Local Field Effect in antimony-germanate glasses co-doped with Rare-Earth ions and silver nanoparticles

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Received December 18, 2017; accepted December 20, 2017; published December 31, 2017

Abstract—The article presents the possible mechanisms of interaction between emission of Eu^{3+} ions and surface plasmon resonance (SPR) from Ag^0 nanoparticles. The antimony-germanate glasses were synthetized by standard melt-quenching method. The influence of high-phonon glass forming compounds on excitation and luminescence spectra was analysed. Also, we showed that Sb_2O_3 is a mild reducing agent of noble metal ions. This mild reduction property enables thermochemical reduction of Ag^+ to Ag^0 in a single-step during the melting process. The energy transfer mechanisms between Eu^{3+} ions and Ag^0 nanoparticles were also discussed in terms of a local field effect of Ag^0 nanoparticles.

In the field of materials engineering for photonics, the main effort is paid to the development of novel materials with unique optical and structural properties. Up to day, a number of glasses, glass-ceramics and crystals doped with Rare-Earth (RE) ions have been proposed as a promising material for light management in a wide spectral range. It includes a nanometric volume of molecules embedded in a glassy material and called as nanocomposites [1]. The presence of some nanoparticles (NPs) of crystals, noble metals or even semiconductors simultaneously with RE ions allows to achieve new luminescent properties resulting from the interaction of light and energy transfer between RE ions and embedded nanoparticles. Especially, in order to improve the quantum efficiency of radiative transitions of RE ions and broaden the spontaneous emission spectrum, low-phonon materials are required. Among oxide glasses the special attention should be paid to antimony-germanate glasses – a matrix of different phonon energies formed as a combination of glass-forming elements. Antimony oxide glasses have attracted considerable interest for their combination of chemical durability, low phonon energies (~600cm^{-1}) and high transparency in a wide range. However, the low field strength (0.73) of Sb^{3+} makes it a poor glass former, unable to exist, particularly in a bulk monolithic form, which is very much essential for practical applications.

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In our earlier investigations, we proposed the solution of this problem and synthesized a glass with a combination of different phonon energy of glass-forming elements [2–4]. The article will show the influence of different high-phonon compounds like phosphorous (P_2O_5 – 1200cm^{-1}), boron (B_2O_3 – 1400cm^{-1}) and silica (SiO_2 – 1100cm^{-1}) on luminescent properties of RE ions doped antimony-germanate glasses. Moreover, special attention has been paid for noble metals such as gold and silver ions. The reason is that the collective oscillation of the noble metal electrons resonantly excited by visible light causes a tremendous enhancement of the electromagnetic near-field in the vicinity of nanoparticles. This phenomenon is called surface plasmon resonance and if it exists in inorganic glasses doped with RE ions, the luminescence signal may be amplified or quenched [5]. Moreover, the most interesting aspect of antimony oxide-based glasses over conventional systems is that Sb_2O_3 is their mild reducing agent. This mild reduction property enables in-situ reduction of Ag^+ ($AgNO_3$) to Ag^0 in a single-step during the melting process, thereby providing a simple, low cost method for the preparation of bulk photonic materials [9]. In our experiment we confirmed that the specific glass composition and the controlled heat-treatment process give a new concept of creating RE – doped optical nanocomposites.

Glasses with based molar composition $25Sb_2O_3$ – $25GeO_2$ – $40(SiO_2/P_2O_5/B_2O_3)$ – $5Al_2O_3$ – $5Na_2O$ were synthesized by a standard melt-quenching method and labelled as SGS, SGP and SGB, respectively. The Eu_2O_3 concentration was fixed on a level of 0.5mol% and $AgNO_3$ content was selected to obtain the optimal interaction effect. All the raw materials were analytical grade reagents (99.99%). A homogenized set was placed in a platinum crucible and melted in an electric furnace at the range 1250°C÷1450°C for 60 min in oxide atmosphere. Next, the glass melt was poured into a brass plate at room temperature (RT) and then annealed at near

transformation temperature for 2 hours to release the internal stress from the quench. Next, the glasses were cooled down to room temperature and polished carefully in order to meet the requirements for optical measurements. The excitation and luminescence spectra of the glasses in a range of 350÷750nm were measured using a JobinYvon Fluoromax4 spectrophotometer.

Figure 1 shows the excitation spectra of each sample doped with 0.5 mol% of Eu_2O_3 monitored at a wavelength of 613nm. In analysed range from 325nm to 550nm the five bands centered at wavelengths of 362nm ($^7F_0 \rightarrow {}^5D_4$), 382nm ($^7F_0 \rightarrow {}^5L_7$), 395nm ($^7F_0 \rightarrow {}^5L_6$), 416nm ($^7F_0 \rightarrow {}^5D_3$) and 464nm ($^7F_0 \rightarrow {}^5D_2$) were observed.

