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LUMINESCENT PROPERTIES OF RARE EARTH DOPED ZnO-B_2O_3-P_2O_5 GLASSES

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ABSTRACT

ZnO-B_2O_3-P_2O_5 (ZBP) glasses are a comparatively new material with a wide application potential for some optic devices. This is so because they are an excellent host matrix for different rear earths, especially for samarium ions, which in turn leads to intense luminescence in the visible region. Based on some previous studies of the structure, chemical durability, thermal stability, physical and optical properties it is found that this matrix is not only a good candidate as a host material for different RE ions but it is also applicable in sensing and valuable documents protection.

The present communication reports results referring to synthesis of new rare earth (Eu, Gd, Tb, Nd) doped and co-doped with Gd/Nd, Gd/Sm, Nd/Eu, Nd/Sm, Tb/Sm ZBP glasses and study of their absorption and fluorescent properties. The synthesis is performed by the conventional melt quenching method at 950^{o}C in a muffle furnace. It is found that all synthesized glasses are homogeneous (with no gases inclusion), while some of them are fully transparent. The luminescent analysis reveals strong fluorescence in the visible and near infra-red region for different doping ions. Rare earth co-doping widens the potential applications of these glasses. ZBPs are also found a good host matrix for laser-active ions.

Keywords: rare earth, zinc borophosphate, luminescence.

INTRODUCTION

The glasses doped with rare earth (RE) elements are widely used in different fields such as fluorescent lamps, displays, lasers and medical diagnostic devices, due to their luminescent properties. Inorganic glasses have been used as optical materials for a long time due mainly to their high transparency in the visible and adjacent, ultraviolet (UV) and near-infrared (NIR) ranges. However, they do not exhibit electronic transitions in this region. Controlled introduction of optically active ions is applied to provide such transitions. Thus in turn determines the optical properties of RE ion-doped inorganic glasses of importance in the field of materials physics [3].

Within the optics industry, RE elements are quickly growing in importance. Lanthanum is used in many high index glasses. A high index glass, when combined with other glass materials, improves the dispersion, which provides efficiency increase and image quality improvement of many achromat and imaging lenses. Cerium can be found in some of the polishing compounds used in the manufacturing process of optical glasses. A number of other optical components and electro-optical devices like night-vision goggles and imaging sensors are also affected. They rely on RE elements including lanthanum, gadolinium, and yttrium [4].

When incorporated in crystalline or amorphous hosts, RE is present in the form of 3^+, or occasionally 2^+ ions. The 3^+ ions exhibit intense narrow-band intra-4f luminescence in a wide variety of hosts, while the shielding provided by the 5s2 and 5p6 electrons indicates that rare-earth radiative transitions in solid hosts resemble those of the free ions. The electron–phonon coupling is also weak. Although some of the divalent species exhibit luminescence (principally samarium and europium), it is the trivalent ions that are of most interest.

The tendency of RE ions to ion–ion interactions is their characteristic feature. Ions of the same RE (as is the case in clustered material) or different ions (as in the sensitization of one rare-earth ion by another) can participate. A loss mechanism describes the former case. It refers to increase of the non-radiative decay channels or luminescence from unwanted transitions [5].

Gadolinium (Gd^{3+}) is used as a dopant of the phosphate system because it emits narrowband ultraviolet B (UVB) radiation needed to treat skin diseases. However, the problem is that this emission intensity is very low. This can affect the general performance and the life span of the UV phototherapy lamps. UVB emission of Gd^{3+} can be improved by co-doping using other rare earth ions such as praseodymium (Pr^{3+}), cerium (Ce^{3+}), terbium (Tb^{3+}), and europium (Eu^{3+}) that can absorb excitation in the high energy region of the electromagnetic spectrum and transfer it to Gd^{3+} by a down-conversion process [6]. Wegh et al. [7] are the first to report visible luminescence from trivalent gadolinium at 600 nm. This paper reports the luminescent properties of RE doped $ZnO-B_2O_3-P_2O_5$ glasses synthesized by the conventional melting quenching method using the information previously obtained on the host material potential.

