Er\textsuperscript{3+}–Al\textsubscript{2}O\textsubscript{3} nanoparticles doping of borosilicate glass

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Abstract. Novel borosilicate glasses were developed by adding in the glass batch Er\textsuperscript{3+}–Al\textsubscript{2}O\textsubscript{3} nanoparticles synthesized by using a soft chemical method. A similar nanoparticle doping with modified chemical vapour deposition (MCVD) process was developed to increase the efficiency of the amplifying silica fibre in comparison to using MCVD and solution doping. It was shown that with the melt quench technique, a Er\textsuperscript{3+}–Al\textsubscript{2}O\textsubscript{3} nanoparticle doping neither leads to an increase in the Er\textsuperscript{3+} luminescence properties nor allows one to control the rare-earth chemical environment in a borosilicate glass. The site of Er\textsuperscript{3+} in the Er\textsuperscript{3+}–Al\textsubscript{2}O\textsubscript{3} nanoparticle containing glass seems to be similar as in glasses with the same composition prepared using standard raw materials. We suspect the Er\textsuperscript{3+} ions to diffuse from the nanoparticles into the glass matrix. There was no clear evidence of the presence of Al\textsubscript{2}O\textsubscript{3} nanoparticles in the glasses after melting.

Keywords. Glass; optical fibre; IR photoluminescence; nanoparticles; doping.

1. Introduction

The development of materials doped with Er\textsuperscript{3+} ions has been of great interest, as these materials can be used for signal amplification at the wavelength of 1.55 \textmu m corresponding to the telecommunication window (the \textsuperscript{4}I\textsubscript{13/2}–\textsuperscript{4}I\textsubscript{15/2} transition).\textsuperscript{1} In the development of optical devices based on rare-earth (RE) ions, the local environment around the RE was found to be of paramount importance for determining the optical properties.\textsuperscript{2} While in homogeneous glasses, RE elements tend to cluster in many compositions, glass ceramics have been found to be a valuable alternative media to control the chemical environment of the RE. In fact, these materials combine the mechanical and optical properties of the glass with some advantages of RE-doped single crystals (higher absorption/emission cross-section and longer lifetimes of luminescent levels).\textsuperscript{3}

The glass ceramics are usually obtained by nucleation and controlled crystallization of the RE-doped glasses. A new modified chemical vapour deposition (MCVD) compatible nanoparticle doping process has been developed to master with higher accuracy of the RE neighbours in fibres independently from the glass composition.\textsuperscript{4}

In this paper, we investigate the effect of Er\textsuperscript{3+}–Al\textsubscript{2}O\textsubscript{3} nanoparticles doping on the thermal, optical, structural and luminescence properties of borosilicate glasses. The effect of the addition of doped Al\textsubscript{2}O\textsubscript{3} as a fused powder primarily in \textalpha-phase, from Aldrich, on those properties of the glasses is also discussed.

2. Experimental

2.1 Glass preparation

Thirty grams of glasses with the composition xAl\textsubscript{2}O\textsubscript{3}–(100 – x) (0.508SiO\textsubscript{2}–0.005P\textsubscript{2}O\textsubscript{5} – 0.273B\textsubscript{2}O\textsubscript{3} –0.212Na\textsubscript{2}O–0.0025Er\textsubscript{2}O\textsubscript{3}) (mol\%) with x = 1.5 and 4.5 were prepared by the standard melt-quenching process (labelled as R-glass1.5 and 4.5, respectively). Na\textsubscript{2}PO\textsubscript{4}, H\textsubscript{2}O (Merck, 99%), H\textsubscript{3}BO\textsubscript{3} (Aldrich, 99.99%), Na\textsubscript{2}CO\textsubscript{3} (Sigma-Aldrich, > 99.5%), Al\textsubscript{2}O\textsubscript{3} (Sigma-Aldrich, > 99%), SiO\textsubscript{2} (Sigma-Aldrich, 99%) and Er\textsubscript{2}O\textsubscript{3} (MV Laboratory, 99.999%) were used as raw materials in the powder form. The batches were first pre-treated at 400°C overnight to decompose the raw materials and successively melted in an ambient atmosphere in a quartz crucible at 1450°C for 30 min. After quenching, the glass was annealed for 3 h at 40°C below its \textalpha\textsubscript{T} to remove the internal stress induced by the quenching. Finally the glass was cut, ground and polished.

