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Towards lead-free oxyfluoride germanate glasses singly doped with Er^{3+} for long-lived near-infrared luminescence

Wojciech A. Pisarski [a,*], Joanna Pisarska [a], Dominik Dorosz [b], Jan Dorosz [b]

[a] Institute of Chemistry, University of Silesia, Szkolna 9, 40-007 Katowice, Poland
[b] Faculty of Electrical Engineering, Bialystok University of Technology, Wiejska 45D, 15-351 Bialystok, Poland

HIGHLIGHTS

- Erbium-doped lead-free germanate glasses modified by BaF_2 were prepared.
- The bonding parameter is reduced with increasing BaF_2 content.
- The $^4I_{15/2} - {}^2H_{11/2}$ hypersensitive transition is blue shifted with increasing BaF_2 content.
- Luminescence spectra due to main $^4I_{13/2} - {}^4I_{15/2}$ laser transition of Er^{3+} were detected.
- Long-lived NIR emission of Er^{3+} is observed for glass samples with low BaF_2 content.

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ABSTRACT

Spectroscopic properties of Er^{3+} ions in lead-free oxyfluoride germanate glasses were studied. The absorption and luminescence spectra of Er^{3+} ions were examined for glass samples with low and high BaF_2 content. From absorption spectra the bonding parameter was calculated and its value is reduced with increasing BaF_2 content. The maximum of absorption peak due to $^4I_{15/2} - {}^2H_{11/2}$ hypersensitive transition is shifted to shorter wavelengths (blue shift) with increasing BaF_2 content. Luminescence spectra and their decays corresponding to main $^4I_{13/2} - {}^4I_{15/2}$ laser transition of Er^{3+} are also presented and discussed. Quite long-lived near-infrared luminescence of Er^{3+} is observed for lead-free glass samples with low BaF_2 concentration.

1. Introduction

An introduction of CdF_2 and/or PbF_2 to inorganic glass host matrices containing rare earth ions influenced strongly on the local structure and their optical properties [1–9]. Among rare earth doped glasses, Er^{3+}-doped oxyfluoride glasses due to main $^4I_{13/2} - {}^4I_{15/2}$ transition at 1500 nm are especially interesting for solid-state NIR laser media [10] and broadband optical amplifiers [11]. With substitution of PbO by PbF_2 in germanate [12], tellurite [13] and borate [14] glasses the thermal stability is improved, whereas near-infrared luminescence and up-conversion processes of Er^{3+} are significantly enhanced. However, glasses containing CdF_2 and/or PbF_2 are classified as toxic raw materials and consequently they are being often eliminated from various practical applications due to their hazardous effect on health and environment. Therefore, lead- and cadmium-free glasses [15] and glass-ceramics [16] are proposed alternatively for potential application in optoelectronics. Fluorophosphate glasses with BaF_2 and other divalent metal fluorides MF_2 (M = Mg, Ca, Sr) having higher thermal stability against crystallization and showing favorable conditions for infrared laser can be considered as alternative amorphous materials for systems with PbF_2 [17], but PbO/BaF_2 [18] or PbF_2/BaF_2 [19] components also coexist in some glass compositions, which are attractive for optical applications. On the other hand, barium fluoride was introduced to silicate glass in order to obtain transparent glass–ceramic systems containing BaF_2 nanocrystals [20,21]. Other crystalline phases such as $BaYF_5$ [22], Ba_2YbF_7 [23] or Ba_2LaF_7 [24] were also evidenced by X-ray diffraction and their occurrence critically depend on MF_3 (M = Y,

* Corresponding author. Tel.: +48 32 3591775.
E-mail addresses: wojciech.pisarski@us.edu.pl, wpisarsk@us.edu.pl (W.A. Pisarski).

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Yb or La) concentration and heat treatment conditions. The spectroscopic investigations indicate that the intensities of luminescence bands are significantly increased due to partial incorporation of Er^{3+} ions into BaF_2 crystalline phase [25,26]. The effects of rare earth doping into fluoride nanocrystals embedded in silicate glasses are of scientific and technical interest and their spectroscopic results are also well presented and discussed for glass-ceramic system with CaF_2 [27].

In this short communication, we present new preliminary spectroscopic results for lead-free germanate glasses containing barium fluoride. In the studied $BaO-Ga_2O_3-GeO_2$ glass system, barium oxide was partially or totally substituted by BaF_2. Absorption and luminescence properties of Er^{3+} ions in oxyfluoride germanate glasses have been examined as a function of BaF_2 concentration. Near-infrared luminescence spectra due to main $^4I_{13/2} - {}^4I_{15/2}$ laser transition of Er^{3+} ions were registered. Based on spectra and their decays, the $^4I_{13/2} - {}^4I_{15/2}$ line widths and luminescence lifetimes for the $^4I_{13/2}$ upper laser state of Er^{3+} were determined. Both spectroscopic parameters were analyzed for glass samples with low (5 and 10 mol%) and high BaF_2 (30 mol%) content. To the best of our knowledge, the spectroscopic properties of rare earth ions in $BaO-Ga_2O_3-GeO_2$ glasses modified by BaF_2 are not often examined. Recently, a new type host of germanate glass ($GeO_2-BaO-BaF_2-Ga_2O_3-La_2O_3$) singly doped with Tm^{3+} ions has been investigated for application as NIR laser material at 1800 nm [28]. Further studies suggest that Tm^{3+}-doped germanate glass fibers with a large core diameter has proved to be promising infrared optical and high-power level laser materials [29].