EXPERIMENTAL

ZnO, B_2O_3, P_2O_5 and R_2O_3 (R = Sm, Tb, Eu, Nd, Gd) of an analytical grade (99.999 % pure) were used in the preparation of the glasses. The batch compositions (in mol %) for the present work were represented as (72.31-x) ZnO + 18 B_2O_3 +9.69 P_2O_5 + x R_2O_3 (0.25 - 0.5) (the system was referred as ZBP:RE). 10 g of each system (Table 1) were weighed accurately on an electronic bal-

Table 1. ZBP glasses content

Sample	Content, mol %							
	ZnO	P_2O_5	B_2O_3	Sm_2O_3	Eu_2O_3	TbF_3	Nd_2O_3	Gd_2O_3
1	71.81	9.69	18.0	0.5	-	-	-	-
2	71.81	9.69	18.0	-	0.5	-	-	-
3	72.06	9.69	18.0	-	0.25	-	-	-
4	71.81	9.69	18.0	-	-	0.5	-	-
5	71.81	9.69	18.0	-	-	-	0.5	-
6	71.81	9.69	18.0	-	-	-	-	0.5
7	71.81	9.69	18.0	0.25	-	-	-	0.25
8	71.81	9.69	18.0	0.25	-	-	0.25	-
9	71.81	9.69	18.0	-	0.25	-	0.25	-

Table 2. Thermal, physical and chemical properties of ZBP glasses

Property	Values
Tg, ^oC	522 - 552
ρ, g/cm^3	1.887 - 1.888
V_m, cm^3	45.83 - 47.40
Dr, $(mg/cm^2.min).10^{-6}$ pH=1.2	360 - 450
Dr, $(mg/cm^2.min).10^{-6}$ pH=1.5	21.6 - 25
Dr, $(mg/cm^2.min).10^{-6}$ pH=7, 10 and 12	8.33 -10

