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OPTICAL PROPERTIES OF SAMARIUM-DOPED GLASSES IN THE SYSTEM $ZnO\text{-}B_2O_3\text{-}P_2O_5$

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Abstract

In this paper the optical properties of Samarium doped glasses were studied by fluorescence spectroscopy. The ternary glass system $ZnO\text{-}B_2O_3\text{-}P_2O_5$ was synthesized with different molar ratios of the doping component. The binary systems $ZnO\text{-}B_2O_3$, $ZnO\text{-}P_2O_5$, $B_2O_3\text{-}P_2O_5$ and the subsolidus phase equilibrium in the $ZnO\text{-}B_2O_3\text{-}P_2O_5$ system are discussed.

Key words: *Sm^{2+} doped borophosphate glasses, Fluorescence spectroscopy, Luminous Down-Shifting materials*

1 INTRODUCTION

Luminescent materials are substances which convert an incident energy input into the emission of electromagnetic waves in the ultraviolet (UV), visible (VIS) or infrared (IR) regions of the spectrum. Depending on the excitation the luminescence can be divided into photoluminescence, radioluminescence, cathodluminescence, electroluminescence, thermoluminescence and optically/photo-simulated luminescence (Edgar 2007).

The luminescence properties of rare earth doted materials have been extensively studied because of their large range of applications. As described by Tonchev et al this materials are used in sensors, lasers and different optical equipment. Other applications are the measurement of very high doses in synchrotron-based techniques for cancer treatment such as Microbeam Radiation Therapy (MRT) and also in some radiation detection systems (D. Tonchev 2012). Ln-doted glasses have been used also as concentrators in the solar cells for enhancing their efficiency. This kind of materials has a capability to convert a broad spectrum of light into photons of a particular wavelength to minimize the losses in the solar-cells-based energy conversion process. In this paper, we will focus on the Sm-doted $ZnO\text{-}B_2O_3\text{-}P_2O_5$ spectral converters, with a possibility for PV applications as down-shifting materials.

1.1 Luminous Down-Shifting (LDS) for higher efficiency

Luminescent down convertors (LDC) offer the potential to increase the absorption efficiency of the solar cell while decreasing self-absorption losses. Rare earth complexes have high photoluminescence efficiency that is spectrally well matched to the bandgap of photovoltaic (PV) cells. The advantage of the LDC is that it decouples the processes of light capture and charge conversion. Undoubtedly, this is an advantage since each process relies on different materials properties to be efficient (Xiaoyong Huang 2013).

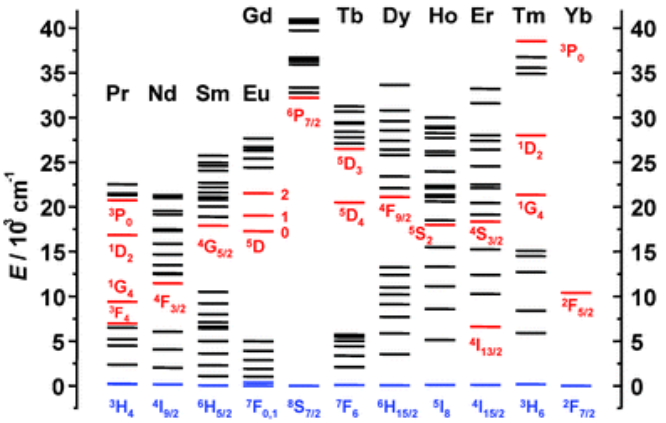

Figure 1-1: Energy level diagrams of the lanthanides. In red are marked transitions levels (K.Binnemans 2009).

Depending on the optical properties (refractive index and optical absorption) we focus on $ZnO-B_2O_3-P_2O_5$ system with low refractive index glass (Crown class). Different kinds of lanthanide rare earth doping agents (K.Binnemans 2009) have been used. Generally Samarium- Sm (predominantly) and Europium-Eu rare earth elements (see Figure 1-1 energy levels) have been used as function of their price and optical characteristics (K.Binnemans 2009).

2 COMPOSITIONS, SYNTHESIS AND PHASE DIAGRAMS

2.1 Compositions and synthesis

Table 1 presents the compositions of Samarium (Sm) doped $ZnO-B_2O_3-P_2O_5$ glasses, which have been synthesized with different molar ratios content of the rare earth element.

Table 1 Molar ratios of glasses doped with Samarium.

