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Germanate glasses co-doped with Ce^{3+}/Ln^{3+} (Ln = Pr, Tb, Dy) for white light emitting diodes

AGATA GÓRNY*, MARTA SOŁTYS, JOANNA PISARSKA, WOJCIECH A. PISARSKI

University of Silesia, Institute of Chemistry, Katowice, Poland

*Corresponding author: agata.gorny@smcebi.edu.pl

Glasses doped with lanthanides ions may be good white light emitters due to their interesting physical and spectroscopic properties. In this paper, the optical spectroscopy of rare earths doped glasses with a special emphasis on application as white LED were presented. The luminescent glass materials containing Ln^{3+} (Ln = Pr, Tb, Dy) and Ce^{3+} ions were obtained. The glasses samples were prepared by a traditional melt-quenching technique. The optical properties of glasses containing various concentrations of rare earth ions were analyzed. It was observed that luminescence bands corresponding to characteristic transitions of Ln^{3+} and cerium ions are present on spectra measured under direct excitation of Ce^{3+}. Therefore, it indicates that the energy transfer process between Ce^{3+}/Pr^{3+}, Ce^{3+}/Tb^{3+}, Ce^{3+}/Dy^{3+} ions in glasses occurs. Some parameters such as correlated color temperature (CCT) and chromaticity coordinates (CIE) that characterize white LEDs were analyzed and discussed in detail.

Keywords: glasses, rare earth ions, white luminescence.

1. Introduction

Inorganic glass systems doped with rare earth ions are a very large group of materials which due to their properties can be used to generate white light [1–4]. Much research provide a spotlight on the correlation between the optical properties and white luminescence. In many cases the white light emission significantly depends on glass host [5–7], concentration of rare earth ions [8–10] or excitation wavelengths [11, 12]. It is worth noting that nowadays many different studies based on glasses doped with lanthanide ions are focused on finding the best matrices as potential white light emitters. Additionally, the possibility of energy transfer between optically active dopant supports the generation of white light emission in inorganic glasses [13–15].

Cerium ions are one of the most important promising lanthanide ions for application in radiation detectors because of their following characteristics properties [16]. The emission spectrum for a system doped with Ce^{3+} ions shows a broadband centered

at the border between UV and visible light domains [17–19]. Moreover, these ions introduced into the matrix as donors, transfer part of energy to other ions which act as an acceptors. In recent years, the investigations were focused on cerium ions for applications especially in scintillators [20–22]. Nowadays, there is more information about glasses [23, 24], crystals [25, 26] and phosphors [27] doped with cerium ions used as materials to generate white light.

In present work, germanate glasses singly doped with Ce^{3+}, Pr^{3+}, Tb^{3+} and Dy^{3+} ions and glass systems doubly doped with Ce^{3+}/Tb^{3+}, Ce^{3+}/Pr^{3+} and Ce^{3+}/Dy^{3+} were prepared. To study the spectroscopic properties of glass systems, the luminescence spectra were recorded. The energy transfer process from cerium to terbium, praseodymium and dysprosium ions in germanate glasses occurs. From the emission spectra, the Commission Internationale de I'Eclairage (CIE) chromaticity coordinates (x, y) were calculated in relation to concentration of acceptor ions. The obtained results indicate that germanate glasses co-doped with Ce^{3+}/Dy^{3+} can be used as potential white light emitters.

2. Experiment

Germanate glasses co-doped with Ce^{3+} and Ln^{3+} (Ln = Tb, Dy, Pr) ions were synthesized using the traditional melt quenching-technique. The glasses with general formula $30BaO–(10-x-y)Ga_2O_3–60GeO_2–xCe_2O_3–yLn_2O_3$ ($x = 0, 0.5$; $y = 0, 0.25, 0.5, 0.75$) in mol%, were prepared by mixing and melting appropriate amounts of metal oxides of high purity (99.99%, Aldrich Chemical Co.). Then, they were melted for 0.45 h at 1250°C. Optical measurements were performed on a PTI QuantaMaster QM40 (Photon Technology International QuantaMaster 40 (QM 40) UV/VIS Steady State Spectrofluorometer) coupled with a 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 UV-VIS PMT (R928) detector controlled by a computer. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Optical properties of Ln^{3+} ions in germanate glasses