In order to analyse the influence of high-phonon glass-forming compounds on the intensity of "hypersensitive" transition ($^7F_0 \rightarrow {}^5D_2$) of europium ions, we normalised the spectra to the strongest excitation band at 395nm ($^7F_0 \rightarrow {}^5D_2$). In our experiment, the increase of phonon energy of the following compounds ($SiO_2 \rightarrow P_2O_5 \rightarrow B_2O_3$) in antimony-germanate glasses leads to a strong reduction of "hypersensitive transition" intensity. This phenomenon confirms the structural distortion of the glass network in the vicinity of Eu^{3+} ions [6].

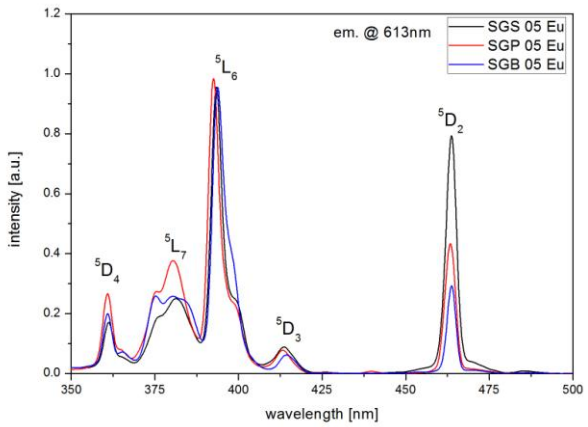

Fig. 1. Excitation spectra of antimony-germanate glasses doped with 0.5mol% Eu_2O_3 and modified by different high-phonon compounds.

The luminescence spectra of fabricated glasses doped with Eu^{3+} ions under excitation by laser radiation with λ_{exc}=397nm were shown in Fig. 2. In a range of 525÷725nm, five characteristic emission bands have been observed at wavelengths of 580, 591, 613, 653, and 703nm originating from the transitions of $^5D_0 \rightarrow {}^7F_0$, $^7F_1$,$^7F_2$, $^7F_3$ and $^7F_4$, respectively. In this case, we also observed changes of emission shape of europium depending on a high-phonon compound. The intensity of $^5D_0 \rightarrow {}^7F_1$ transition is largely independent of the local environment of Eu^{3+} hence all spectra were scaled (integrated) [8]. It is worth noticing that the emission band at 612nm ($^5D_0 \rightarrow {}^7F_1$) is characterized by significant intensity changes indicating structural changes in the vicinity of Eu^{3+}. The ratio R between the integrated intensity of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) transitions, gives a factor of distortion degree from the inversion symmetry of the local environment of europium ions [7]. In our experiment, the intensity ratio R is highest for SGS glass (R=3.36) and decreases rapidly for SGB glass (R=1.76). It suggests that for glass with boron oxide the local environment of Eu^{3+} ions is characterized by a less covalent character. This property is favourable for the mechanism of nanoparticles formation. Besides, due to the specific function of antimony ions as a mild reduction agent the thermochemical reduction of noble metals in the SGB glass was chosen to analyse the local field effect of Ag^0 nanoparticles.

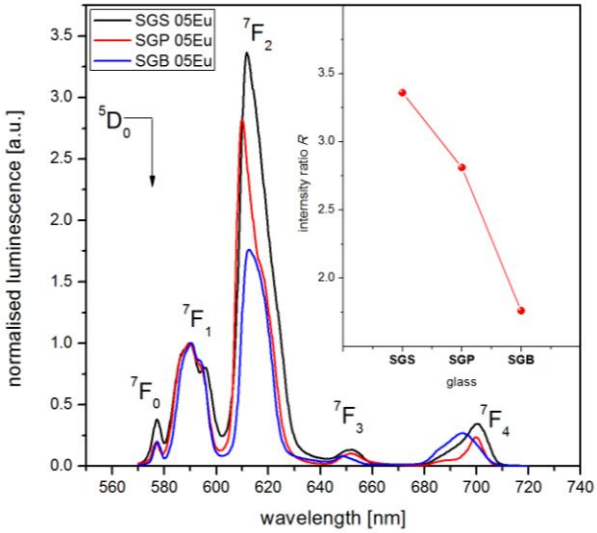

Fig. 2. The luminescence spectra of fabricated glasses normalized to $^5D_0 \rightarrow {}^7F_1$ transition. The intensity ratio R of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) transitions (inset).

A probable mechanism of selective chemical reduction of Ag^+ to Au^0 by Sb^{3+} can be explained by considering the reduction potentials (E^o) of the respective redox systems as follows:

$$Sb^{3+} + 2Ag^+ \rightarrow Sb^{5+} + 2Ag^0 \qquad E^o = 0.95\ V, \qquad (1)$$

where

$$Sb^{5+} + 2e^- \rightarrow Sb^{3+} \qquad E^o = 0.649\ V \qquad (2)$$

$$Ag^+ + 1e^- \rightarrow Ag^0 \qquad E^o = 0.7996\ V \qquad (3)$$

Figure 3 presents a comparison of luminescence spectra of SGB glasses doped with Eu^{3+}, Eu^{3+}/Ag^0 and Eu^{3+}/Ag^0 after the heat-treatment process. Unfortunately, the quenching of luminescence was observed at all emission bands in SGB glass co-doped with Eu^{3+} and Ag^0 nanoparticles. Also, the additional heat-treatment process leads to a further decrease of the luminescence signal of europium ions. It confirmed that the major effect in

interaction mechanisms results from energy transfer between Eu^{3+} ions and a surface plasmon resonance (SPR) band of Ag^0 NPs. However, an interesting effect was observed in the intensity ratio of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) transitions. The introduction of Ag ions to SGB glass leads to an increase of *R*, all the more prominent after the heat-treatment process. It could be correlated to energy transfer between europium ions and silver nanoparticles.

