

Influence of ZnF₂ concentration on excitation energy transfer between Er³⁺ and Tm³⁺ ions in antimony-germanate glass ceramic

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Abstract—New broadband-emitting materials are still in demand for industrial, medical, and telecommunications solutions. Thus, new materials that improve the luminescence of lanthanide ions are in demand. Equally important seems to be the co-doping of the host material with different lanthanides, for example, Er³⁺ and Tm³⁺. In co-doped materials, energy transfers between ions depend on lanthanide ion concentrations, host material chemical composition, and structure. Low-phonon matrices should be used to improve energy transfer efficiency and radiative transitions. One of the various solutions is using oxide-fluoride matrices, where the oxide part of the matrix provides the desired thermal and mechanical stability, and the fluoride part provides a low-phonon environment for the ions. In this report, the influence of the concentration of ZnF₂ on the co-doped oxide matrix was investigated in terms of luminescence changes.

Oxy-fluoride glasses and glass-ceramic are promising fields of research because of their possibility of creating new types of glasses with unique parameters. Oxy-fluoride glasses combine low phonon-energy [1], improved radiative emission, and luminescence shaping from fluoride glasses with the mechanical and thermal stability usually found in oxide glasses [2]. Broadband light sources are desired in various fields like medicine, sensors, and optical amplifiers [3–4]. The doping of lanthanide ions is used to get a light source with a broad spectrum. Co-doping the material with different lanthanides opens up new possibilities for energy transfer between ions. These transfers can be crucial for obtaining broadband emission and disordered luminescence quenching. Energy transfers depend on the chemical composition of the host, its structure, and the concentration of lanthanides.

In this experiment, the effect of changing the amount of zinc fluoride on the luminescence properties of oxide glass while doping with erbium and thulium ions has been studied. Luminescence shape changes were observed, and excitation and ZnF₂ modifier concentration parameters were determined.

In this experiment, Sigma-Aldrich compounds with 99.999% purity were used. Samples were prepared with (34.8–*x*)SiO₂ – 0.30GeO₂ – 20Sb₂O₃ – 5Ga₂O₃ – 5K₂O – (*x*)ZnF₂ + (0.1Er₂O₃ – 0.1Tm₂O₃) chemical composition, where *x*={5, 10, 15}. All compounds were homogenized in an agate mortar and were melted in an electric furnace at

1450°C. Melted liquid material was poured onto a steel plate and annealed at 400°C for 8 hours to reduce internal stresses. After annealing, samples were heat-treated at 655°C (HTL) at 1 hour and 685°C (HTH) also at 1 hour for glass-ceramic fabrication. The prepared samples were 2.5mm in thickness. Samples were excited by solid-state laser light sources with 796nm, 808nm, and 980nm wavelengths. Yokogawa AQ9675B registered luminescence shapes. DSC (SETARAM Labsys) tests were also performed. DSC results are shown in Fig. 1. There are visible changes in DSC shapes with increasing concentrations of ZnF₂.

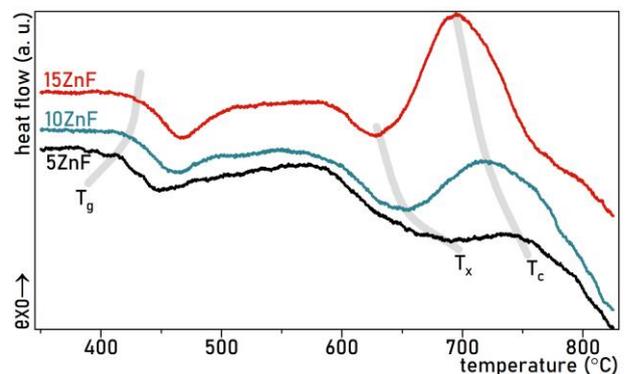


Fig. 1. DSC curves of samples modified with ZnF₂.

With increasing ZnF₂ concentration, crystallization peaks increase and shift to lower temperatures. Transition temperature (*T_g*) also shifts but into higher temperatures. All *T_g* and *T_x* temperature changes, decreasing thermal stability ΔT of the material with increasing ZnF₂ concentration.

Table 1. Thermal stability of samples modified with ZnF₂.

	<i>T_g</i>	<i>T_x</i>	$\Delta T = T_x - T_g$
5ZnF	412	686	274
10ZnF	422	653	231
15ZnF	430	630	200

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The luminescence shapes study was performed with laser excitation. The noise seen in Figs. 2–4 in the 1820–1920nm range is connected to the switching detectors in the measuring instrument. All charts were normalized at erbium ${}^4I_{15/2} \rightarrow {}^4I_{13/2}$ radiative transition to allow comparison of samples with different levels of transparency.