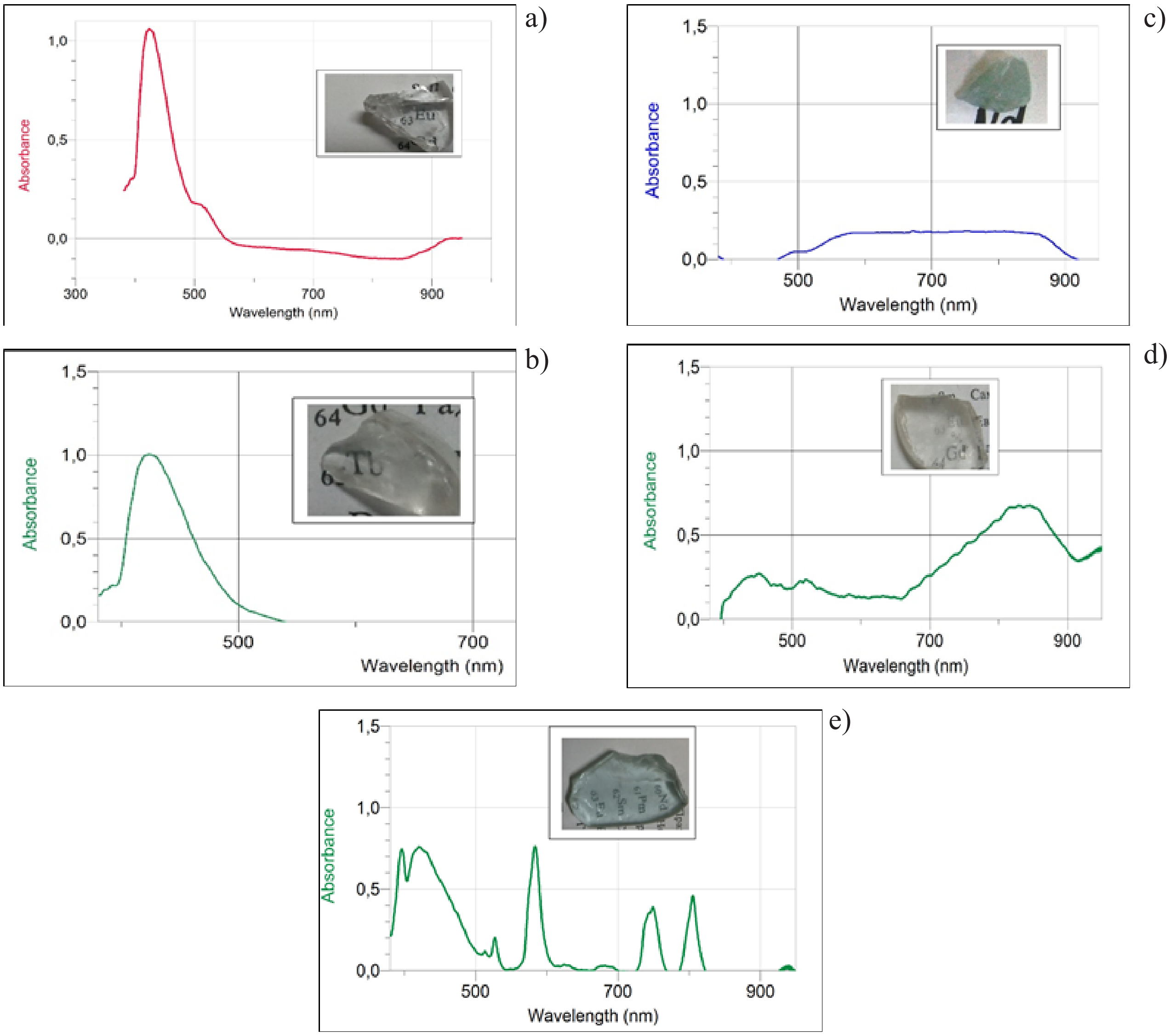

Fig. 1. Absorption spectra of a) ZBP:Eu; b) ZBP:Tb; c) ZBP:Nd; d) ZBP:Gd; e) ZBP:Nd, Eu.

ance prior to mixing and grinding to a fine powder. The batches were placed in alumina crucibles and melted in a muffle furnace in air atmosphere for 3 h at 950°C. The melt was then quenched on a graphite plate. The glasses were annealed for 2 h at 250°C to remove thermal strains and stress, and then cooled down to room temperature using a muffle furnace. The prepared glass samples were highly transparent and of a good optical quality. The density of the glass samples was measured by employing the Archimedes principle using deionized water as an immersion liquid.

Differential scanning calorimetry (DSC) was performed with a Thermal Analysis TA Instrument DSC Q100 with an attached fast air cooling system (FACS) at heating rates of 2 K/min, a period of 60 s and ±1 amplitude. The optical absorption and photoluminescence spectra were recorded using Go Direct SpectroVis Plus spectrophotometer with two excitation sources (λ = 405 nm and 500 nm) in the wavelength range of 380 nm - 950 nm.

RESULTS AND DISCUSSION

Physical and chemical properties

The structural properties of the glass matrix are studied in detail [1, 2]. Table 2 lists ZBP glasses general physical and chemical properties. The results show a high glass transition temperature (T_g) which is indicative of these samples thermal stability. On the other hand, the chemical stability is characterized by the rate of decomposition (D_r). The latter values show that ZBP glasses are less resistant in an acidic medium, while they are sustainable in neutral and alkaline media.

Absorption spectra

The optical absorption spectra are recorded in the range of 380nm-950nm. Those of ZBP glasses doped and co-doped with different RE elements are present in Fig. 1(a-e). The Tb^{3+} and Eu^{3+} doped glasses show full absorbance in the range of 403 nm - 461nm. These samples are fully transparent, uncolored and homogenous as can be seen on Figs. 1(a) and 1(b). Nd^{3+} doped glass (Fig. 1(c)) is colored and not transparent when compared to Gd^{3+}:ZBP. On the Fig. 1(d) shows less absorbance at the near infrared wavelengths. The glass with Nd and Eu dopants gives narrow absorption peaks because of the co-doping (Fig. 1(e)). This glass is transparent and less colored due to presence of Nd^{3+} in the structure.