Glasses with the same compositions were prepared using Al\textsubscript{2}O\textsubscript{3} nanoparticles doped with Er\textsuperscript{3+}, which were

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prepared using the protocol described in Jolivet et al.\(^6\) (labelled as NP-glass1.5 and NP-glass4.5). The preparation of the Al\(_2\)O\(_3\) nanoparticles with the composition 85.7Al\(_2\)O\(_3\)-14.3Er\(_2\)O\(_3\) (mol\%) implies to first dissolve 60 mM of Al(NO\(_3\))\(_3\)·9H\(_2\)O and erbium acetylacetonate Er\(_2\)(C\(_5\)H\(_7\))\(_2\)O\(_6\) in 250 ml of distilled water in stoichiometric proportion and then mix, by magnetic stirring, the whole solution for 30 min. The solution was then heated during 15 days at 100°C in a tight flask. The solution was successively evaporated at 150°C during 5 h and finally heated at 200°C during 10 h in a furnace with a continuous air flow. At this stage, the compounds were single phased corresponding to the boehmite (AlO(OH)) reference [49-0133] as seen in figure 1. The average size of the particles, measured using the Scherrer formula, was \(\sim(9 \pm 2)\) nm. The particles were heat treated at 1300°C for 5 h. As seen in the XRD pattern (figure 1), the phases present in the samples are corundum Al\(_2\)O\(_3\) [10-0173] and ErAlO\(_3\) [24-396]. The nanoparticle-doped glasses (NP-glasses) were prepared by mixing the raw materials and Er\(_3\)+–Al\(_2\)O\(_3\) nanoparticles and then melted the glass batch using the melting process described in the previous paragraph. In order to prepare the glass with \(x = 4.5\) with the same amount of Er\(_3\)+ ions and Al\(_2\)O\(_3\) (mol\%), Al\(_2\)O\(_3\) as a fused powder primarily in \(\alpha\)-phase from Aldrich was added in the glass batch prior to the melting (labelled as NP-glass4.5).

2.2. Characterizations

The glass transition \(T_g\) and crystallization \(T_p\) temperatures were measured by differential thermal analysis (Mettler Toledo TGA/SDTA851) at a 15°C min\(^{-1}\) heating rate. The \(T_g\) was taken at the inflection point of the endo-therm, as obtained by taking the first derivative of the differential scanning calorimetry (DSC) curve and \(T_p\) was defined as the maximum of the exothermic peak. The temperatures were determined with an accuracy of 4°C.

The crystalline phases were identified using an X-ray diffraction analyzer (Philips X’pert) with CuK\(\alpha\) radiation \((\lambda = 1.5418\) Å\). The scans were performed from \(2\theta = 0–60^\circ\) with a step size of 0.02°.

The density of the bulk glass materials was measured after Archimedes’ method in water. The accuracy was better than 0.3%.

The UV–visible–infrared (IR) absorption spectra of the glass samples were recorded using a Perkin Elmer spectrometer over the 250–2500 nm spectral region. The measurements were performed at room temperature and were corrected for the Fresnel losses and the glass thickness.

The emission spectra in the 1400–1700 nm range were measured with an Edinburgh Instruments monochromator (M300) and a liquid nitrogen cooled germanium detector (ADC 403L) at room temperature using an excitation source emitting at 365 nm.

3. Results and discussion

In this paper, we investigate the effect of Al\(_2\)O\(_3\) and Er\(_3\)+-Al\(_2\)O\(_3\) nanoparticles on the Er\(_3\)+ luminescence properties of borosilicate glasses. The nanoparticles-doped glasses were prepared using a two-step process: preparation of the Er\(_3\)+–Al\(_2\)O\(_3\) nanoparticles and melting of the borosilicate glass batch which contains the nanoparticles. Al\(_2\)O\(_3\) nanoparticles were chosen due to their ability to resist to high temperature and stress condition as suggested by Pastouret et al.\(^6\) Alumina is also known to permit high content solubilization of RE ions in a well-dispersed state\(^1\) and can be transformed in a highly thermally resistant phases through appropriate thermal treatment avoiding its destruction during the glass processing.\(^7\)

The density of the glasses and some of their thermal properties are listed in table 1. While the addition of Er\(_3\)+-doped Al\(_2\)O\(_3\) nanoparticles has no impact on the density, \(T_g\) and \(T_p\), an increase of the Al\(_2\)O\(_3\) content from 1.5 to 4.5 mol\% in (regular and NP containing) glasses decreases slightly the density and \(T_g\), but has no strong impact on \(T_p\). It increases \(\Delta T\) which is an indication of an increase in the resistance of the glass to crystallization. This is in agreement with our previous work.\(^8\) We explained that an increase in the Al\(_2\)O\(_3\) content in the glass matrix leads to the formation of negatively charged AlO\(_2\) units, leading to an increase of the Si–BO units in the network. This

![Figure 1. XRD of the heat-treated nanoparticles.](image-url)
transformation from Si–NBO to Si–BO results from the charge compensation mechanism taking place to neutralize the negative charges of the AlO₃ units. The introduction of Al₂O₃ in borosilicate glasses is also expected to turn the charged four-coordinated boron units into neutral three-coordinated boron. These changes in the glass network result in a reduction of the density and \( T_g \).

The absorption spectra of the investigated glasses were measured and the UV absorption edge was found to remain almost constant at ~315 nm, independently of the glass composition. The absorption cross-section at 365 nm is measured from the absorption spectra using

\[
\alpha_{abs}(\lambda) = 2.303 \times \log(I_0/I)(\mathrm{NL}) = \alpha(\lambda)L,
\]

where log\((I_0/I)\) is the absorbance, \( N \) the RE ion concentration, \( L \) the thickness of the sample and \( \alpha_{abs}(\lambda) \) the absorption coefficient.

