Bulgarian Chemical Communications, Volume 47, Special Issue B (pp. 9–14) 2015

Analysis of fluorescence spectra of oxyfluoride compositions doped with samarium oxide (Sm_2O_3) and samarium fluoride (SmF_3)

T. Pashova[1]*, I. Kostova[2,3], T. Eftimov[1], D. Tonchev[2,3]

[1] *Faculty of Physics, Paisii Hilendarski University of Plovdiv, 24 Tsar Asen Str., BG-4000 Plovdiv, Bulgaria*
[2] *Faculty of Chemistry, Paisii Hilendarski University of Plovdiv, 24 Tsar Asen Str., BG-4000 Plovdiv, Bulgaria*
[3] *Laboratory for Electronic and Optic Materials, University of Saskachewan, 54 College Dr, Saskatoon, Canada*

ZnO-ZnF_2-P_2O_5-B_2O_3 compositions, doped with a varying quantity of samarium oxide (Sm_2O_3) and samarium fluoride (SmF_3) have been synthesized. The thermal properties of the obtained compositions have been measured using DSC analysis. Fluorescence spectra measured at different excitation wavelengths are shown. The fluorescence excitation efficiency for varying quantity of Samarium in the samples and the pumping wavelength has been studied. With optical pumping in the 370–490 nm range fluorescence spectra indicating the presence of Sm^{3+} have been obtained. The widening of the pumping range to higher wavelengths a new fluorescence peak was observed. The range in which the peak is observed was established from the performed analysis and the excitation wavelength of maximum efficiency was determined.

Key words: samarium, fluorescence, emission spectra, optical materials

INTRODUCTION

The interest towards luminescence properties of novel non-organic materials with rare earth elements has grown considerably during the last several years because of their possible applications in laser technologies, optoelectronics, eco-technologies and other developing areas [1].

This paper presents the optical properties of ZnO-ZnF_2-P_2O_5-B_2O_3: Sm_2O_3 and SmF_3 compositions. Several samples with this composition have been synthesized differing by the content of Sm_2O_3 and SmF_3, for $x = 0.025, 0.075, 0.125, 0.175$, and 0.25 mol%, correspondingly. After the samples were obtained their thermal properties were studied using DSC analysis, as well as their optical properties by excitation at the following wavelengths: 370, 395, 405, 410, 415, 425, 435, 450, 470, 490, 505, 515, 525, 535, 565, 572, 590, 605, 615, 632, 660, and 700 nm.

Spectral analysis shows that with excitation in the 370 to 500 nm range four characteristic peaks for Sm^{3+} [2, 3]. The study of the 500-600 nm excitation range exhibits a new fluorescence peak in the 670 - 680 nm range which suggests a Sm^{2+} ion [4].

EXPERIMENTAL PART

Synthesis

For the synthesis of ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 glasses the following reagents have been used: ZnO (Alfa Aesar, 99.9%), ZnF_2 (Alfa Aesar, 99%), P_2O_5 (Alfa Aesar, 98%), B_2O_3 (Alfa Aesar, 99.98%), Sm_2O_3 (Alfa Aesar, 99.99%), SmF_3 (Alfa Aesar, 99.99%). For the purpose of complete homogenization of the mixture, the synthesis was performed in a zirconium furnace Zircar 110 (temperature range from 0 to 1750°C) at a temperature of 950°C for a period of 3 h. The samples were cast at 1200°C and cooled at room temperature. Five compositions with different content of Sm_2O_3 and SmF_3 were obtained as is shown in Table 1.

Table 1. ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 copositions

Sample No	**ZnO,** mol%	**ZnF_2,** mol%	**P_2O_5,** mol%	**B_2O_3,** mol%	**Sm_2O_3,** mol%	**SmF_3,** mol%
1	36.23	36.23	9.69	18.00	0.025	0.025
2	36.13	36.13	9.69	18.00	0.075	0.075
3	36.03	36.03	9.69	18.00	0.125	0.125
4	35.93	35.93	9.69	18.00	0.175	0.175
5	35.78	35.78	9.69	18.00	0.25	0.25

The synthesis of the new compositions shows the optimum content of rare earth elements in so much as transparency is concerned. It is somewhat surprising that the optimum content is 0.125 mol% which neither the minimum, nor the maximum quantity of both dopants (sample 3). This is shown in Fig. 1. It can be seen that sample 3 is a transparent and gas bubbles free.

