Journal of Luminescence 193 (2018) 34–38

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Influence of excitation wavelengths on up-converted luminescence sensing behavior of Er^{3+} ions in lead-free germanate glass

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ARTICLE INFO

Keywords:
Glasses
Er^{3+} ions
Up-conversion luminescence
Optical temperature sensors

ABSTRACT

Temperature-dependent up-conversion luminescence spectra of Er^{3+} in lead-free germanate glass have been examined under 800 nm and 980 nm diode laser excitation. Green up-conversion luminescence spectra measured in the 500–580 nm ranges correspond to transitions originating from thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels to $^4I_{15/2}$ ground level of Er^{3+}. The relative emission band intensities of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} are changed with temperature. The rate of fluorescence intensity ratio varying with temperature was calculated for glass sample excited at 800 nm and 980 nm, respectively. The maximum temperature sensitivity is nearly 20% higher for glass sample pumped at 980 nm than 800 nm.

1. Introduction

Since the radiative and non-radiative processes between rare earth ions (Ln^{3+}) in inorganic glasses were revealed by Reisfeld et al. [1–7] in seventieth years, much more effort has been directed towards Ln^{3+}-doped glasses, which can efficiently convert near infrared (NIR) light into visible light under low-cost infrared laser diodes. The mechanisms of up-conversion processes, namely the excited state absorption (ESA), energy transfer up-conversion (ETU) and photon avalanche (PA), have been well presented and discussed in the review published by Auzel [8]. Among Ln^{3+} ions, trivalent Er^{3+} is the most popular ion showing up-conversion luminescence. Several previously published works demonstrate the enhanced green and/or red up-conversion luminescence properties of Er^{3+} ions in various glass-host matrices [9–19]. Up-converted luminescence bands correspond to $^4H_{11/2}$,$^4S_{3/2} \rightarrow {}^4I_{15/2}$ (green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (red) transitions of Er^{3+}. Green and/or red up-conversion luminescence spectra of Er^{3+} can be measured under 980 nm [20] or 800 nm [21] diode-laser excitation. Further investigations suggest that differences in the intensities of up-converted emission bands are associated to different radiative transition rates changing significantly with temperature. In particular, Er^{3+}-doped systems are promising for optical temperature sensors due to thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ levels, whose populations meet the Boltzmann distribution law. The temperature can be determined by processing the fluorescence intensity ratio (FIR) of the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}. The fluorescence intensity ratio of these green emission lines fulfills a temperature-dependent function, because the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels is quite small (about 800 cm^{-1}). A few works is devoted to temperature-dependent up-conversion luminescence processes of Er^{3+} which confirm the ability of the studied oxide or oxyfluoride glass systems to be used as optical temperature sensors [22–27].

Among glass-host matrices, rare earth doped lead-free oxyfluoride germanate glasses belong to excellent optical materials emitting visible light or near-infrared radiation. Recently, spectroscopic properties of Pr^{3+}, Eu^{3+} and Er^{3+} ions in oxyfluoride germanate glass based on GeO_2 – BaO – BaF_2 – Ga_2O_3 were presented and discussed in details [28–31]. Several spectroscopic parameters of rare earth ions were examined in glass samples, where BaO was partially or totally replaced by BaF_2. The spectral analysis suggests that the positions of luminescence bands and their relative intensities are changed significantly with BaF_2 content. The relative integrated emission intensities of $^3P_0 \rightarrow {}^3H_4$ transition (blue) to the $^3P_0 \rightarrow {}^3F_2$ transition (red) of Pr^{3+} strongly depend on fluoride modifier BaF_2 in glass composition [28]. Further investigations indicate that the ratio of integrated emission intensity of the $^5D_0 \rightarrow {}^7F_2$ transition to that of the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+} decrease significantly with increasing BaF_2 content [29]. The same situation is observed for $^5D_0$ luminescence lifetime of Eu^{3+}, which reduced from 1.22 to 0.54 ms under total replacement BaO by BaF_2. From absorption spectra of Er^{3+} ions the bonding parameter was calculated and its value is reduced with increasing BaF_2 content [30]. The absorption (Er^{3+}) and emission (Pr^{3+}) 'hypersensitive transitions' of rare

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http://dx.doi.org/10.1016/j.jlumin.2017.09.003
Received 20 April 2017; Received in revised form 7 July 2017; Accepted 1 September 2017
Available online 06 September 2017

earths are shifted in direction to shorter wavelengths with increasing BaF_2 content in glass composition [31].

