Optical and Structural Properties of Er\textsuperscript{3+}-doped SiO\textsubscript{2}-ZrO\textsubscript{2} Glass-Ceramic Thin Film

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Abstract. The Er\textsuperscript{3+}-activate dielectric thin film can be applied to produce planar waveguide amplifiers that can be integrated with other active or passive devices on the same chip. However, Er\textsuperscript{3+} tend to cluster in host material especially in silica when doped at high concentration. This issue can be overcome by introducing ZrO\textsubscript{2} as a co-host material in a silica glass matrix by helping to disperse Er\textsuperscript{3+} homogeneously and consequently enhance the output intensity. In this work, we present a study on 70SiO\textsubscript{2}-30ZrO\textsubscript{2} glass ceramic doped with a various concentration of Er\textsuperscript{3+} prepared by the sol-gel dip coating technique and each film obtained were annealed at 900°C. Full film densification was achieved for the deposited film, which indicates the hydroxyl group was successfully removed as shown in Raman spectra. Refractive index of the film increase with the increment of rare earth ion and this permit the guiding of light in the film. Red and green emissions of Er\textsuperscript{3+} were detected upon 514.5 nm excitation. Nevertheless, the presence of higher Er\textsuperscript{3+} (0.58 mol\%) induces concentration quenching phenomena as shown in the PL spectra where there is a decline in green emission peak.

1. Introduction

Optical communication systems have proven a great potential for high speed and data transmission over the last decade. The vast number of end users acquire faster internet and higher data capacity which coax the world of information and communication technology (ICT) to divert their attention towards photonic integrated circuit (PIC). The growing demand in PIC necessitated the improvement of optical materials which plays an important role in producing high-performance PIC components. One of important PIC component is an optical amplifier that is very useful to boost the signal power. Among various optical amplifier, erbium doped waveguide amplifier (EDWA) is seen to be a great candidate due to its low noise and high gain in the C-band region (1530-1565 nm) of optical communication [1,2].

Rare-earth (RE) doped glass-ceramic is a nanocomposite system that has specific morphological, structural and spectroscopic properties. These materials consist of nanocrystal embedded in amorphous silica [3]. Due to the mixture of these two phases, the transparent glass ceramic thin film will have tremendous potential applications.

Glass-ceramic materials doped with Er\textsuperscript{3+} for communication networks have attracted the interest of many researchers [4], especially for EDWA application. Er\textsuperscript{3+} has been reported as the most suitable rare-
earth (RE) ion for optical signal amplification at 1.55 μm [5,6], due to its ion-ion transition that emits photon energy at this wavelength range, and furthermore, it coincides, within the low-loss wavelength region of silica optical fibres [7]. The other Er$^{3+}$ transitions in the blue, green and red spectral regions were also discovered to have potential in other applications [8–10]. However, Er$^{3+}$ tend to cluster in silica when it is doped at high concentration [11]. It is due to silica rigid network structure which has strong Si-O-Si covalent bond that failed to accommodate Er$^{3+}$ ions effectively. Hence, Er$^{3+}$ is more likely to locate themselves close to each other and prone to achieve their favourite six-fold coordinated structure. Upon clustering, the energy transfer process between Er-Er ion are likely to occur and ultimately hampers the luminescence emission intensity via non-radiative transition.

This issue can be overcome by introducing other oxide material to the silica such as Al$_2$O$_3$ [12], P$_2$O$_5$ [13], HfO$_2$ [14] and TiO$_2$ [15] which can neutralize Er$^{3+}$ positive charges by providing more non-bridging sites in the SiO$_2$. The study by Armelao et al [12] reported that the addition of Al$_2$O$_3$ in silica reduce the clustering effect by supplying NBO bonds. In addition, the use of P$_2$O$_5$ as a co-host with silica causes emission intensity of RE ions to increase as studied by Glorieux et al [13]. Tosello also reported high luminescence intensity and broad bandwidth were observed at 1550 nm for Er$^{3+}$ doped SiO$_2$-TiO$_2$ waveguide. It shows that the SiO$_2$-TiO$_2$ mixture promotes the dispersion Er$^{3+}$ in the network [15]. Moreover, the influence of hafnium in silica was also investigated by Zampedri et al [14]. They discovered hafnium alter the structure of SiO$_2$ and assist the incorporation of Er$^{3+}$ in the network. Therefore, the use of ZrO$_2$ as a co-host material with silica glass matrix could help to disperse Er$^{3+}$ ions homogeneously [16] and consequently enhance the output intensity. Furthermore, addition zirconia in the network could reduce the phonon energy and lower the non-radiative relaxation process.