Luminescence spectra

The fluorescent spectra of the samples are measured at 405 nm and 500 nm. The spectra are recorded in the range of 380 nm - 950 nm. Most of the samples show visible fluorescence when excited at 405 nm. ZBP:Tb (sample 3) is the only exception. The results are presented in Figs. 2 and 3.

Two samples of ZBP:Eu are presented in Fig. 2. It

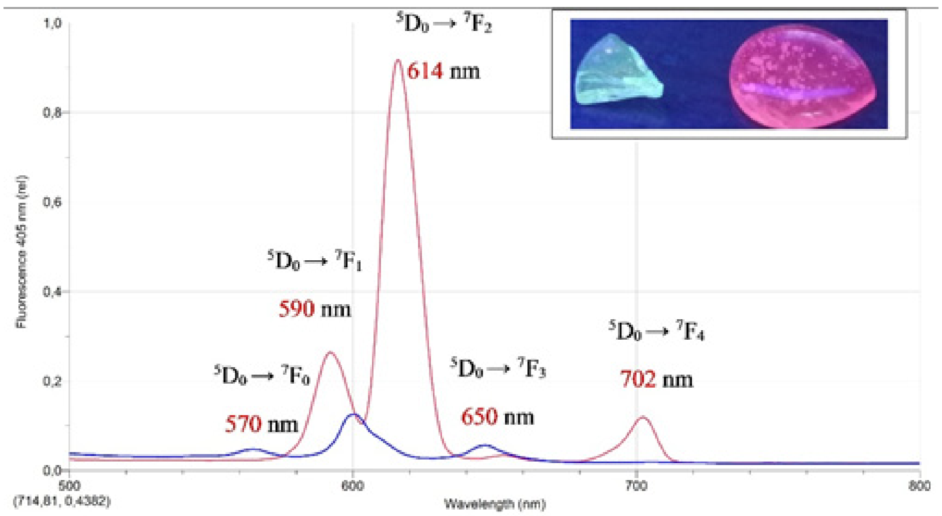

Fig. 2. Fluorescence spectra of ZBP:Eu glasses at λ_{exc} = 405 nm.

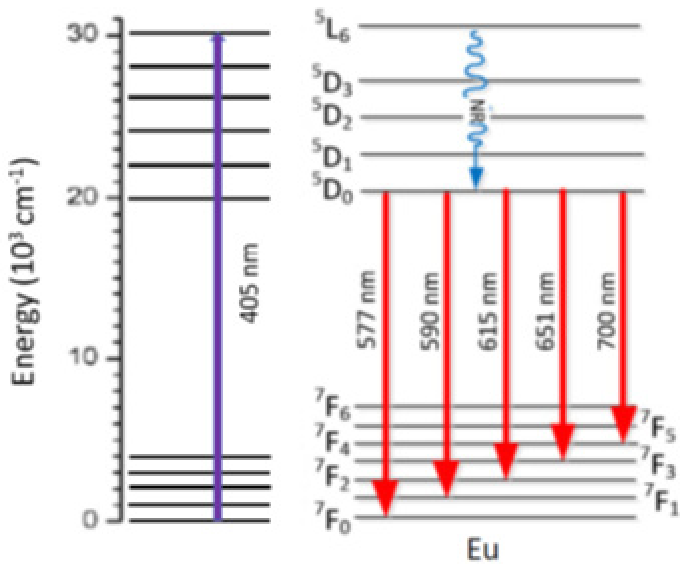

Fig. 3. An energy level diagram of Eu^{3+}.