The spectroscopic properties of germanate glasses singly and doubly doped with Ln^{3+} (Ln = Ce, Tb, Pr, Dy) ions were investigated. First of all, the excitation and emission spectra were measured for germanate glass singly doped with Ce^{3+} ions (Fig. 1). The excitation spectrum for cerium ions was monitored at 440 nm. The spectrum consists of an asymmetric broadband corresponding to the transition from 4*f* ground state to the excited 5*d* level of Ce^{3+} ions. Observably, from the excitation spectrum, the co-excitation band of Ce^{3+} ions is at the wavelength of 380 nm. The emission spectrum of germanate glass shows a broadband luminescence of cerium ions in the range from 400

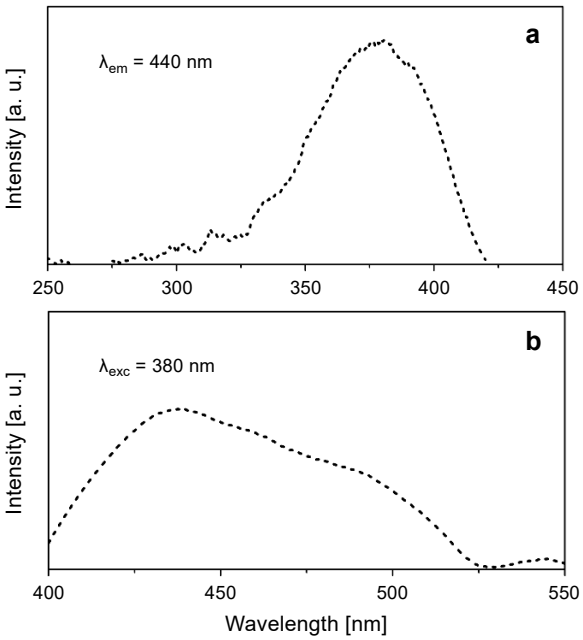

Fig. 1. Excitation spectrum (**a**) and emission spectrum (**b**) for germanate glasses doped with Ce^{3+} ions.

to 550 nm. The emission of Ce^{3+} are assigned to two transitions from 5*d* level to $^2F_{5/2}$ and $^2F_{7/2}$, respectively. In order to examine that the energy transfer process is possible between Ce^{3+} as donor ions and Ln^{3+} (Ln = Tb, Pr, Dy) as acceptor ions in germanate glasses, the excitation spectra for glass systems singly doped with terbium, praseodymium and dysprosium ions were registered (Fig. 2). The excitation spectrum of the glass host singly doped with Tb^{3+} ions was obtained by monitoring the wavelength at 543 nm. The spectrum presents eight bands at 338, 343, 352, 359, 368, 375, 378 and 485 nm assigned to transition from $^7F_6$ ground state to $^5L_7$, $^5L_8$, $^5L_9$, $^5G_5$, $^5L_{10}$, $^5G_6$, $^5D_3$, $^5D_4$ excited state, respectively. On the other hand, the excitation spectrum of dysprosium ions in germanate glass (λ_{em} = 572 nm) consists of six bands originating from electronic transition from $^6H_{15/2}$ ground state of Dy^{3+}. The registered bands due to $^6H_{15/2} \rightarrow {}^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}$, $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$ located at 350, 364, 388, 425, 453, 473 nm, respectively. What is more, the excitation spectrum for germanate glass singly doped with praseodymium ions was also registered at an emission wavelength 610 nm in the range 400–500 nm. It has three excitation bands corresponding to the transitions $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ at the wavelengths 447, 472 and 484 nm, respectively. Among all the excitation bands, the band at 484 nm corresponding to the transition $^3H_4 \rightarrow {}^3P_0$ is more intense. Furthermore, it was observed that in the range from 450 to 500 nm for terbium ions, 400–500 nm for dysprosium ions and 425–500 nm for praseodymium ions excitation bands of these rare earth ions and emission band of cerium ions overlap,

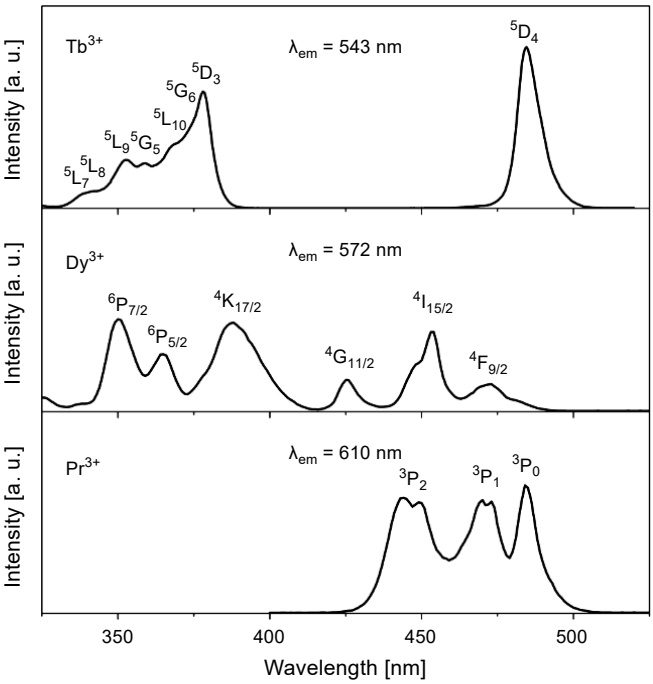

Fig. 2. Excitation spectra for Ln^{3+} ions in germanate glasses.