2. Experimental

Series of samples: $x BaF_2-(30 - x)BaO-60GeO_2-9.5Ga_2O_3-0.5Er_2O_3$ ($x = 0, 5, 10, 30$ mol%) were prepared by mixing and melting appropriate amounts of metal anhydrous oxides and fluorides of high purity (99.99%, Aldrich Chemical Co.) as starting materials. In order to prepare glass samples, appropriate amounts of all components were mixed homogeneously together. Due to the hygroscopicity of the fluorides and, in order to minimize the adsorbed water content, all glass components were weighted and stored in glove box, in a protective atmosphere of dried argon. Then, they were melted at 1200 °C for 45 min. Transparent glassy plates of 10×10 mm dimension were obtained. Each glass sample of 2 mm in thickness was polished for optical measurements.

Optical absorption spectra were recorded using a Varian 5000 UV–VIS–NIR spectrophotometer. The emission spectra were performed using the QuantaMaster™ system, Photon Technology International, Inc., their decay curves were registered using Opolette™ (HE) 355 II + UV system. The spectral measurements were carried out with a resolution of 0.1 nm. Luminescence lifetimes were determined with accuracy of 1 μs. All measurements were carried out at room temperature.

3. Results and discussion

Lead-free oxyfluoride germanate glasses singly doped with Er^{3+} ions were synthesized and then studied using absorption and emission spectroscopy. The spectroscopic properties of Er^{3+} have been examined for glass samples with low (5 and 10 mol%) and high BaF_2 (30 mol%) BaF_2 content.

The optical absorption spectra of Er^{3+} ions in lead-free germanate glasses recorded at room temperature in the (a) UV–visible and (b) NIR wavelength region are presented in Fig. 1. Clearly resolved absorption bands are attributed to the electronic transitions from the $^4I_{15/2}$ ground state to the high-lying excited levels of Er^{3+} ions. Inset of Fig. 1a shows absorption bands corresponding to the $^4I_{15/2} - {}^2H_{11/2}$ transition, so called 'hypersensitive transition' of Er^{3+}, which is sensitive to small changes of the glass environment around rare earth ions. The absorption bands related to hypersensitive transition of Er^{3+} ions are shifted to shorter wavelengths (blue shift) with increasing BaF_2 concentration. From absorption

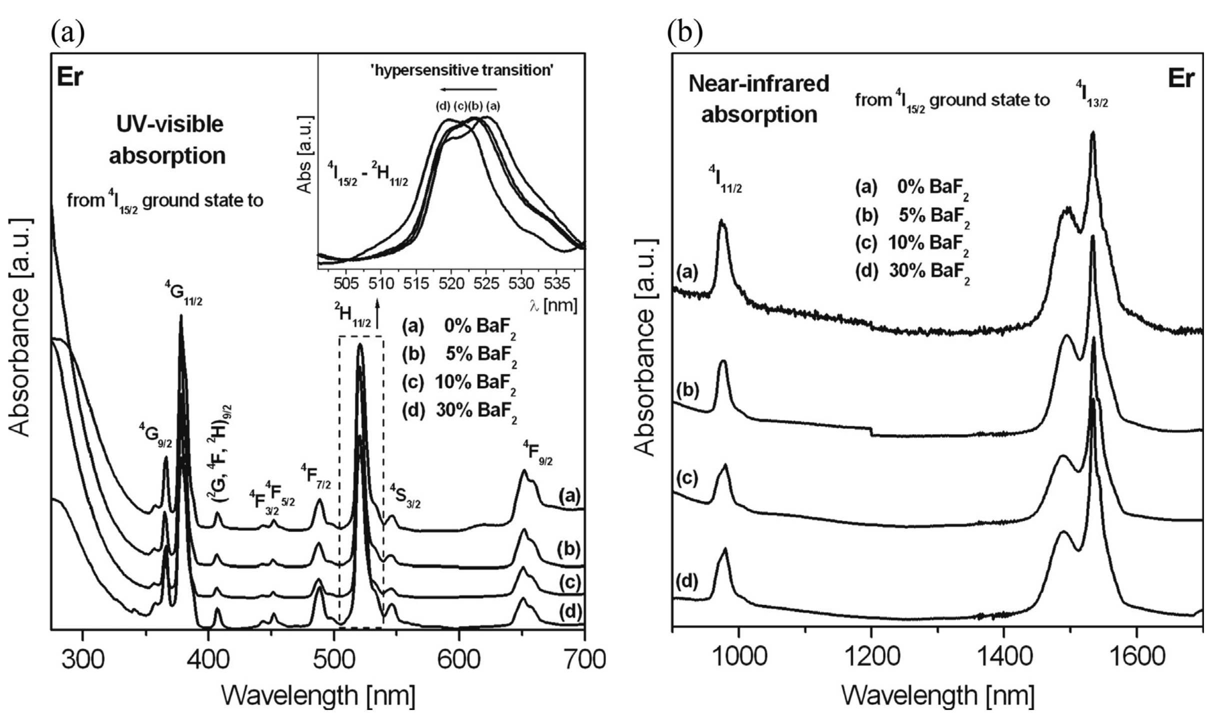

Fig. 1. Absorption spectra for Er^{3+} ions in lead-free germanate glasses measured in (a) UV–visible and (b) NIR region. Inset shows absorption band due to $^4I_{15/2} - {}^2H_{11/2}$ hypersensitive transition of Er^{3+}.