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Spectral analysis of Pr³⁺ doped germanate glasses modified by BaO and BaF₂Joanna Pisarska^{a,*}, Wojciech A. Pisarski^a, Dominik Dorosz^b, Jan Dorosz^b^a University of Silesia, Institute of Chemistry, Szkolna 9 Street, 40-007 Katowice, Poland^b Bialystok University of Technology, Faculty of Electrical Engineering, Wiejska 45D Street, 15-351 Bialystok, Poland

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ABSTRACT

Luminescence properties of Pr³⁺ ions in germanate glasses modified by BaF₂ were investigated. Several luminescence bands originating to transitions from the ³P₀ state to the lower-lying states of Pr³⁺ were registered under 450 nm excitation. The spectral analysis suggests that the positions of luminescence bands and their relative intensities are changed significantly with BaF₂ content. The relative integrated luminescence intensities of ³P₀→³H₄ transition (blue) to the ³P₀→³F₂ transition (red) of Pr³⁺ ions strongly depend on fluoride modifier BaF₂ in glass composition. The luminescence bands of Pr³⁺ ions are shifted to shorter wavelengths with increasing BaF₂ content.

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1. Introduction

The energy level scheme of trivalent praseodymium belonging to 4f² electronic configuration contains several metastable levels that provide the possibility of simultaneous luminescent transitions in the blue, orange, red and near-infrared spectral ranges [1–3]. The Pr³⁺ ions in some glass matrices exhibit mainly efficient visible emission. Several observed luminescence bands correspond to transitions originating from ³P₀ and ¹D₂ excited states of Pr³⁺ [3]. Under the commercial blue LED excitation, the radiant flux and the quantum yield for red luminescence of Pr³⁺ ions in heavy metal germanium tellurite glasses are solved to be 219 μW and 11.8%, respectively. Moreover, 85.24% photons of the luminescence in the visible spectral region are demonstrated to be located in 600–720 nm wavelength range, which indicate that Pr³⁺-doped heavy metal germanium tellurite glass is promising for irradiative light source in minimally invasive photodynamic therapy surgery [4]. The second group of glass materials exhibits broadband near-infrared luminescence of Pr³⁺ covering a wavelength range from 1.2 μm to 1.7 μm, which is important for optical fiber amplifiers operating at O-, E-, S-, C-, and L-band [5]. Among several inorganic glass systems, glasses containing CdF₂ and/or PbF₂ 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, but at the same time these

fluoride components were established to play important role in glass formation and further strengthening of glass host network [6]. Alternatively, lead- and cadmium-free glasses are proposed for potential applications in photonics [7]. Recently, luminescence properties of trivalent Pr³⁺ ions in lead-free [8–17] and lead based [18–24] glass host matrices were reported.

Here, our research has been focused on excitation and luminescence of germanate glasses doped with Pr³⁺. The spectroscopic properties of Pr³⁺ ions in glass samples modified by BaO and/or BaF₂ are presented and discussed in details.

2. Experimental

Germanate glasses with the following chemical composition: 60GeO₂–(30–x)BaO–xBaF₂–9.5Ga₂O₃–0.5Pr₂O₃, where x=0, 5, 10, 20, 30 (given in mol%) and 60GeO₂–(30–x)BaO–xBaF₂–9.9Ga₂O₃–0.1Pr₂O₃ (x=0 and 5), were prepared by mixing and melting appropriate amounts of metal oxides and BaF₂ of high purity (99.99%, Aldrich Chemical Co.). In order to prepare the glass samples, appropriate amounts of all components were mixed homogeneously. Due to the hygroscopicity of the fluoride component and, in order to minimize the adsorbed water content, batches of 5 g were weighted and stored in glove box, in a protective atmosphere of dried argon. Then, they were melted at 1200 °C for 0.45 h. Transparent glassy plates of 10 × 10 mm dimension were obtained. Each glass sample of 2 mm in thickness was polished for optical measurements. The nature of the studied samples was identified using the X-ray diffraction analysis (X'Pert

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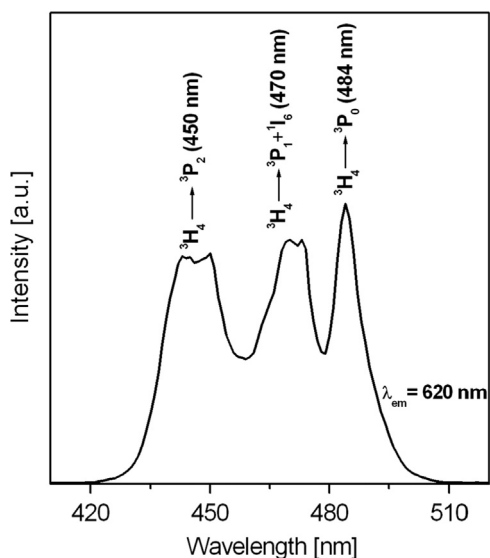


Fig. 1. Typical excitation spectrum for Pr^{3+} ions in germanate glass.

X-ray diffractometer). Absorption spectra were recorded using a Varian 5000 UV–VIS–NIR spectrophotometer. Excitation and luminescence measurements were performed on a PTI Quanta-Master QM40 coupled with tunable pulsed optical parametric oscillator (OPO), pumped by a third harmonic of a Nd:YAG laser (Opotek Opolette 355 LD). The luminescence was dispersed by double 200 mm monochromators. The luminescence spectra were recorded using a multimode UVIS PMT (R928) and Hamamatsu H10330B-75 detectors controlled by a computer. All measurements were carried out at room temperature.

