

Er-doped zinc-silicate glass-ceramics with enhanced emission in the near-infrared region

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Abstract. Erbium-doped lasers and amplifiers exhibit emission around 1.5 μm , which makes them perspective in various applications, such as telecommunications, material processing or defence. The conventionally used silica glass suffers from various drawbacks, such as low solubility of erbium ions or high phonon energy of the silica lattice, which limit the luminescence properties. The zinc-silicate glass-ceramics containing ZnO or Zn₂SiO₄ nanocrystals represent a suitable alternative. The incorporation of erbium ions into the nanocrystals should result in the enhancement of luminescence properties. In this work, we prepared a zinc-silicate glass-ceramic material containing Zn₂SiO₄ nanocrystals by the controlled heat treatment of a precursor glass. The luminescence properties of the 1.5 μm emission were measured and the influence of the crystallization on the near-infrared emission was evaluated.

1 INTRODUCTION

Erbium-doped lasers and amplifiers exhibit emission around 1.5 μm , which makes them perspective for use in telecommunications, material processing or defence. Silica glass remains a frequently used material as host for erbium thanks to high thermal stability, chemical resistance or low-cost. However, silica suffers from several drawbacks, such as the tendency towards clustering even at low erbium concentrations and high phonon energy of the silica lattice, which cause quenching of the emission by non-radiative mechanisms [1].

The glass-ceramics with erbium ions embedded in low-phonon nanocrystals represents a perspective alternative to conventional silica glass [2]. Regarding the zinc-silicate system, the crystallization of ZnO nanocrystals was demonstrated in a K₂O-ZnO-Al₂O₃-SiO₂ system [3]. However, the Er³⁺ ions remained incorporated in the residual amorphous phase, rather than becoming embedded in the nanocrystals, which caused deterioration of luminescence properties [4,5]. The impact of Zn₂SiO₄ nanocrystals on the luminescence properties of erbium is yet to be demonstrated.

In this work, we prepared a Zn₂SiO₄-containing glass-ceramics by controlled heat treatment of precursor glass. The glass-ceramics were analysed by XRD. The luminescence properties were measured, and the influence of Zn₂SiO₄ crystallization on the luminescence of erbium was evaluated.

2 EXPERIMENT

The composition of the precursor glass was (in mol. %): 14 Na₂O – 35 ZnO – 48.6 SiO₂ – 0.6 Al₂O₃ – 0.1 Er₂O₃ – 1.6 Yb₂O₃. The glass was prepared by standard melt-quenching method at 1500 °C for approx. 10 hours. The glass melt was manually stirred every 30 min. to ensure homogenization. The crystallization was induced by controlled heat treatment at 800 °C for 4 hours, with a 1.5 °C·min⁻¹ cooling rate.

The samples were analyzed on a Bruker-AXS D2 Phaser powder diffractometer using Co-K α radiation. A custom-built Horiba Fluorolog spectrofluorometer with a Xenon lamp and extended InGaAs detector was used to measure emission spectra. Fluorescence decay curves were measured in a setup containing ILX Lightwave 3900 power source, Agilent 33512B pulse generator, Teledyne Lecroy HDO6034 oscilloscope, InGaAs photodiode detector, and EM4 P161-600-976 diode emitting at 976 nm as excitation source.

3 RESULTS

The as-melted glass was transparent with pink coloration. The heat-treated glass-ceramic sample became opaque and non-transparent, presumably due to the effects of crystallization.

The XRD spectra of the as-melted glass as well as the glass-ceramic sample are shown in Figure 1. The as-melted glass exhibited a fully amorphous character with a typical broad band around 35 °. The heat-treated sample

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exhibited a highly crystalline character with well-defined, sharp peaks, which were assigned to rhombohedral modification of Zn_2SiO_4 , also called willemite (PDF: 008-0329).