Figure 2 presented results of luminescence measurement samples with 5% mol of ZnF_2 for 796, 808, and 980 nm excitation. Heat-treatment processes have a small impact on luminescence shape.

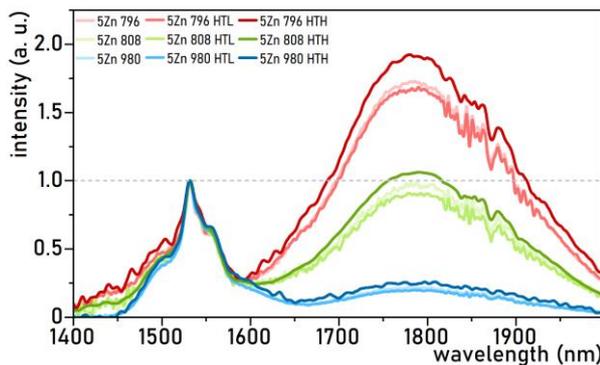


Fig. 2. Luminescence spectra of samples modified with 5% mol of ZnF_2 .

In general, samples heat-treated at lower temperatures (HTL) have almost no change in luminescence shape. After being heat-treated at higher (HTH) temperatures, samples have a slightly higher intensity of luminescence transition originating from thulium ions.

In Figure 3, the visible luminescence shapes of the samples change with 10% molar of ZnF_2 . Samples under 980nm laser excitation showed no visible changes in melted and heat-treated samples. There are visible changes in luminescence shape at 796nm and 808nm excitation on the samples after heat treatment at 685°C.

Figure 4 shows the luminescence shapes of samples with 15% molar of ZnF_2 . Samples excited with 980 nm show an increase in luminescence connected with Tm^{3+} . More significant changes are for 808 nm excitation.

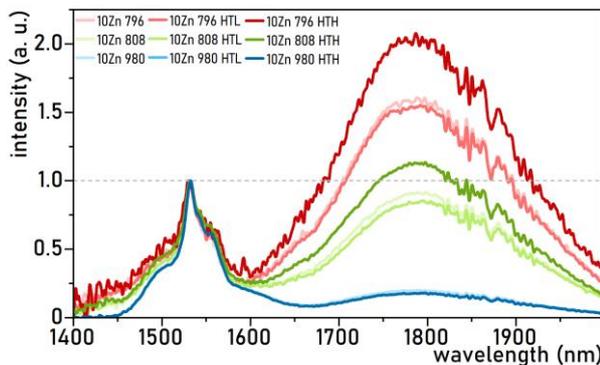


Fig. 3. Luminescence spectra of samples modified with 10% mol of ZnF_2 .

Whereas melted samples and glass-ceramic samples have almost the same luminescence shape as samples with a lower concentration of ZnF_2 . However, samples heat treated at 685°C have substantial luminescence change in the ratio around 1:1 for 5% and 10% ZnF_2 samples to almost 2:1 ratio between the Er^{3+} band and Tm^{3+} band.

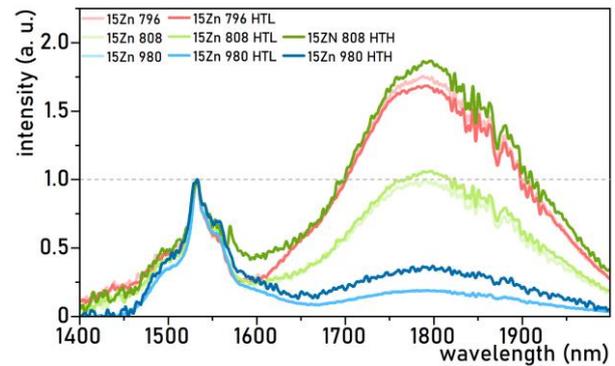


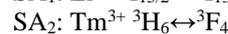
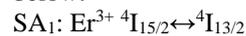
Fig. 4. Luminescence spectra of samples modified with 15% mol of ZnF_2 .

The luminescence shape of 15% of the ZnF_2 sample under 796 nm excitation is missing because of the weak signal level caused by the sample being opaque and too low signal of the laser pump.

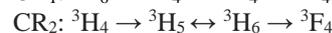
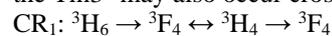
Usually, the low thermal stability of glass leads to a fast crystallization process [1, 5], losing transparency. In our case, the samples annealed at T_x (HTL) temperature kept their transparent character. Still, the higher temperature (HTH) closer to T_c made them translucent for 5% of ZnF_2 and opaque for higher concentrations of ZnF_2 .

In materials co-doped with lanthanide ions, energy transfer can occur between ions of different lanthanides and between ions of the same lanthanide [4]. For this process to occur, the absorption bands of the acceptor should overlap the emission band of the donor [6]. Erbium and thulium have several bands in common that make such energy transfer possible. Also, the concentration of ions, their ion radius, and ion distance have a crucial impact on energy transfer, luminescence quenching, or emission and absorption cross-section.