so that the energy transfer between Ce^{3+} and Tb^{3+}, Dy^{3+}, Pr^{3+} is possible. Moreover, the energy level of these three lanthanide ions is lying significantly lower that the energy level of cerium. From this point of view, the energy transfer between these optical active dopants could be effective due to the radiation emitted by donor ions (Ce^{3+}) which can excite the acceptor ions (Tb^{3+}, Dy^{3+}, Pr^{3+}).

3.2. Influence of acceptor ions on white light generation

To investigate the influence of acceptor ions on white light generation, the emission spectra for co-doped germanate glasses were registered under direct excitation of cerium ions. Figure 3 presents the emission spectra for germanate glasses doubly doped with Ce^{3+} and Tb^{3+}, which have been examined as a function of activator concentration. The emission spectra were registered under direct excitation by 390 nm. The spectra consist of five characteristic luminescence bands corresponding to blue emission ($5d \rightarrow {}^4F_{7/2}$, ${}^4F_{5/2}$) of cerium ions at 439 nm and blue (${}^5D_4 \rightarrow {}^7F_6$), green (${}^5D_4 \rightarrow {}^7F_5$) yellow (${}^5D_4 \rightarrow {}^7F_4$) and red (${}^5D_4 \rightarrow {}^7F_3$) emission of terbium ions at 489, 544, 580 and 620 nm, respectively. Additionally, the influence of concentration of rare earth ions on intensity of luminescence was investigated. It was stated that the content of terbium ions changes the shape of luminescence bands of optical active dopants. Therefore, there is a possibility of tuning the color emission by changing chromaticity parameters of the glasses by varying the acceptor concentration. From this point of view, the Commission

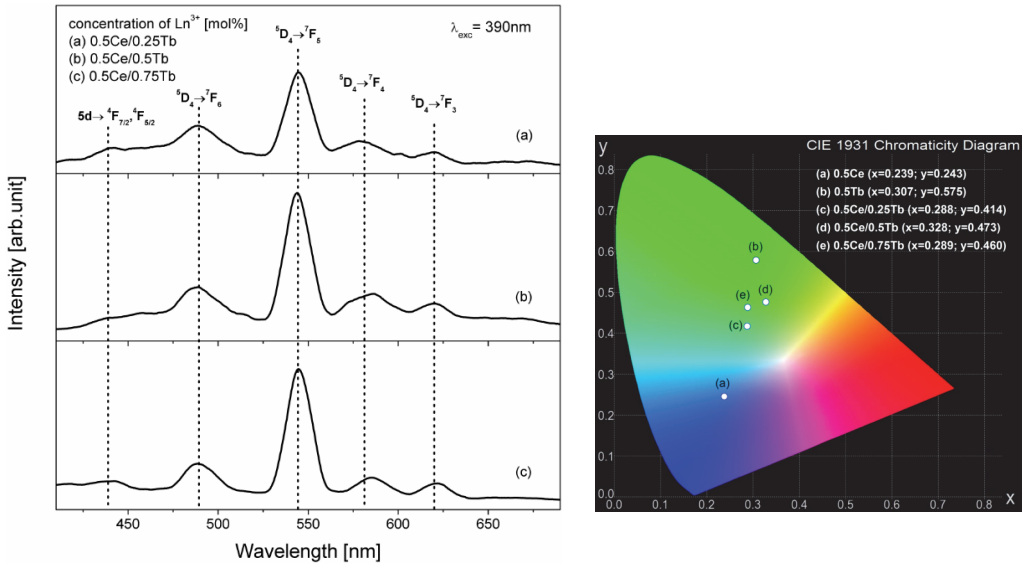

Fig. 3. Emission spectra and CIE chromaticity diagram of germanate glasses co-doped with Ce^{3+} and Pr^{3+}.