* To whom all correspondence should be sent:
teodora_pashova@abv.bg

Fig. 1. A picture of the tested compositions.

Differential scanning calorimetry

The thermal properties of the obtained samples were measured using a Differential scanning calorimeter (TA Instrument DSC Q100) with a fast cooling system (FACS) for a heating rate of 2 K/min and modulation period of 60 s. The results of the analysis are processed using the TA Instruments Universal Analysis (UA) software.

Sample preparation

The glass samples obtained are in the form of round plates having a diameter of about 1 cm. To perform the optical measurements, a piece of the plate is taken and is ground to a fine homogeneous powder. A bowl and a pestle are used for the purpose.

Experimental optical set up

Figure 2 represents schematically the experimental set-up for the study of the optical properties of samples of the ZnO-ZnF_2-P_2O_5-B_2O_3:Sm_2O_3 and the SmF_3 compositions.

Light emitting diodes (LEDs) emitting in the spectral range from 370 nm to 700 nm were used to

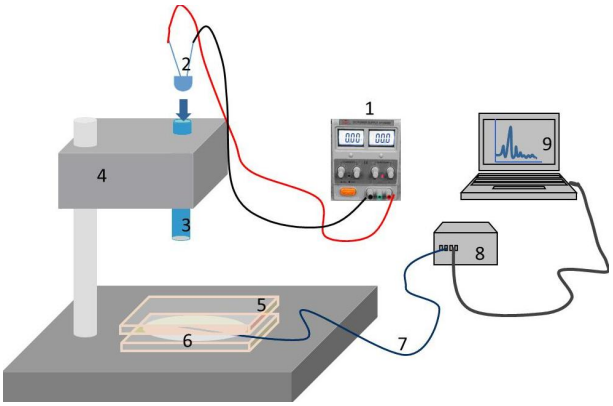

Fig. 2. Experimental set up: 1 – power supply, 2 – light source, 3 – a lens collimating system, 4 – holder of the light source, 5 – fused silica plates, 6 – powder sample of the studied material, 7 – a detecting optical fiber, 8 – Spectrometer, 9 – read and write software.