In this paper, Er$^{3+}$-doped SiO$_2$-ZrO$_2$ with various concentration Er$^{3+}$ (0.52, 0.54, 0.56 and 0.58 mol%) were synthesis and deposited by using sol-gel method and dip-coating technique, respectively. The optical and structural properties as a function of Er$^{3+}$ amount were studied.

2. Experimental details
A mixture of 70SiO$_2$-30ZrO$_2$ doped x(Er$^{3+}$) (x = 0.52, 0.54, 0.56 and 0.58 mol%) was obtained by using sol-gel method. The SiO$_2$ solution was prepared by mixing tetraethyloorthosilicate (TEOS, Fluka, 98% purity), deionized water (H$_2$O), ethanol (EtOH, HmbG, 100% purity) and hydrochloric acid (HCl, the concentration of 37%) with the molar ratio 1:2:37:9:0.01. EtOH and HCl were acting as solvent and catalyst, respectively. The mixture was then being magnetically stirred at 65°C for 1 hour with the stirring speed of 400 rpm. After 1 hour, zirconium oxychloride octahydrate (ZrOCl$_2$∙8H$_2$O) was dissolved in EtOH and later the mixture was added in the SiO$_2$ solution. Erbium chloride hexahydrate (ErCl$_3$∙6H$_2$O) in aqueous solution was inserted into the final solution with specific concentration (0.52, 0.54, 0.56 and 0.58 mol%). Then, the resulting mixture was left stirred for 16 hours at room temperature at the speed of 400 rpm to obtain transparent and homogeneous solution. Prior to coating process, the solution was filtered with membrane Whatman filter with the pore size of 0.1 μm. This step is important in order to remove contamination and impurities that may present in the mixture.

The solution was deposited on the cleaned fused silica substrate (rectangular shape (2 x 3 cm) with the thickness of 1 mm) by using dip-coating (KSV dip coater) method with the uniform speed of 40 mm/min. The cleaned substrates have been coated for 30 layers which each layer was annealed for 50 seconds at 900°C to eliminate OH ions in the obtained layer and also to restrain the layer to be cracked. The final layer underwent further heat treatment at 950°C in order to achieve full film densification.

Optical transparency of these samples was analyzed using UV-VIS-NIR spectrometer (Cary 5000 spectrophotometer Version 1.12) and photoluminescence spectra were obtained using Horiba Jobin Yvon spectrophotometer (514.5 nm excitation of Argon ion). Prism coupler (SAIRON SPA 4000-R) was used to measure the film thickness and refractive index. Morphology and surface roughness of films were performed by atomic force microscopy (AFM XE-100). X-ray diffraction (XRD Pan Analytical X’Pert Pro MPD) and Raman spectroscopy (Raman Horiba Jobin Yvon Spectrometer) were employed to characterize the structural properties of the samples.
3. Results and Discussion

Table 1 displays the list of samples for different concentration of Er$^{3+}$ in 70SiO$_2$-30ZrO$_2$. All samples exhibit cracks-free and homogeneous layer. Film thickness, the refractive index in transverse electric (TE) and transverse magnetic (TM) mode and birefringence at a wavelength of 632.8 nm and 1550 nm were tabulated in Table 2.

Table 1. List of samples with different Er$^{3+}$ concentration

| Samples | Er$^{3+}$ concentration (mol %) |
|---------|--------------------------------|
| A1      | 0.52                           |
| A2      | 0.54                           |
| A3      | 0.56                           |
| A4      | 0.58                           |

Table 2. Film thickness (t), refractive index (n) and birefringence $|n_{TE}-n_{TM}|$ for sample A1-A4 measured at TE and TM polarizations at the wavelength of 632.8 nm and 1550 nm.