Based on the analysis of the luminescence shapes (Figs. 2–4) and the energy diagram shown in Fig. 5, it is possible to describe the energy transfers between Er^{3+} and Tm^{3+} ions. Also, it is possible to find self-absorption transfers, as below:



Self-absorption processes are unwanted transfers because they decrease emission at 1520nm [7] and 1780 nm [4]. In the Tm^{3+} may also occur cross-relaxation transfers:



At excitation with a 980nm laser, low energy transfer from erbium ions to thulium ions is visible. That suggests ET_3

and ET_4 transfers have low intensity and do not enhance the emission at 1800nm. This transfer is slightly increased for HTH samples with 15% of ZnF_2 . This allows us to conclude that in the case of strong crystallization, a change in the ion's environment affects energy transfer.

The ratio between erbium and thulium peaks is about 1:0.2. Resonant Energy Transfer (RET) is expected to be the primary and robust mechanism for energy transfer between Er^{3+} and Tm^{3+} ions. In RET, energy transfer occurs directly from a donor ion to an acceptor ion without the emission of photons, necessitating a close alignment of their energy levels. However, observations from the emission spectrum reveal that this form of energy transfer appears to be notably weak. This could suggest an alteration in the energy levels of erbium and thulium, potentially due to unexpected structural changes in the material.

The ET_1 energy transfer appears to have no apparent significance or CR_1 decreasing emission intensity at 1450nm [4, 6] or the existence of ET_2 . That is confirmed by the lack of visible spectral changes around 1450nm. In theory, pumping at 980nm should be more effective than pumping at 808nm because 808nm pumping leads to multi-phonon relaxation. A 980nm pump should enormously improve energy transfer from Erbium to Thulium. However, this phenomenon can be explained by the energy transfer from $4I_{13/2}$ to the OH group [8]. As a result, the energy transfer to the holmium is slight.

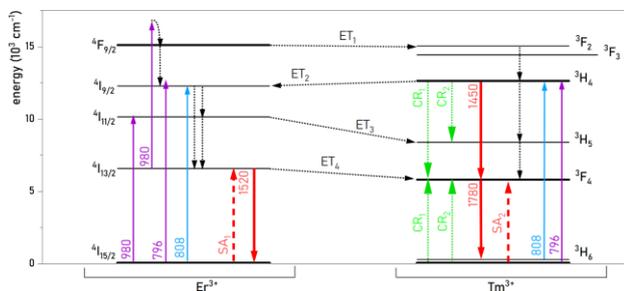


Fig. 5. Energy diagram of erbium and thulium, where ET stands for energy transfer, CR stands for cross-relaxation, and SA stands for self-absorption.

The luminescence spectrum at 808nm excitation differs from that at 980nm excitation. It indicates substantial energy transfer (ET_4) from $4I_{13/2}$ erbium energy level to $3F_4$ thulium energy level. The ratio is about 1:1 for most samples except the HTH sample with 15% of ZnF_2 , where the ratio is about 1:2. ET_3 energy transfer cannot be ruled out; however, because of the short lifetimes of the $4I_{11/2}$ level, there is a greater chance of non-radiative relaxation to the $4I_{13/2}$ level than the chances of energy transfer to the $3H_5$ level. Low emission intensity at 1450 can be caused by ET_2 , CR_1 , and CR_2 transfers, which reduces the chance of radiative transition $3H_4 \rightarrow 3F_4$ [4, 6, 8].

The main difference between 796nm and 808nm excitation is the apparent increase in the intensity of the $3F_4 \rightarrow 3H_6$ transition for 796nm excitation. The ratio is around 1:1.6. Analyzing the luminescence shapes for the 808nm and

796nm excitations, there are no significant differences between them, indicating changes in the energy transfers from thulium to erbium. At the same time, this may be why the 796nm and 808nm pumps have very similar wavelengths and, as a result, may cause a similar effect with excitation.

In summary, fluorides can improve the luminescence shape of the co-doped oxide host. The best result is for 15% ZnF_2 concentration in the chemical formula, which significantly enhances luminescence intensity from 1650nm to 1950nm. This change shows structural changes in host material caused by the heat-treat process at 685°C at 1 hour. Heat treatment processes in lower temperatures and for lower ZnF_2 concentrations have almost no effect on luminescence shape.

Further studies are planned to broaden the emission spectrum of Er^{3+} and Tm^{3+} to complement the low-intensity luminescence around 1600 nm. This would provide a broad emission band from about 1500 to 1900nm. Also intriguing is the possibility of excitation of co-doped material by two pumps, 980 nm and 796/808 nm.

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