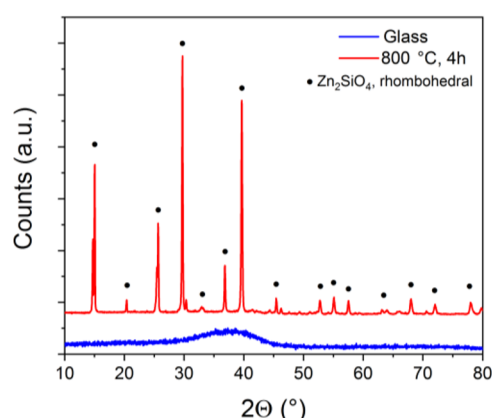


Figure 1 – XRD spectra of the as-melted glass and glass-ceramic sample heat-treated at 900 °C.

The emission spectra of the $Er^{3+}:^3I_{13/2} \rightarrow ^3I_{15/2}$ transition around 1.5 μm are depicted in Figure 2. The heat treatment and crystallization lead to a 300 % increase of emission intensity. The FWHM of the emission band was slightly decreased, but the overall shape with lack of Stark splitting suggests that the Er^{3+} ions remain embedded primarily in the residual amorphous phase.

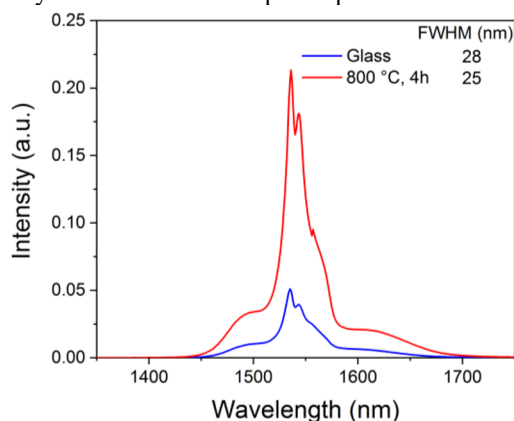


Figure 2 – emission spectra of the as-melted glass and glass-ceramic sample heat-treated at 900 °C, $\lambda(exc.) = 978$ nm.

The corresponding fluorescence decay curves of the $Er^{3+}:^3I_{13/2} \rightarrow ^3I_{15/2}$ transition are depicted in Figure 3. The decay curves of both samples were single-exponential, which indicates Er^{3+} ions in a single optically-active environment. The crystallization lead to a slight decrease of fluorescence lifetime, which indicates that the environment of Er^{3+} ions was not significantly changed.

In summary, the crystallization of Zn_2SiO_4 led to an increase of emission intensity, but other characteristics such as band-shape (FWHM) and fluorescence lifetime were only slightly changed. This result indicates that the Er^{3+} ions remain embedded primarily in the residual amorphous phase or at the grain boundaries, rather than becoming embedded in the Zn_2SiO_4 nanocrystals. This

phenomenon can be explained by the low solubility of Er^{3+} ions in the Zn_2SiO_4 structure. The low solubility of Er^{3+} ions was previously demonstrated for ZnO [4,6].

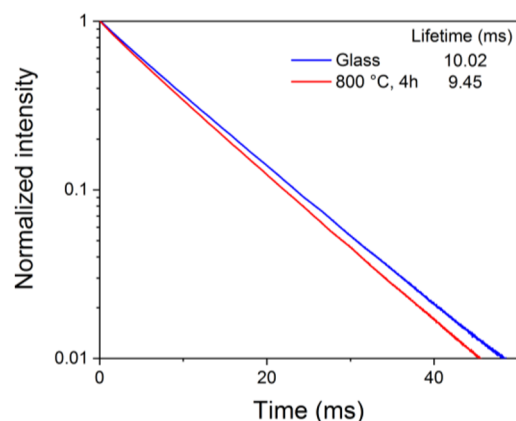


Figure 3 – fluorescence decay curves of the as-melted glass and glass-ceramic sample heat-treated at 900 °C, $\lambda(exc.) = 978$ nm.

4 CONCLUSION

The Zn_2SiO_4 -containing glass-ceramics were prepared by controlled heat treatment of precursor glass. The crystallization of Zn_2SiO_4 lead to a 300 % increase of emission intensity, but other emission characteristics such as band-shape or fluorescence lifetime were only slightly changed. The Er^{3+} ions remain embedded in the residual amorphous phase due to the low solubility in Zn_2SiO_4 crystalline lattice.

Acknowledgements

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