| Samples | t (± 0.05 µm) | n (TE, 632.8 nm, ± 0.05 µm) | n (TM, 632.8 nm, ± 0.05 µm) | $|n_{TE}-n_{TM}|$ (632.8 nm, ± 0.005 µm) | n (TE, 1550 nm, ± 0.05 µm) | n (TM, 1550 nm, ± 0.05 µm) | $|n_{TE}-n_{TM}|$ (1550 nm, ± 0.005 µm) |
|---------|--------------|------------------------------|-------------------------------|----------------------------------------|-----------------------------|-----------------------------|---------------------------------|
| A1      | 4.39         | 1.505                        | 1.485                         | 0.020                                  | 1.520                       | 1.495                       | 0.025                           |
| A2      | 3.78         | 1.545                        | 1.535                         | 0.010                                  | 1.525                       | 1.520                       | 0.005                           |
| A3      | 3.58         | 1.575                        | 1.570                         | 0.005                                  | 1.555                       | 1.550                       | 0.005                           |
| A4      | 2.17         | 1.605                        | 1.580                         | 0.025                                  | 1.690                       | 1.730                       | 0.040                           |

The total thickness of 30 coated layer decreased with the addition of Er$^{3+}$. However, the opposite trend was observed for refractive index whereby it is increasing as the thickness of the film is decreased which represent the films achieved full film densification. Higher Er$^{3+}$ content raises the optical density of the material which reduces the velocity of light that propagates in the film, thus increase the refractive index. The relationship between the velocity of light and refractive index can be shown by the equation; $n = c/v$ whereas $c$ and $v$ is the velocity of light in the vacuum and velocity of light in the particular medium, respectively. Figure 1 displays the refractive indices of sample A1-A4 measured at a wavelength of 632.8 nm at both TE and TM mode. There is a difference of the refractive index value for both modes that denote the birefringence properties of the obtained films. The difference occurs because of the existence of stress in the film that might be originated from crystallization due to annealing.
Figure 1: Refractive indices of the films as a function of Er\(^{3+}\) for both TE and TM modes, measured at 632.8 nm

Figure 2 shows the PL emission spectra for sample A1-A4 under 514.5 nm excitation. All the samples exhibit strong red and green emission bands with similar emission bandwidth. The narrow and sharp peaks indicate that most of Er\(^{3+}\) are incorporated in the crystalline phase whereby the ordered environment contribute to the reduction of emission spectra width. The crystalline environment around Er\(^{3+}\) could also decrease the phonon energies of the surrounding environment.

The green emission around 562 nm is produced by the \(^{4}S_{3/2} \rightarrow ^{4}I_{15/2}\) Er\(^{3+}\) transition while the red emission consists a few peaks at around 645, 650, 655 and 678 nm were attributed to the \(^{4}F_{9/2} \rightarrow ^{4}I_{15/2}\) transitions [17,18]. The red emission band was split into several peaks due to the Stark splitting of the degenerate 4f levels under the crystal field [19]. For green emission, the emission intensity is increased proportionally with Er\(^{3+}\) concentration but exhibit decrements when the Er\(^{3+}\) content reaches 0.58 mol\%. This probably due to Er\(^{3+}\) clustering that commonly occurs at high Er\(^{3+}\) concentration [20]. The average
spacing between Er-Er ions was reduced when higher Er$^{3+}$ content in the network resulting concentration quenching effect in which energy transfer between Er-Er ions [21]. This process causes depopulation of the $^4S_{3/2}$ level that leads to the cross relaxation which in turn quenching the green emission [22]. Meanwhile, the emission intensity for red emission does not show significant change with the increment of Er$^{3+}$ doping.

The transmission spectra of the thin films of 70SiO$_2$-30ZrO$_2$: Er$^{3+}$ (0.52-0.58 mol%) is shown in Figure 3. All the samples present high transmittance at UV-VIS-NIR wavelength range and show a similar pattern of the spectrum. From the obtained transmittance percentage range (65% to 79%), it shows that all samples have high optical transparency. However, the transmittance is lowest for sample A4 due to the increase of crystallization in the resultant film.

![Figure 3: Spectral transmittance of the sample A1-A4 measured by UV-VIS-NIR spectrometer](image)

The three dimensional (3D) images of AFM of the surface for sample A1-A4, measured for an area of 5 μm × 5 μm are shown in Figure 4. The uneven and rough surface has been detected for A4 samples. This is believed to be due to the inhomogeneous ion distribution caused by Er$^{3+}$ clustering in the silica-zirconia matrix which has also been proven in PL emission spectra as shown in Figure 2. Scattered white spots were detected on the surfaces for all the thin films which probably link with the presence of precipitated particles or dust during film deposition, annealing process or AFM measurement.
Figure 4: 3D topography images measured by AFM of the samples with different Er\(^{3+}\) content. Sample A1 was doped with 0.52 mol% while sample A2, A3 and A4 were doped with 0.54 mol%, 0.56 mol%, and 0.58 mol%, respectively.