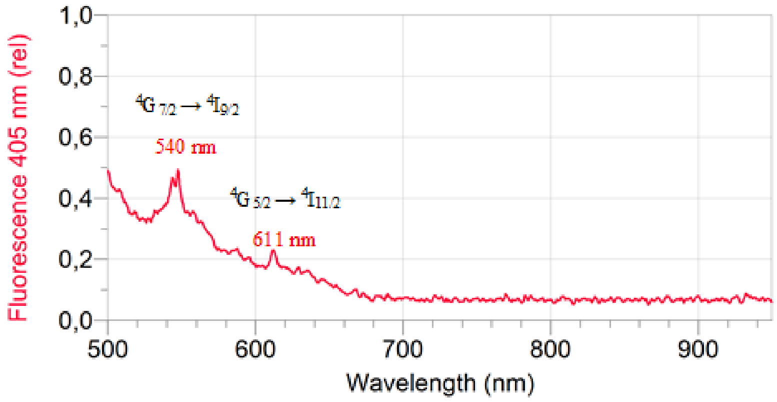

Fig. 4. A fluorescent spectrum of ZBP:Nd glass at λ_{exc} = 405 nm.

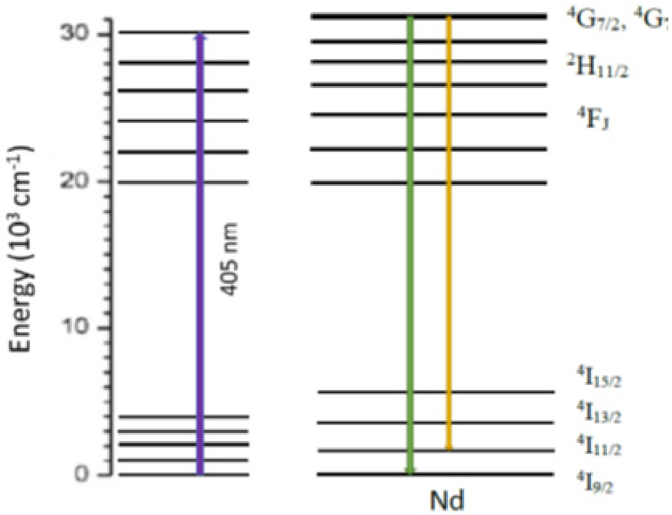

Fig. 5. An energy level diagram of Nd^{3+}.

is evident that these glass samples emit different wavelength by excitation with 405 nm. This is attributed to Eu^{3+} (0.25 mol % or 0.5 mol %) concentration in the samples. The glass containing a higher concentration shows more intensive peaks in the orange–red range. These peaks refer to the electronic transitions from the excited $^5D_1$ and $^5D_0$ levels to ^7F_J (J = 0 - 6) levels (Fig. 3). The strong emission peak at 610nm-620 nm shown in Fig. 2 can be ascribed to the hypersensitive electric dipole $^5D_0 \rightarrow ^7F_2$ transition [8].

The emission peak at 590 nm - 600 nm is due to the magnetic dipole transition of $^5D_0 \rightarrow ^5F_1$, which is lower than that that referring to $^5D_0 \rightarrow ^7F_2$. This indicates that Eu^{3+} ions are located at the non-inversion symmetric sites.

Low intensive fluorescent peaks are observed in case of ZBP:Nd glass (Fig. 4).

Nd^{3+} emitted in the visible spectrum through excitation at 405 nm at 540 nm (green) and 611 nm (orange) are due to transitions from ($^4G_{5/2}$ + $^4G_{7/2}$) and $^4G_{7/2}$ to ^4I_J multiplets (Fig. 5) [9, 10].

Fig. 6 presents Pl emission spectra of ZBP glass doped with Gd^{3+}. They are obtained at excitation at 405 nm and 500 nm. Gd^{3+} emission due to $^6P_{7/2} \rightarrow ^8S_{7/2}$ transition is well known and is situated at ca 312 nm. The same is valid for $^6G_j \rightarrow ^8S_{7/2}$ emission at 200 nm. These two emissions are in the ultraviolet region [7, 11]. It is possible to expect visible emission in orange/red due to ^6G_J — ^6P_J transition followed by emission of a second photon from the ^6P_J level. This is in correspondence with the energy level diagram (Fig. 7) of Gd^{3+}.