3. Results and discussion

Germanate glasses singly doped with Pr^{3+} ions were studied using excitation and luminescence spectroscopy. Fig. 1 presents typical excitation spectrum for trivalent Pr^{3+} ions in germanate glass. The spectrum was monitored at 620 nm emission wavelength. In 420–510 nm ranges, the excitation spectrum consists of three characteristic bands, which correspond to transitions originating from the $^3\text{H}_4$ ground state to the higher-lying $^3\text{P}_2$, $^3\text{P}_1+^1\text{I}_6$ and $^3\text{P}_0$ states of Pr^{3+} . The energy gaps between excited states of Pr^{3+} are very small and the excitation energy transfers very fast from the $^3\text{P}_2$ state via $^3\text{P}_1+^1\text{I}_6$ states to the $^3\text{P}_0$ state by non-radiative relaxation. Next, the $^3\text{P}_0$ excited state is depopulated giving several radiative transitions to the lower-lying states of Pr^{3+} . Fig. 2 shows luminescence spectra for Pr^{3+} doped germanate glasses in the absence and presence of BaF_2 . The glass samples were excited at 450 nm ($^3\text{P}_2$ state of Pr^{3+}). The spectra consist of several emission bands, which are due to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{H}_5$, $^1\text{D}_2 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{H}_6$ and $^3\text{P}_0 \rightarrow ^3\text{F}_2$ transitions of trivalent Pr^{3+} , respectively. The broad luminescence band at 525 nm–560 nm can contain a contribution from $^3\text{P}_1 \rightarrow ^3\text{H}_5$ transition, whereas the shoulder at about 473 nm is due to $^3\text{P}_1 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} . All transitions are schematized on the energy level scheme of Pr^{3+} (Fig. 3). Generally, visible luminescence originating from the $^3\text{P}_0$ state of Pr^{3+} ions can be successfully observed. The relative integrated luminescence band intensities of Pr^{3+} ions are different for glass samples without and with BaF_2 . You can evidently see that the changes in luminescence intensities are significant, when even a small amounts of BaF_2 (5 mol%) is added to the germanate glass host. Moreover, the luminescence spectra

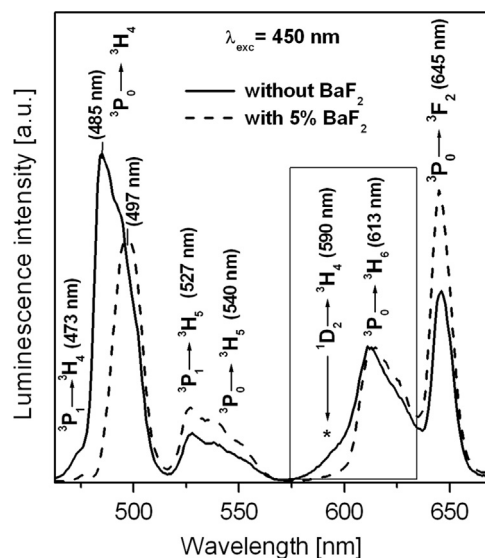


Fig. 2. Luminescence spectra for Pr^{3+} ions in germanate glasses in the absence (solid line) and presence of BaF_2 (dashed line).

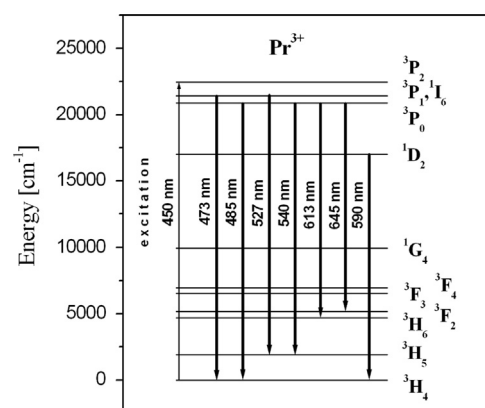


Fig. 3. Energy level scheme for Pr^{3+} ions in germanate glass. All transitions are also indicated.

at about 590 nm referred as (*) are drastically changed. Luminescence band due to $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} is also located in this spectral region. This band was identified only for the oxide glass sample containing BaO. It is interesting to see that luminescence due to $^1\text{D}_2 \rightarrow ^3\text{H}_4$ transition of Pr^{3+} ions is not observed for glass samples, where BaO was partially (or totally) substituted by BaF_2 in glass composition. Fig. 4 shows the luminescence decay profiles of the excited states of Pr^{3+} ions in germanate glass without BaF_2 measured under different excitation and monitoring emission wavelengths. Luminescence decay curves for the glass sample excited at 450 nm ($^3\text{P}_2$ state of Pr^{3+}) depend critically on monitoring emission wavelengths (a) 620 nm and (b) 590 nm. The luminescence decay is longer for glass sample under monitoring emission wavelength 590 nm than 620 nm, respectively. The detailed analysis confirmed that longer decay is identical than that one obtained for the glass sample under direct excitation at 590 nm ($^1\text{D}_2$ state of Pr^{3+}). Based on decay measurements, luminescence lifetimes for 0.5 mol% of Pr^{3+} ions in germanate glass containing BaO were determined. Measured lifetimes for the $^3\text{P}_0$ and $^1\text{D}_2$ states of Pr^{3+} are close to 8 μs and 21 μs , respectively. Their values are in a good agreement with the experimental results 8 μs ($^3\text{P}_0$) and 32 μs ($^1\text{D}_2$) obtained for Pr^{3+} ions (0.5 mol%) in heavy metal glasses containing PbO and TiO_2 [25]. In contrast to oxide glass sample, only shorter decays (below 10 μs) from the $^3\text{P}_0$ state of Pr^{3+} ions in glass samples containing BaF_2 were measured,

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