Internationale de I'Eclairage (CIE) chromaticity coordinates are calculated [6]. The diagram of CIE coordinates for glasses doubly doped with 0.5 mol% of Ce^{3+} ions and different concentrations of Tb^{3+} ions were also shown in Fig. 3. The obtained color coordinates are closed $x = 0.288$, $y = 0.414$ for sample with 0.25 mol% of Tb^{3+}, $x = 0.328$, $y = 0.473$ for 0.5 mol% of Tb^{3+}, and $x = 0.289$, $y = 0.460$ for 0.75 mol% Tb^{3+}. Moreover, it was observed that the CIE chromaticity coordinates are mainly in the green region. On the contrary, the results obtained by ZHANG *et al*. [28] show that for glass ceramics containing YPO_4 nanocrystals the chromaticity coordinates were found closer the white region than for our germanate glasses. The best CIE coordinates were found to be (0.3201, 0.3749). These results suggest that the glass ceramics may be a promising luminescence material for white LEDs.

Figure 4 shows the results obtained for germanate glasses doubly doped with cerium and praseodymium ions. The emission spectra for glass samples with different concentrations of acceptor ions (Pr^{3+}) were registered under direct excitation of cerium ions (380 nm). Figure 4 presents the influence of concentration of praseodymium ions on bands in the emission spectra. However, the bands corresponding to characteristic transitions of cerium ions are separated into two distinct bands, contrary to bands registered for glasses co-doped with Ce^{3+} and Tb^{3+} ions. The CIE chromaticity coordinates for all obtained glass systems were calculated. It was observed that in this case the coordinates are also far from the white region on the CIE diagram. The white light emission was not observed for germanate glasses doped with cerium and praseodymium ions.

Quite different behaviour for glass samples doubly doped with cerium and dysprosium ions was noticed. The emission spectra for glass systems containing 0.5 mol% of Ce^{3+} ions and 0.5 mol% of Dy^{3+} ions show a broad luminescence band correspond-

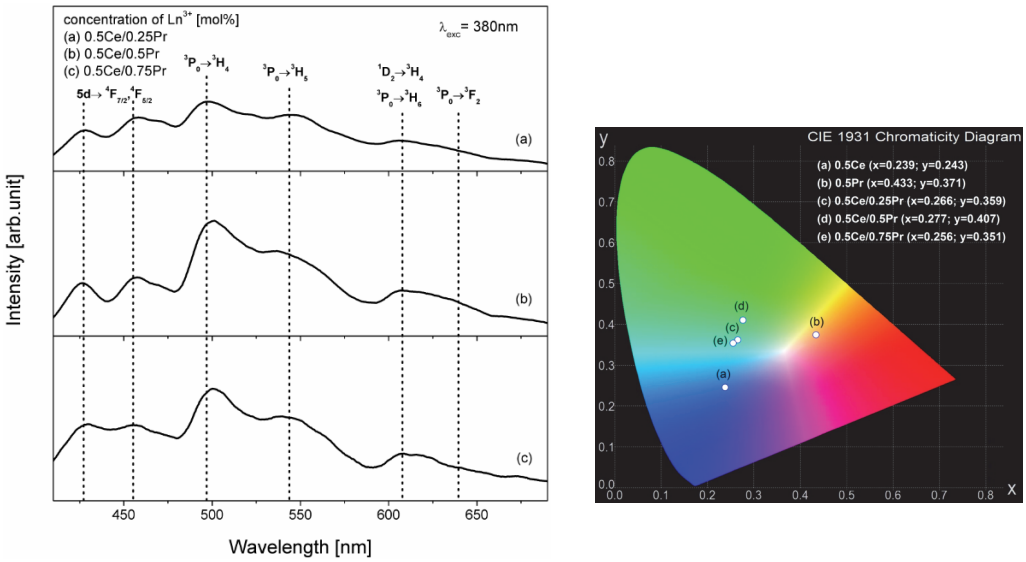

Fig. 4. Emission spectra and CIE chromaticity diagram of germanate glasses co-doped with Ce^{3+} and Tb^{3+}.

ing to characteristic blue emission (435 nm) due to transitions of Ce^{3+} ions (Fig. 5). Additionally, the luminescence bands due to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ (blue emission at 480 nm), ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ (yellow emission at 570 nm), and ${}^4F_{9/2} \rightarrow {}^6H_{11/2}$ (red emission at 663 nm) transitions of trivalent dysprosium ions are observed for all studied glasses. It was stated that the intensity of visible emission originating from transitions of both