On the Fig. 6 This visible emission is seen in Fig. 6.

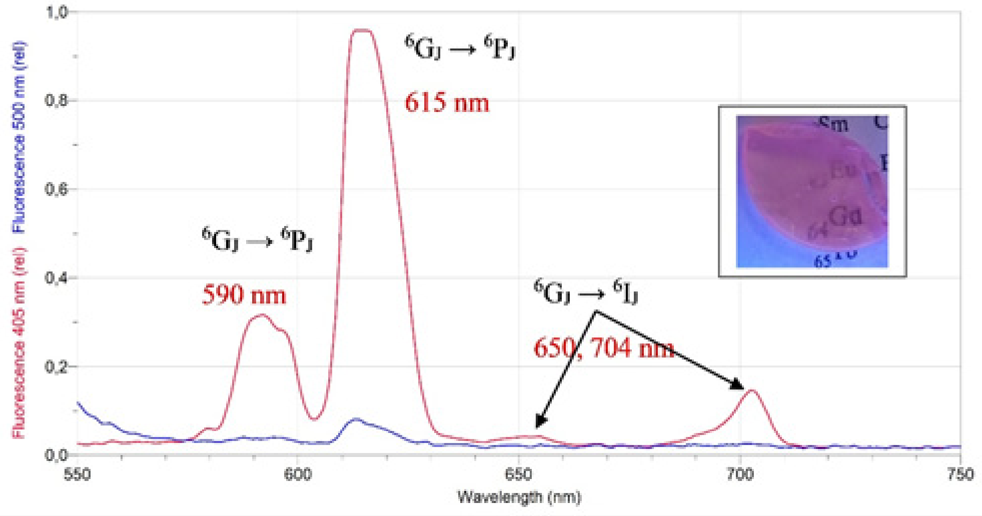

Fig. 6. This visible emission is seen in Fig. 6. It is of a high intensity at λ_{exc} = 405 nm. The intensity at λ_{exc} = 500 nm is low.

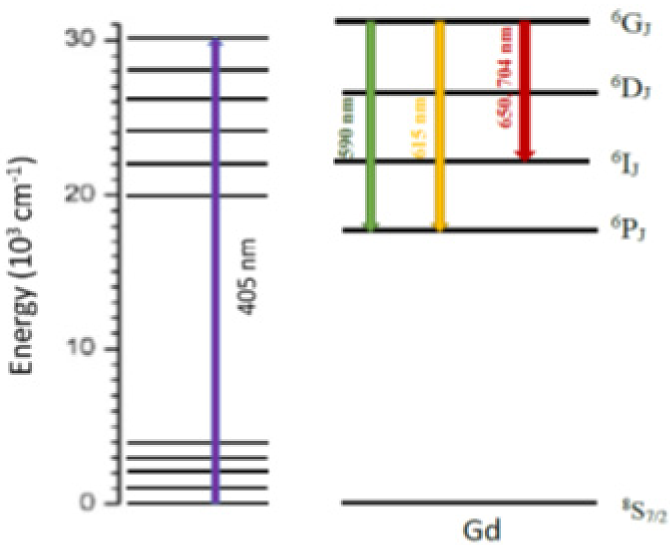

Fig. 7. An energy level diagram of Gd^{3+}.

It is of a high intensity at λ_{exc} = 405 nm. The intensity at λ_{exc} = 500 nm is low. The effect of ZBP glasses co-doping can be illustrated by Figs. 8 and 9.

The emission bands at 580 nm, 600 nm, and 650 nm can be attributed to Sm^{3+}: $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$, $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transitions in absence of Gd^{3+} and Nd^{3+} peaks. The emission intensities of Sm^{3+} are high due to co-doping as evident from Fig. 8. Gd^{3+} and Nd^{3+} change the shape of Sm^{3+} peaks.

The emission spectrum of ZBP:Nd, Eu glass is given in Fig. 9. The co-doping of this sample does not change the PL spectrum. As evident, the peaks refer to Eu^{3+} in the orange-red region.