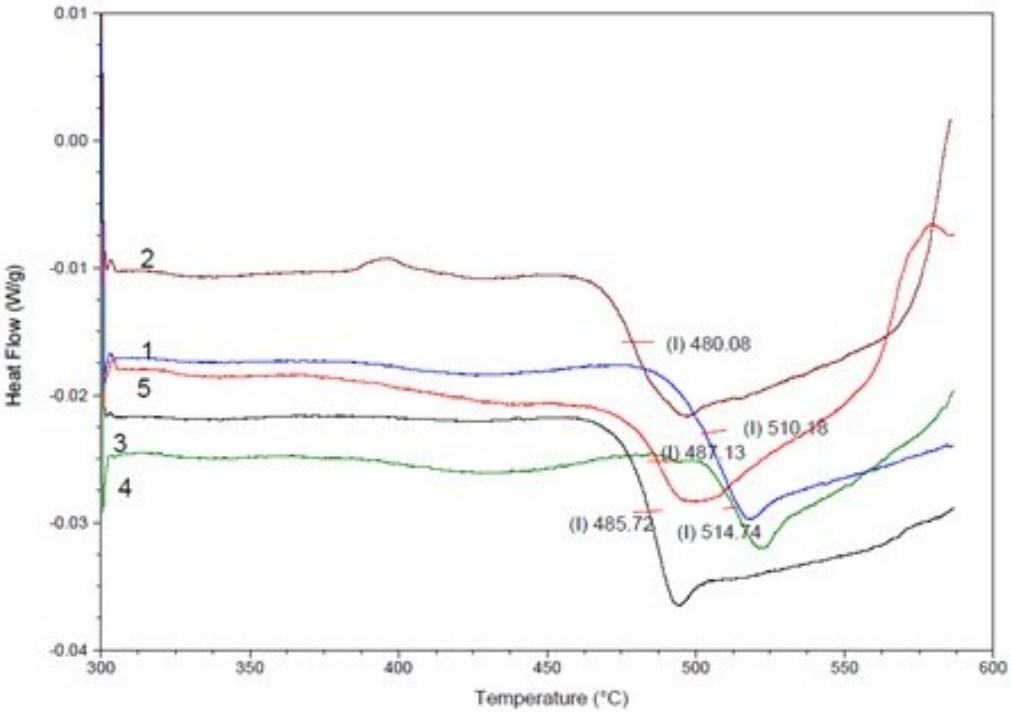

Fig. 3. Dependence of T_g on the content of Sm_2O_3 and SmF_3 in the composition.

directly excite the sample. A lens system was used to collimate the divergent light from the LEDs. The output light spot has a diameter of about 1–2 mm. The glass plates were used to position the samples and the detecting fiber and to ensure a uniform thickness of the layer. The detecting system consists of a detecting optical fiber (7), a fiber-optic spectrometer (8) (AvaSpec) in the 200 - 1160 nm spectral range, powered by a computer via a USB port, and using a specialized software AvaSoft-basic (9).

The purpose of the experimental set-up is to check the excitation efficiency of the ZnO-ZnF_2-P_2O_5-B_2O_3:Sm_2O_3 and SmF_3 compositions; to check if the quantity of Sm_2O_3 and SmF_3 produces an effect on the emission fluorescence spectra.

RESULTS AND ANALYSIS

Thermal analysis

The data from the DSC are presented in Fig. 3. As is seen, the glass transition temperature (T_g) is in the 485 to 514°C range and no linear dependence is observed on the content of the rare earth ions (Sm_2O_3 and SmF_3) in the composition.

Fluorescence analysis

Fluorescence spectra are taken after excitation of each of the samples with a collection of 22 LEDs in the range from 370 nm to 700 nm. The data obtained are summarized in three sub-ranges, namely: (1) [370–490 nm]; (2) [505–590 nm]; (3) [605–700 nm].

The resulting fluorescence spectra are presented after normalization to maximum intensity of the scattered excitation light.

1. Spectra in the 370 to 490 nm. Experimental data are shown graphically as presented in Fig. 4. A strong fluorescence typical for the Sm ions of third valency is seen from the graphs. Four peaks are observed at 564, 600, 645, and 704 nm [2, 3, 5].

The most intensive fluorescence spectrum is for excitation at 405 nm. As is seen form the graph, there is a tendency for the peaks to diminish in intensity as the excitation wavelength increases. The deviations are due to the different optical power launched in the samples under study and the imperfections in the experimental set up as the degree of collimation of the excitation light of LEDs, positioning of detecting optical fiber, stability of power unit and etc.

2. Spectra in the 505 to 590 nm range. Fig. 5 represents the fluorescence spectra in the 505 to 590 nm range. It is seen that for an excitation of 505 nm a fluorescence peak at 650 nm is observed although weak. It is further noticed that with the increase of the excitation wavelength a new peak around 670-680 nm appears, which is not characteristic for the Sm ion of third valency.

