in Figure 2. The modes at 1626 cm^{-1} and 3404 cm^{-1} are assigned to the OH group vibrations. These modes are still present in the samples heat-treated at 600ºC. With higher annealing temperature, starting from 800ºC, they disappear because of the elimination of water from inside the thin films [8].

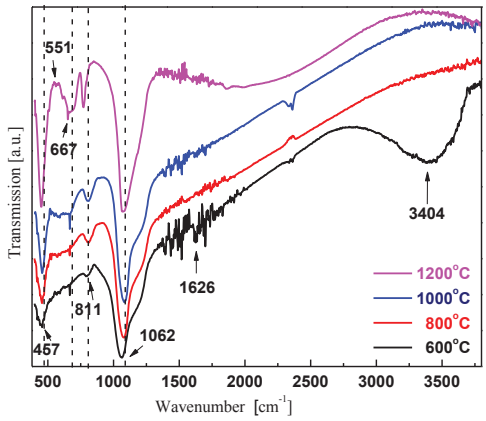

Fig. 2 Infrared spectra of the $30SnO_2$-$70SiO_2$ thin film doped with 1% Er^{3+} heat-treated in air at different temperature for 1 hour.

The broad absorption band at 1062 cm^{-1} is assigned to asymmetric stretching vibration of ≡Si−O−Si≡ linking bonds. There are also other absorption bands concerning Si−O−Si bonding: 811 cm^{-1} and 457 cm^{-1} assigned to the symmetric stretching and to the δ vibrational mode, respectively. The weak band at about 667 cm^{-1} is due to the vibration absorption band of δ(O–Sn–O) bonding, which indicates the growth of SnO_2 nanocrystals [4]. The FTIR feature indicates that after heat treatment at 1200°C a fully densified film is obtained.

3.1.2 XRD

The X-Ray diffraction patterns of $30SnO_2$-$70SiO_2$ thin film doped with 1% Er^{3+} (Figure 3), heat-treated in air at temperature ranging from 800ºC to 1200ºC for 1 hour, show that SnO_2 nanocrystals only appear in sample annealed at temperature higher than 1000ºC.

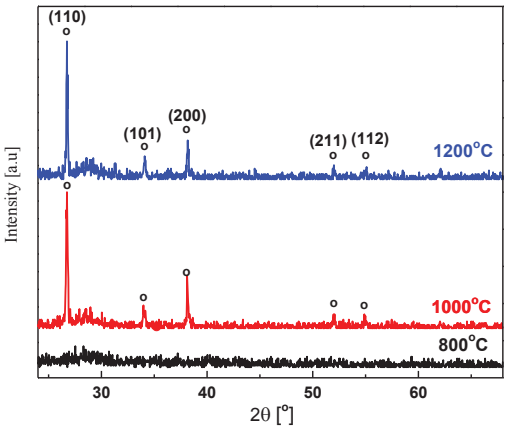

Fig. 3 X-Ray diffraction patterns of $30SnO_2$-$70SiO_2$ thin film doped with 1 mol% Er^{3+}, heat-treated in air at different temperature for 1 hour.

Figure 4 shows XRD spectra of $xSnO_2$-(100-x)SiO_2 (x = 10, 20 and 30 mol%) thin films, doped with 1% $Er^{3+}$and annealed at 1200 °C for 1 hour. The diffraction peaks at 2θ = 26.9°, 34.1°, 38.2° and 52.0° correspond to the network side (110), (101), (200), (211) and (112) of SnO_2 rutile crystal phase (JCPDS 41-1445).
As expected, the higher concentration of SnO_2 is, the larger number of SnO_2 nanocrystals are formed.