CONCLUSIONS

Zinc-boron-phosphate glasses modified by different rare earth elements are synthesized. Most of the glass samples are transparent and homogeneous with no gasses inclusion. The results of the emission spectra show a potential application in optics and laser technology due to the high photoluminescence intensity of the doped or co-doped glass matrix. In addition, ZBP is an excellent host material for laser active ions.

Acknowledgements

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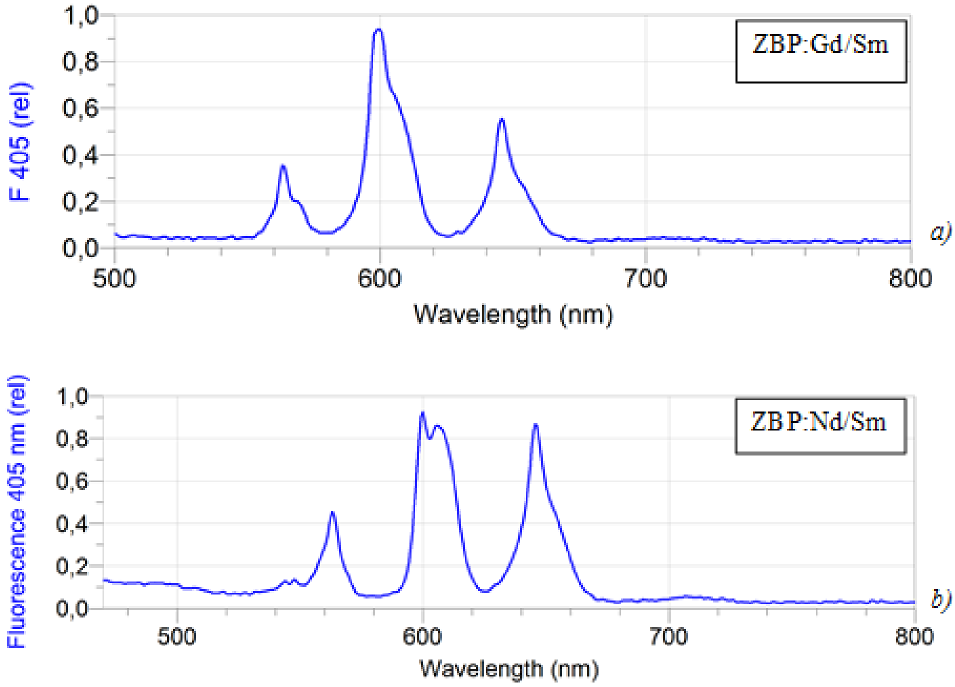

Fig. 8. A fluorescent spectrum of a) ZBP:Gd, Sm and b) ZBP:Nd,Sm.

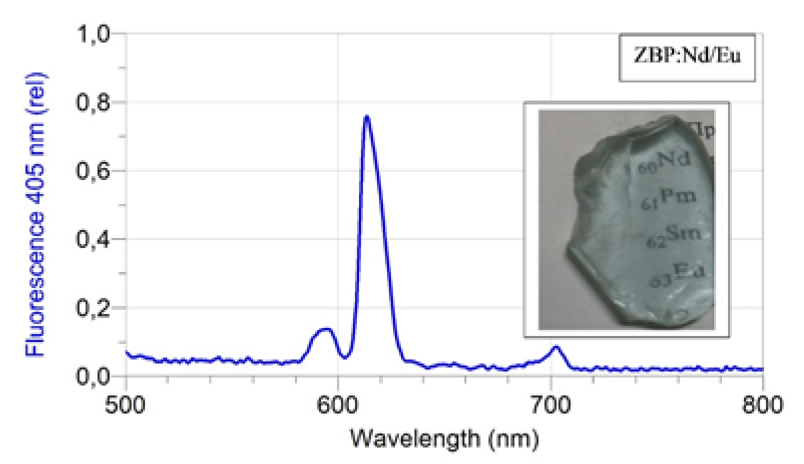

Fig. 9. A fluorescent spectrum of ZBP:Nd, Eu.

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