In this work, we propose environmentally-friendly multicomponent lead-free oxyfluoride germanate glass singly doped with erbium that may be promising for optical temperature sensing. The up-converted luminescence sensing behavior of Er^{3+} ions in lead-free germanate glass has been examined as a function of excitation wavelengths. The temperature-dependent up-conversion emission spectra of Er^{3+} were measured under 800 nm and 980 nm diode-laser excitation. The temperature sensitivity is dependent on the excitation wavelengths. These aspects are really important from the luminescent sensor point of view. They were not examined earlier, to the best of our knowledge.

2. Experimental

Lead-free oxyfluoride germanate glass in $60GeO_2 – 25BaO – 5BaF_2 – 9{,}5Ga_2O_3 – 0{,}5Er_2O_3$ (in %mol) system was prepared. Anhydrous oxides and fluorides (99.99% purity, Aldrich) were used as the starting materials. To prepare samples, the appropriate amounts of all components were mixed homogeneously together and were fabricated in a glow box in a protective atmosphere of dried argon. The glasses were melted at 1200 °C in Al_2O_3 crucibles for 45 min. After this procedure, the samples were slowly cooled to the room temperature.

The refractive index at a wavelength of 632.8 nm was determined using the Metricon 2010 prism coupler. Transmission spectrum was performed on the Nicolet iS50 ATR spectrometer in a infrared frequency region. Raman spectrum was measured using DXRxi Raman Imaging Microscope. A microscope objective (50x) focused the λ = 514.5 nm exciting light in order to obtain the Raman line. The optical absorption spectrum was recorded using a Varian 5000 UV–VIS–NIR spectrophotometer. Up-conversion luminescence has been excited with cw diode laser at 800 nm or 980 nm, respectively. Then dispersed by a 1-m double grating monochromator and detected with a photomultiplier with S-20 spectral response. Luminescence spectra were recorded using a Stanford SRS 250 boxcar integrator with an accuracy of 0.2 nm, controlled by a computer. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Glass characterization

Transmission and Raman spectra were measured in order to characterize multicomponent glass system based on $GeO_2 – BaO – BaF_2 – Ga_2O_3 – Er_2O_3$. Lead-free oxyfluoride germanate glass presents relatively broad transparency from 0.35 to 8 μm. The light transmission is above 80% at wavelengths nearly up to 8 μm (Fig. 1). It indicates that the studied glass shows more transparency in the infrared region, compared with traditional oxide silica glasses. The previous investigations for lead fluorogermanate glass [32] also suggested that infrared transparency was improved with the substitution of fluorine for oxygen in glass composition. The inset of Fig. 1 (on right) presents Raman spectrum measured at higher frequencies (above 700 cm^{-1}). From literature data it is well-known that the highest bands of germanate based glasses lie usually in the 700–900 cm^{-1} frequency region, which may be assigned to antisymmetric stretching motions of GeO_4 tetrahedra containing bridging (i.e. Ge–O–Ge bond) and non-bridging (i.e. Ge–O^- bonding) oxygens [33]. The position of the highest Raman band is important because the non-radiative multiphonon decays of rare earth ions depend strongly on the maximum phonon energy of the glass-host. In our case, the highest Raman band is located below 800 cm^{-1}. The maximum of Raman peak related to phonon energy is close to 787 cm^{-1}. It is in a good agreement with the results obtained for similar lead germanate glass systems [34–36]. The energy of the highest Raman peak in pure germanate glass is 980 cm^{-1}, whereas for lead germanate glass is near 820 cm^{-1} [34]. The presence of lead oxide in germanate based glasses makes the Ge-O bond weaker, shifting its band to 760 cm^{-1} [35]. Further studies for lead germanate glass indicate that the Raman scattering from Ge-O stretching modes has slightly been shifted toward lower frequencies to 736 cm^{-1} with an increase in PbF_2 doping [36].