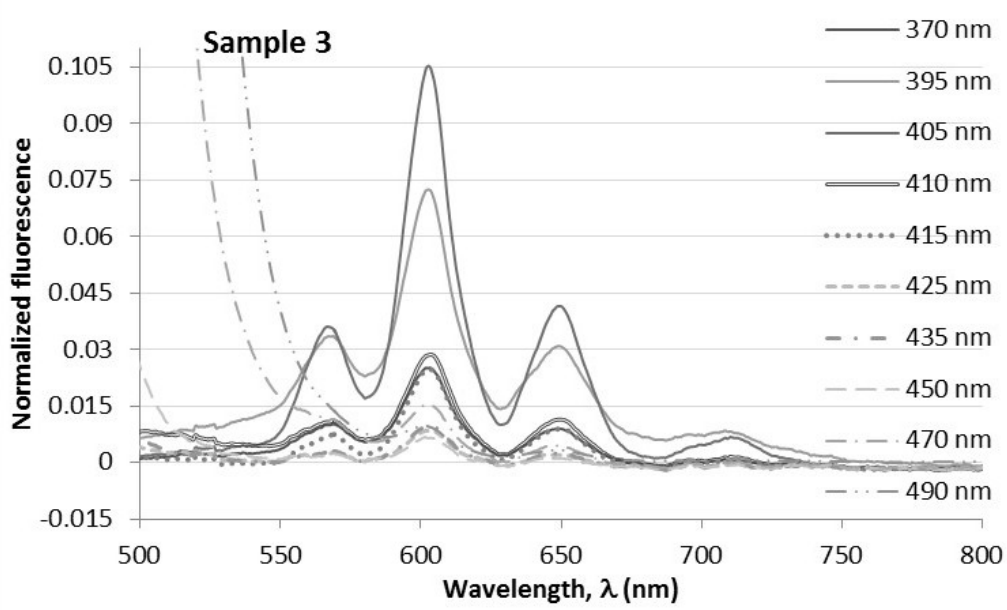

Fig. 4. Fluorescence spectra of ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 glasses normalized to the scattered excitation maximum intensity for excitation in the 370 nm - 490 nm range.

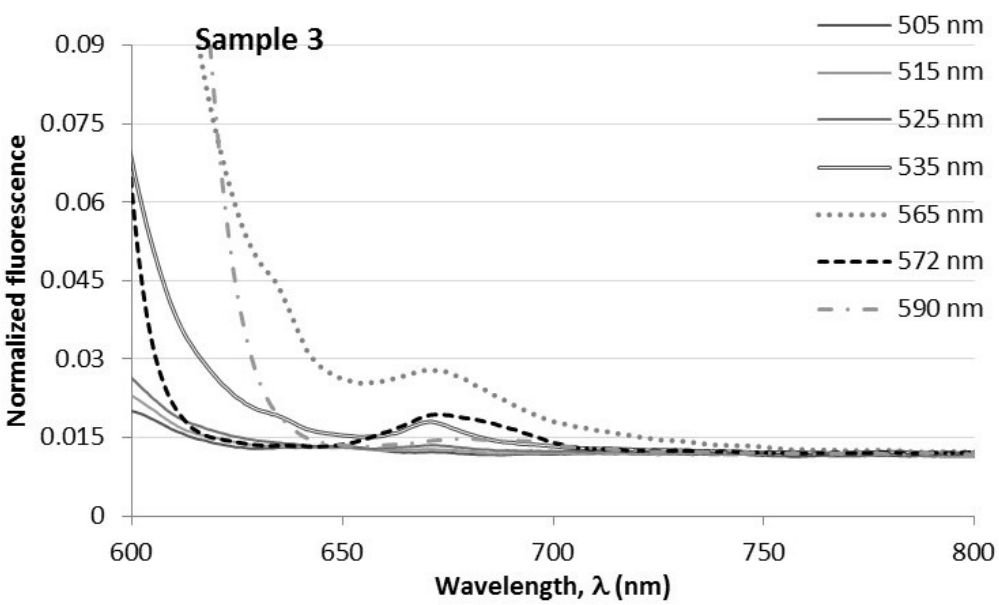

Fig. 5. Normalized fluorescence spectra of ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 glasses for excitation wavelengths in the 505 nm to 590 nm range.

From the literature it is known that this wavelength is situated in the region characterizing the fluorescence of the Sm ions from the second valency [4].

The new peak is most intense upon excitation of 565 nm, but the well-formed at 572 nm.