Raman spectra of the glass-ceramic 70SiO\(_2\)-30ZrO\(_2\) doped with various mol percent of Er\(^{3+}\) thin films are shown in Figure 5. All samples show similar spectra pattern and the existence of an intense peak represent the crystallization of the thin film. The Raman intensity was increased with the Er\(^{3+}\) amount until it reaches 0.58 mol% in which it demonstrates a slight decrease in the intensity. This is suggested that the addition of higher Er\(^{3+}\) disturbs the short-range order and thus reduce the Raman intensity [20]. Wavenumber of 300 cm\(^{-1}\) to 400 cm\(^{-1}\) was attributed to the devitrification process associated with zirconia ZrO\(_2\) crystal vibration. Meanwhile, a small peak at 310 cm\(^{-1}\) was referred to as Zr-O-Zr vibration. Bands around 400 cm\(^{-1}\), 1060 cm\(^{-1}\) and 1190 cm\(^{-1}\) were appointed to SiO\(_2\) network [21]. A small band around 315 cm\(^{-1}\) and broadband at 640-645 cm\(^{-1}\) were assigned to the tetragonal phase of ZrO\(_2\). Shoulder around 1100 cm\(^{-1}\) represents the Si-O bond (stretching mode) [22]. On the other hand, Si-O-Si symmetrical bend modes were usually associated with the intense peaks between 950 cm\(^{-1}\) to 1100 cm\(^{-1}\). In addition, a weaker peak at 975 cm\(^{-1}\) corresponds to the vibrational mode of Si-O-Zr stretching motion [26]. Peak around 1600 cm\(^{-1}\) was attributed to carbon contaminations [27] which was suggested because of the high-temperature annealing process of the samples (900 and 950°C).

Besides that, Raman spectroscopy was used to examine the densification of the film and also the existence of OH- groups inside the obtained film that is widely known significantly decrease the Er\(^{3+}\) luminescence [25]. The presence of hydroxide could develop phonon energy level that enhanced the non-radiative de-excitation of Er\(^{3+}\). The OH- group bands in silicate glasses which commonly found at 3400 cm\(^{-1}\) were absent [11,23]. This indicates OH- have successfully been eliminated through high-temperature annealing process [21].
XRD patterns of the samples of 70SiO$_2$-30ZrO$_2$ with various concentrations of Er$^{3+}$-doping are illustrated in Figure 6. The glass-ceramic exhibits several diffraction patterns associated with the ZrO$_2$ phases. Halo centred at $2\theta = 22.0^\circ$ corresponded to the amorphous phase of the SiO$_2$ component of the film and the fused silica substrate [17]. The peaks around 30$^\circ$, 34.5$^\circ$, 50$^\circ$ and 60$^\circ$ were associated with ZrO$_2$ tetragonal phase [26]. Zirconia is well known to be in the tetragonal phase at temperature up to 2370°C. Presence of RE in the network assist to stabilize the tetragonal ZrO$_2$ at a lower temperature. In addition, tetragonal ZrO$_2$ can be formed when underwent a process of rapid thermal annealing [27].

4. Conclusion
The study of 70 SiO$_2$-30 ZrO$_2$ doped with various Er$^{3+}$ concentration shows the increment of refractive index for higher Er$^{3+}$ concentration due to a presence of larger cation in the matrix that contributes to the dense packing of the film. The high refractive index provides good optical confinement inside the film. Red and green emissions of Er$^{3+}$ were detected upon 514.5 nm excitation. However, the green emission is quenched for 0.58 mol % sample which is related to the energy transfer between Er-Er ions.
From Raman spectra, the OH- group bands in all samples were found to be absent and this indicates OH- have successfully been eliminated. The present results show the potential applications of Er3+-doped SiO2-HfO2 for EDWA applications.

Acknowledgement
The authors would like to express gratitude to Research Management Center and Faculty of Applied Sciences, Universiti Teknologi Mara for assistance and facilities throughout the research. This work was financially support by LESTARI grant (600-IRMI/MyRA 5/3/LESTARI (073/2017).

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