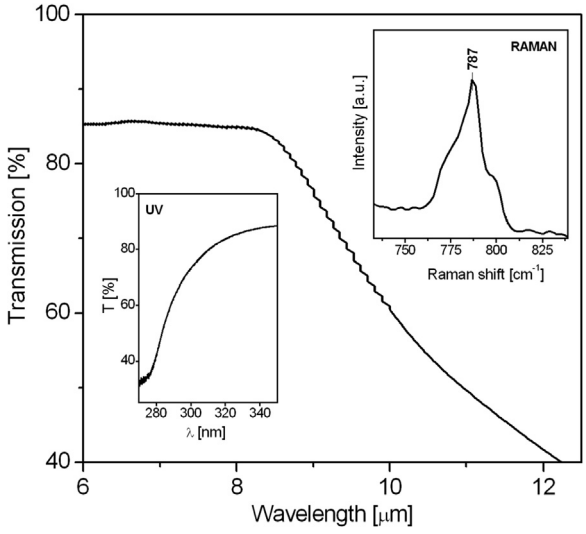

Fig. 1. Transmission spectrum of lead-free oxyfluoride germanate glass in the infrared range. Inset shows transmission spectrum in the UV range (on left) and the Raman spectrum near 800 cm^{-1} frequency region (on right).

The advantage of lead-free oxyfluoride germanate glasses are large transparency from UV to near-infrared spectral ranges and quite easy incorporation of rare earth ions. The refractive index for the studied glass is close to n = 1.736. Especially, the Er^{3+} ions are incorporated to oxyfluoride germanate glass in order to obtain near-infrared (NIR) radiation at about 1.5 μm. Several spectroscopic parameters for the main $^4I_{13/2} \rightarrow {}^4I_{15/2}$ NIR laser transition of Er^{3+} ions in lead-free oxyfluoride germanate glass were determined. In particular, the measured lifetime for the upper $^4I_{13/2}$ laser state of Er^{3+} ions in lead-free oxyfluoride germanate glass is quite long (τ_m = 6.48 ms) and quantum efficiency of $^4I_{13/2}$ state is relatively high (η = 71%) compared to other glass-host matrices [37–44]. It suggests that lead-free oxyfluoride germanate glasses singly doped with Er^{3+} are promising for near-infrared luminescence [45]. The results are summarized in Table 1.

3.2. Up-conversion luminescence

Multicomponent lead-free germanate glass based on $GeO_2 – BaO – BaF_2 – Ga_2O_3 – Er_2O_3$ were examined for optical temperature sensing. In general, the activator concentration is a relevant factor that must be taken into account when developing an Er^{3+} optical temperature glass

Table 1
Spectroscopic parameters for main $^4I_{13/2} \rightarrow {}^4I_{15/2}$ NIR laser transition of Er^{3+} ions in various glass hosts.

Glass host	λ_p [nm]	$\Delta\lambda_p$ [nm]	τ_{rad} [ms]	τ_m [ms]	η (%)	σ_{em} 10^{-20} cm^2	Ref.
$ZnO-Al_2O_3-Bi_2O_3$	1530	57	0,34	0,31	91	0,11	[37]
$Nb_2O_3-K_2O-ZnF_2-LiF-SiO_2$	1540	93,0	–	2,12	–	0,74	[38]
TeO_2-ZnO	1530	76	2,23	3,33	46	–	[39]
$CaO-SiO_2-P_2O_5$	1570	72	–	7,7	–	0.60	[40]
$P_2O_5-K_2O-Al_2O_3-PbO-Na_2O$	1530	46	6,91	2,06	30	0.67	[41]
GeO_2-MgO	1550	81	–	4,45	–	0.85	[42]
$SiO_2-GeO_2-CaO-BaO-Nb_2O_5-Li_2O$	1530	77	5,36	0,78	15	0.95	[43]
GeO_2-PbF_2	1533	57	5,72	5,70	100	–	[44]
$B_2O_3-BaO-BaF_2-Ga_2O_3$	1530	116	12.5	0.38	3	–	[45]
$GeO_2-BaO-BaF_2-Ga_2O_3$	1530	48	9.10	6.48	71	–	[45]