3. Spectra in the 605 to 700 nm range. The plots in Fig. 6 show that fluorescence is very weak in 605 to 700 nm range.

As is evidenced from Fig. 7, the most interesting range is the one from 370 nm to 500 nm.

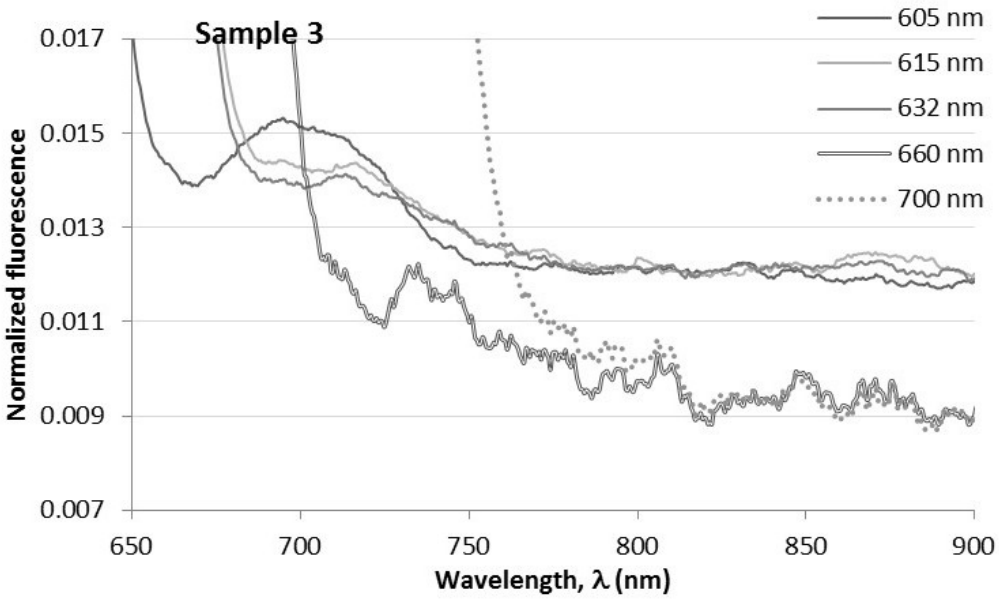

Fig. 6. Normalized fluorescence spectra of ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 glasses for excitation wavelengths in the 605 nm to 700 nm range.

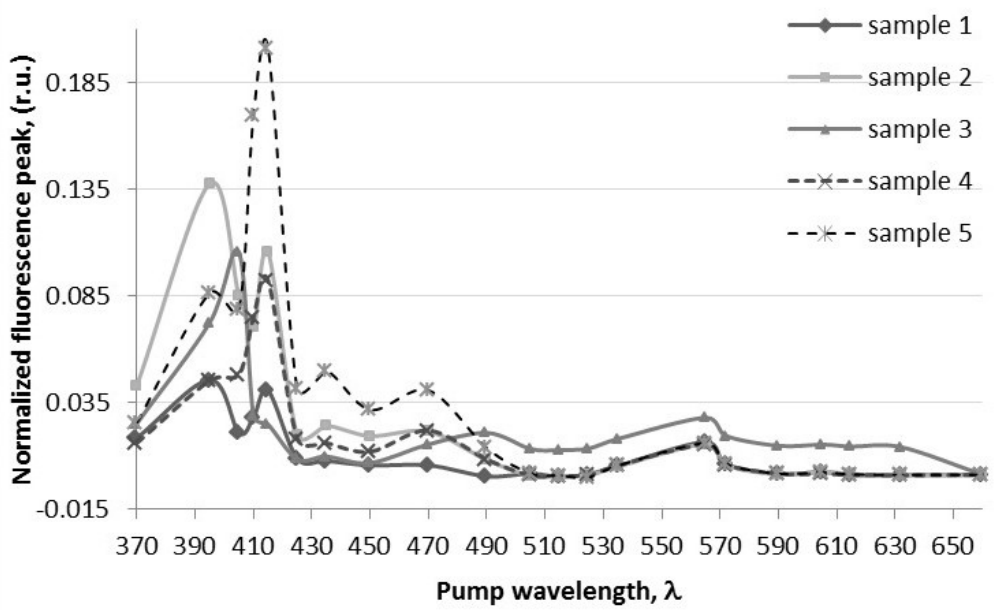

Fig. 7. Plot of the maximum of the fluorescence peak vs. the excitation wavelength.