The absorption cross-section also remains constant at ~1.20 \( \times \) \( 10^{-20} \) cm\(^2\) at \( \pm 10\% \) independently of the glass composition. As illustrated in figure 2, no change in the shape of the absorption band can be seen due to the addition of \( \text{Er}^{3+}-\text{Al}_2\text{O}_3 \) nanoparticles in both glasses (\( x = 1.5 \) and 4.5). However, an increase in the Al₂O₃ content leads to small changes in the absorption band. Similar changes can be seen in the normalized emission band exhibited in figure 3a. This suggests that Al³⁺ ions have a noticeable impact on the crystallographic site of Er³⁺ by modifying the coordination shell of Er³⁺, in agreement with Bourhis et al. However, one can notice that the shape of the emission band of the \( \text{Er}^{3+}-\text{Al}_2\text{O}_3 \) nanoparticle-doped glasses with \( x = 1.5 \) and 4.5 is similar to that of the regular glasses but is different from the emission recorded directly from the \( \text{Er}^{3+} \) doped \( \text{Al}_2\text{O}_3 \) nanoparticles, presented in figure 3b. This tends to indicate that the site of the \( \text{Er}^{3+} \) in the \( \text{Er}^{3+}-\text{Al}_2\text{O}_3 \) nanoparticle-doped glasses (NP-glass1.5 and 4.5) is similar than in the regular glasses (R-glass1.5 and 4.5) prepared using \( \text{Al}_2\text{O}_3 \) as fused powder. A comparison of the relative intensity of the emission at 1530 nm is presented in figure 3c. While the glasses have similar absorption cross-section at 365 nm which corresponds to the excitation wavelength, an increase in the \( \text{Al}_2\text{O}_3 \) content from 1.5 to 4.5 mol% leads to a slight decrease in the intensity of the emission at 1530 nm. As explained in Bourhis et al., an increase in the \( \text{Al}_2\text{O}_3 \) content is suspected to increase the content of OH hydroxyl groups, well-known to be serious quenchers of Er³⁺ ions luminescence. Surprisingly, no increase in the emission intensity at 1530 nm was observed when the glasses (\( x = 1.5 \) and 4.5) were doped with \( \text{Er}^{3+}-\text{Al}_2\text{O}_3 \) nanoparticles, while an increased amplifying medium efficiency compared to conventional doped fibres was obtained in silica fibre prepared with similar nanoparticles.

We suspect the Er³⁺ ions to diffuse from the crystalline \( \text{Al}_2\text{O}_3 \) nanoparticles into the glass during the glass melting. We also suspect the \( \text{Al}_2\text{O}_3 \) nanoparticles to decompose inside the glass network as (1) no change in the glass structure was observed using IR and Raman spectroscopies and (2) the sharp peaks of the sample holder were the only peaks seen in the XRD pattern of the \( \text{Er}^{3+}-\text{Al}_2\text{O}_3 \) nanoparticle-doped glasses (\( x = 1.5 \) and 4.5) as depicted in figure 1 for the NP-glass1.5.

4. Conclusion

Borosilicate glasses with different compositions were prepared to investigate the effect of the glass composition on the Er³⁺ spectroscopic properties. Regular glasses were developed using standard raw materials with two

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Table 1. Density and some thermal properties of the glasses.

<table>
<thead>
<tr>
<th>Glass code</th>
<th>([\text{Er}^{3+}] \times 10^{19} \text{ ions cm}^{-3}) (±5%)</th>
<th>Density (g cm(^{-3})) (±0.02)</th>
<th>Thermal properties</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Glasses with x = 1.5</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-glass1.5</td>
<td>4.63</td>
<td>2.5</td>
<td>578 727 149</td>
</tr>
<tr>
<td>NP-glass1.5</td>
<td>4.63</td>
<td>2.5</td>
<td>580 724 147</td>
</tr>
<tr>
<td><strong>Glasses with x = 4.5</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-glass4.5</td>
<td>4.37</td>
<td>2.47</td>
<td>573 728 156</td>
</tr>
<tr>
<td>NP-glass4.5</td>
<td>4.37</td>
<td>2.45</td>
<td>573 735 165</td>
</tr>
</tbody>
</table>

Figure 2. Normalized absorption band of the glasses.
different concentrations of Al$_2$O$_3$ and glasses with the same compositions were prepared using Er$^{3+}$–Al$_2$O$_3$ nanoparticles. While an increase in the Al$_2$O$_3$ content had an impact on the Er$^{3+}$ crystallographic site in the borosilicate network, no evidence that the Er$^{3+}$–Al$_2$O$_3$ nanoparticles would remain in the glass after melting was found. From the luminescence properties, the Er$^{3+}$ ions are suspected to diffuse from the nanoparticles into the glass matrix. Compared to previous work on this topic, no enhancement of the Er$^{3+}$ spectroscopic properties was observed in the Er$^{3+}$–Al$_2$O$_3$ nanoparticles containing borosilicate glass. In this paper, it is shown that it is not possible to control the site of the Er$^{3+}$ using nanoparticles doping process in glasses prepared by the standard melting process compared as to the similar work on MCVD compatible nanoparticle doping process.

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References