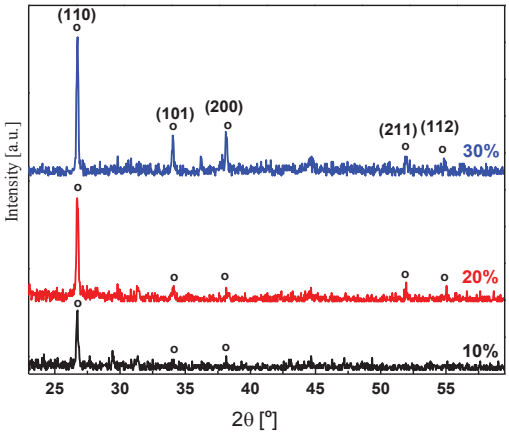

Fig. 4 X-Ray diffraction patterns of $xSnO_2$-(100-x)SiO_2 (x = 10, 20 and 30 mol%) glass-ceramic thin films doped with 1% Er^{3+}.

3.2. Transparency

The UV-Vis transmittance spectra of the thin films deposited on the high purity silica with different concentration of SnO_2, ranging from 10 to 20 mol% activated by 1 mol% of Er^{3+} and annealed at 500°C are shown in Figure 5. It can be seen that the transmittance of these samples remains around 90% over the 400 nm – 1.1 µm region.

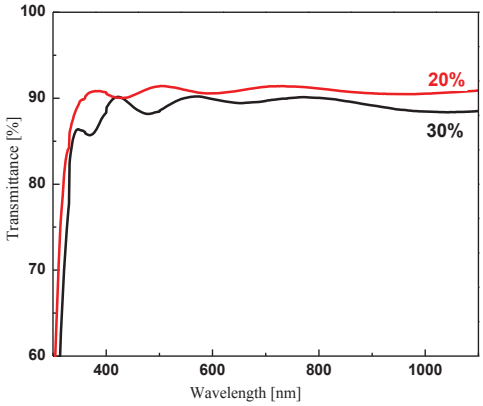

Fig. 5 UV-Vis transmittance spectra of $xSnO_2$-(100-x)SiO_2 (x = 20 and 30 mol%) doped with 1 mol% Er^3 thin films, annealed at 500°C.

3.3. Photoluminescence

Figure 6 shows the 1.5 µm photoluminescence spectra of $30SnO_2$ -$70SiO_2$ glass-ceramic thin films doped with different concentration of Er^{3+} ranging from 1 up to 3 mol% upon excitation at 300 nm. The luminescence spectra indicates an efficient energy transfer from the SnO_2 nanocrystals to the rare earth ions [5]. Moreover, the narrowing of the emission peaks, associated to the Stark multiplets, evidences that the rare earth ions are embedded in the SnO_2 nanocrystals. It is well known that, increasing the concentration of rare earth ions, the luminescence quenching is observed due to clustering effect and ions-ions interaction. Although SnO_2 nanocrystals helps in dispersing Er^{3+} ions, the emission intensity decreases slightly when the concentration of Er^{3+} reaches the percentage of 2 mol% and it shows a strong quenching for the 3 mol% sample.

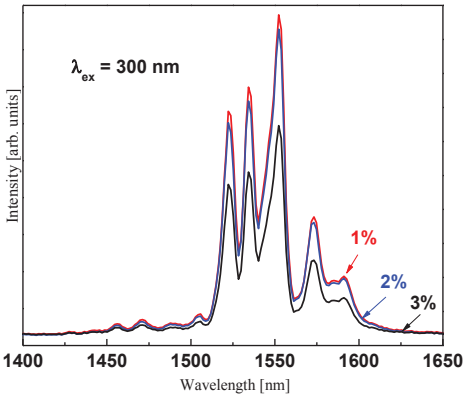

Fig. 6 Photoluminescence spectra of $30SnO_2$ -$70SiO_2$ thin films doped with different concentration of Er^{3+} heat-treated at 1200ºC.

4. Conclusion

We have figured out the fabrication protocol to obtain fully densified thin film with the highest concentrations of SnO_2 and Er^{3+}: 30 mol% and 2 mol%, respectively. The viability of SnO_2 based glasses in form of thin films was investigated. The films are crack-free and exhibit a transmittance of around 90% over the 400 nm – 1.1 µm region. The role of SnO_2 nanocrystals as Er^{3+} luminescence sensitizers was experimentally confirmed.

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