In the opaque compositions containing Sm_2O_3 and SmF_3 under 0.12 mol%, a competition between the pumping sources at 395 nm and 415 nm causing a maximum fluorescence is observed. This competition is overcome for a content of Sm_2O_3 and SmF_3 above 0.13 mol%. This means that with the increase of the concentration of the rare earth ion in the composition the wavelength of the most efficient excitation source increases as well.

CONCLUSIONS

Five samples ZnO-ZnF_2-P_2O_5-B_2O_3-Sm_2O_3-SmF_3 with different content of Sm_2O_3 and SmF_3 have been synthesized. From the measurements made and the analyses performed, the following conclusions can be drawn::

1. The range of glass transition temperature is $T_g = [485–514]$ °C;
2. There is no linear dependence between T_g and the content of the rare earth ions (Sm_2O_3 and SmF_3) in the composition;
3. The intensity of the fluorescence spectrum of the synthesized compounds depends on the content of Sm_2O_3 and SmF_3;
4. The most efficient excitation is in the 390-420 nm range and depends on the concentration of the rare-earth ion.

REFERENCES

[1] Y. Deng, Sh. Yi, Y. Wang and J. Xian, *Opt. Mater.* **36**, 1378–1383 (2014).

[2] M. Jayasimhadri, L. R. Moorthy, S. A. Saleem and R. V. S. S. Ravikumar, *Spectrochim. Acta A* **64**, 939–944 (2006).

[3] T. Pashova, I. Kostova, T. Eftimov, D. Tonchev and G. Patronov, *Fundamental Sciences and Applications* **18**, 137–142 (2012).

[4] Y. Huang, K. Jang, W. Zhao, E. Cho, H. S. Lee, X. Wang, D. Qin, Y. Zhang, Ch. Jiang and H. J. Seo, *J. Solid State Chem.* **180**, 3325–3332 (2007).

[5] S. Arunkumar and K. Marimuthu, *J. Alloy Compd.* **565**, 104–114 (2013).

АНАЛИЗ НА ФЛУОРЕСЦЕНТНИ СПЕКТРИ НА ОКСИФЛУОРИДНИ КОМПОЗИЦИИ, ЛЕГИРАНИ СЪС САМАРИЕВ ОКИС (Sm_2O_3) И САМАРИЕВ ФЛУОРИД (SmF_3)

Т. Пашова[1], И. Костова[2], Т. Ефтимов[1], Д. Тончев[2]

[1] *Физически факултет, Пловдивски университет "Паисий Хилендарски", ул. "Цар Асен" №24, 4000 Пловдив, България*
[2] *Химически факултет, Пловдивски университет "Паисий Хилендарски", ул. "Цар Асен" №24, 4000 Пловдив, България*

(Резюме)

Синтезирани са $ZnO\text{-}ZnF_2\text{-}P_2O_5\text{-}B_2O_3$ стъкла, легирани с различно количество самариев окис (Sm_2O_3) и самариев флуорид (SmF_3). Представени са флуоресцентните спектри, снети за различни дължини на напомпване. Изследвана е ефективността на възбуждане на флуоресценция в зависимост от количественото съдържание на самарий в пробите и промяна в дължината на възбуждащия източник. При оптично напомпване в диапазона 370–490 nm се получават флуоресцентни спектри, характеризиращи наличие на Sm^{3+}. При разширяване на областта на напомпване, към по-големите дължини на вълните, се наблюдава поява на нов неизследван от нас флуоресцентен пик. От проведения анализ се установи областта, в която се получава пика и е определена най-ефективната дължина на възбуждане.