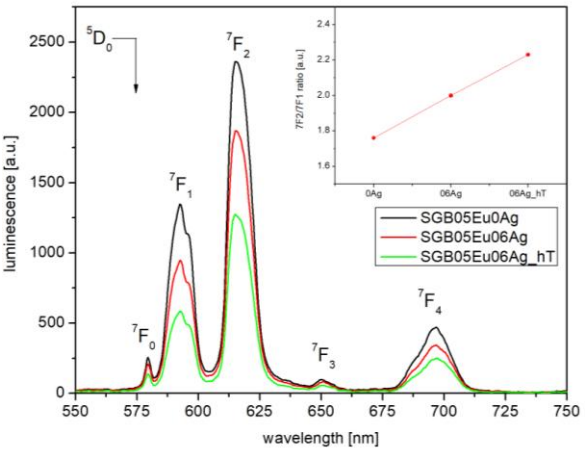

Fig. 3. Luminescence spectra of SGB glass without Ag, with Ag ions before and after heat-treatment. The intensity ratio *R* of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) transitions (inset).

In order to understand the absorption and emission processes in Eu^{3+}-doped SGB glass in the vicinity of Ag^0 NPs, a simplified energy level diagram of the system is presented in Fig. 4.

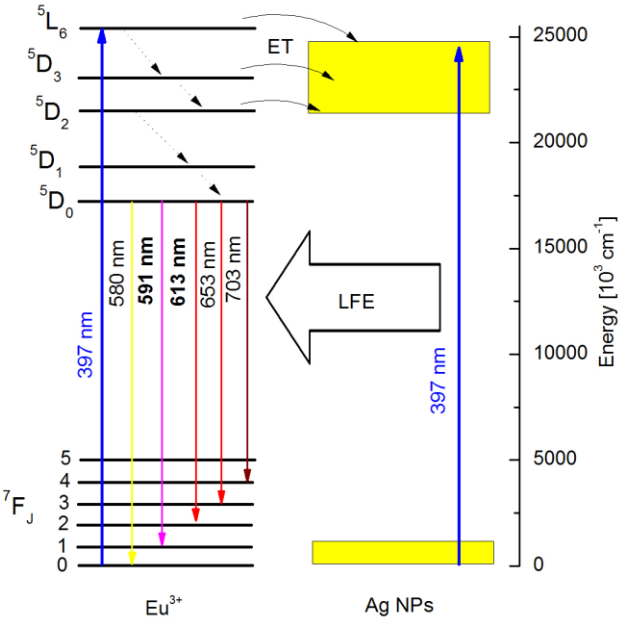

Fig. 4. Simplified energy levels diagram with possible mechanisms of interaction between europium ions and silver nanoparticles.

Possible amplification or quench mechanisms induced by light interaction can be explained by the following processes: (i) after ground state absorption from $^7F_0 \rightarrow {}^5L_6$ transition under 397nm laser excitation, the $^5D_0$ metastable energy level is fast populated from transitions $^5D_3 \rightarrow {}^5D_2 \rightarrow {}^5D_1 \rightarrow {}^5D_0$. The large energy difference between $^5D_0$ and $^7F_5$ levels allows excited Eu^{3+} ion to relax radiatively, while visible emission is observed (Fig. 3); (ii) simultaneously, the interaction of excitation light with silver NPs results in a large localized electric field induced at the surface of the metal; (iii) the energy transfer (ET) between RE ions and Ag^0 NPs contributes to quenching the luminescence peak intensity.

In conclusions, series of antimony-germanate glasses modified by high-phonon energy compounds ($SiO_2/P_2O_5/B_2O_3$) were synthetized by a standard melting and quenching method. A strong intensity reduction of "hypersensitive" transition ($^7F_0 \rightarrow {}^5D_2$) of europium ions leads to a structural distortion of glass network for SGB glass. The decrease in the intensity ratio of ($^5D_0 \rightarrow {}^7F_2$)/($^5D_0 \rightarrow {}^7F_1$) transitions confirms that for glass with boron oxide the local environment of Eu^{3+} ions is characterized by a less covalent character. According to luminescent measure-ments, the decrease of a luminescence signal due to a local field effect has been observed in SGB glass doped with $0.6AgNO_3$ before and after the heat-treatment process. Our experiment shows that Ag NPs creation is possible in a one-step melting method of SGB glass. It could be helpful in further investigations on the technology of optical fibre with Ag nanoparticles.

The project was funded by the National Science Centre (Poland) granted on the basis of the decision No. DEC-2016/21/D/ST7/03453. The COST Action MP1401 "Advanced fibre laser and coherent source as tools for society, manufacturing and life science" is also acknowledged.

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