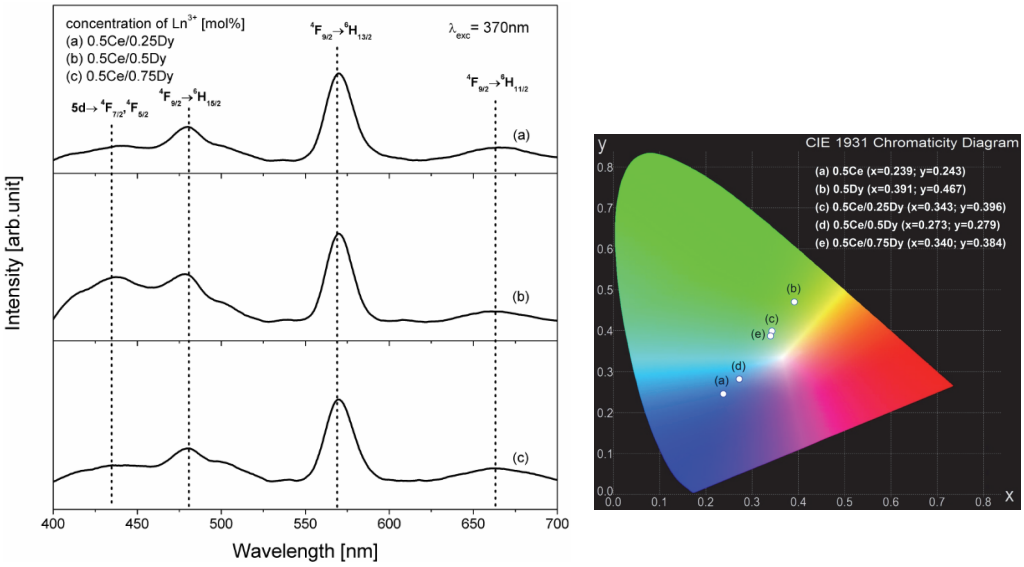

Fig. 5. Emission spectra and CIE chromaticity diagram of germanate glasses co-doped with Ce^{3+} and Dy^{3+}.

ions (Ce^{3+} and Dy^{3+}) significantly changes when the molar content of dysprosium ions increases. Furthermore, the CIE chromaticity coordinates for all glasses co-doped with Ce^{3+} and Dy^{3+} ions show that the glass hosts with these rare earth ions are better than glasses co-doped with Ce^{3+}/Pr^{3+} and Ce^{3+}/Tb^{3+} as materials for emitting white light. In the case of glasses doubly doped with 0.5 mol% Ce^{3+} and 0.75 mol% Dy^{3+}, the chromaticity coordinates are located the nearest the white region in the CIE diagram ($x = 0.340$, $y = 0.384$). On the other hand, the results obtained for silicate glasses by He *et al*. [29] indicate that for Ce^{3+} and Dy^{3+} co-doped glasses, the combination of Ce^{3+} blue and Dy^{3+} blue and yellow can achieve the white light when excited with 327 nm. The exhibits of pure white with CIE coordinates of (0.308, 0.280) for 0.5 mol% Dy^{3+} and 0.5 mol% Ce^{3+} were obtained. Our previous work confirms that white light can be generated by the appropriate combination of blue and yellow light when barium gallo -germanate glass systems were doubly doped with Ce^{3+} and Dy^{3+} ions. The typical white light emission can be achieved in our doubly doped barium gallo-germanate glasses. The chromaticity coordinates of 0.5Dy/0.75Ce co-doped glass system are close to the white light point (0.333, 0.333) [30]. Our results confirm that the CIE coordinates can be tuned by changing the Ce^{3+} and Dy^{3+} concentration.

4. Conclusion

The optical properties of Ce^{3+}/Pr^{3+}, Ce^{3+}/Tb^{3+} and Ce^{3+}/Dy^{3+} ions in germanate glasses were examined in detail. Luminescence spectra were recorded and analyzed. The obtained experimental results indicate that the energy transfer between Ce^{3+} and Ln^{3+} ions (Ln = Tb, Dy, Pr) is possible. It was observed that luminescence bands corresponding to characteristic transitions of Ln^{3+} and Ce^{3+} ions are present in the emission spectra measured under direct excitation of cerium ions. Furthermore, the influence of concentration of rare earth ions on luminescence properties of glasses was examined. From the emission spectra, the Commission Internationale de I'Eclairage (CIE) chromaticity coordinates (x, y) were calculated. Moreover, it has been proved that our glass system exhibits nearly warm or cool white emission originating from the simultaneous generation of several bands of Ce^{3+} and Ln^{3+} (Ln = Tb, Dy, Pr) under the UV-visible light excitation.

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