Sample		**ZnO**	**B_2O_3**	**P_2O_5**	**Sm_2O_3**
1	mol %	59,5	20	20	0,50
2	mol %	58,5	20	20	1,5

Raw materials as ZnO, $NH_4H_2PO_4$, H_3BO_3 and Sm_2O_3 with analytical grade purity have been used. Conventional melt quench method was applied using the following procedure: First, calculated quantities of the reactants were weighted and mixed. For a better homogenization, planetary mill (FRITSCH) was used as the precursors were placed in agate mortar with grist balls of various sizes and milled for 30 min (see Figure 2-1). The mixture was placed in platinum crucible and heated at 1000°C for one hour in a high temperature muffle furnace. The process was controlled by program applied. In the end, the melted glass was quenched on a graphite plate.



Figure 2-1: The precursors were milled for 30 min in agate mortar with grist balls of various sizes.

The obtained two samples are homogeneous glasses and exhibit strong luminescence when are excited with UV light. Sample 1 with content of 0.5% Sm_2O_3 is transparent and sample 2 with content of 1.5% Sm_2O_3 is milky white. Preliminary tests of sample 1, shows a good emissions after UV illumination (see Figure 2-2).

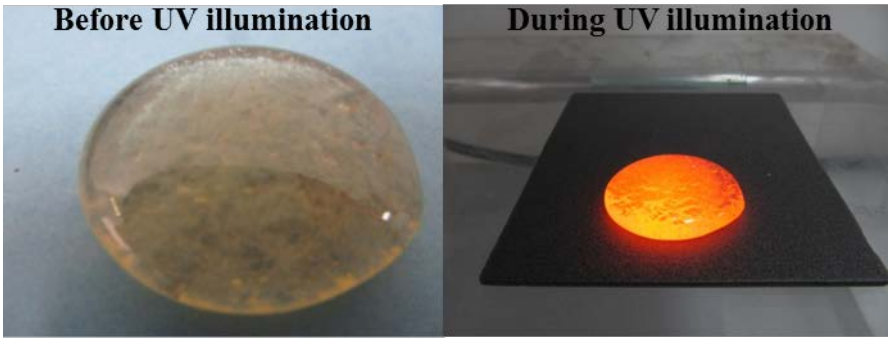

Figure 2-2: Tests behavior with UV light of glass samples 1 containing 0.5 %. Sm_2O_3. Emission in visible spectrum occurs during UV illumination.

It is interesting to serve some information about the phase diagram of the systems, in order to analyze glass synthesis about both technological (glass forming regions determination, melting process and crystallization) and practical (industrial) point of view.

2.2 ZnO-B_2O_3, ZnO-P_2O_5 and B_2O_3-P_2O_5 Binary Systems

ZnO–B_2O_3 system

Harrison and Hummel reported the phase diagram of ZnO-B_2O_3 system (D.E. Harrison 1956). Two compounds with the $ZnO:B_2O_3$ molar ratios of 5:2 and 1:1 were obtained and the 3:2 and 2:1 compounds were mentioned. The melting point of $ZnO{\cdot}B_2O_3$ is 982 ◦C . Composition $5ZnO{\cdot}2B_2O_3$ is melts incongruently at 1045 ◦C (D.E. Harrison 1956).

ZnO–P_2O_5 system

For this system, four compounds were reported with the $ZnO:P_2O_5$ molar ratios of 3:1 (orthophosphate), 2:1 (pyrophosphate), 1:1 (metaphosphate) and 1:2 respectively. The orthophosphate is melts at 1060 ◦C, the pyrophosphate melts at 1017 ◦C and the metaphosphate melts at 872 ◦C (Hummel 1958). The 3:1 compound has three polymorphic forms as α, β and γ, respectively. Katnack and Hummel reported that the α-phase inverted rapidly and reversibly to the β-phase at 132 ^{0}C.

B_2O_3–P_2O_5 system

Only one compound BPO_4 was reported in this system. Two solid-state transitions of boron phosphate occur at 1260°C and 1300°C. The congruent melting point of BPO_4 is 1470°C (G. Baret 1991).

2.3 ZnO-B_2O_3-P_2O_5 Ternary System

The subsolidus phase equilibria in the ZnO-B_2O_3-P_2O_5 ternary system have been studied from Ji et al. (L. N. Ji 2008). The ternary phase diagram is shown in Figure 2-3. There are seven binary compounds and one ternary compound (Zn_3BPO_7) in the system. Ten ternary phase regions were determined and no solid-solution composition ranges were found. The small region ZnO-$Zn_3(BO_3)_2$-$Zn_3(PO_4)_2$ contains the relatively low-melting compounds $Zn_3(BO_3)_2$, $Zn_3(PO_4)_2$, and Zn_3BPO_7.

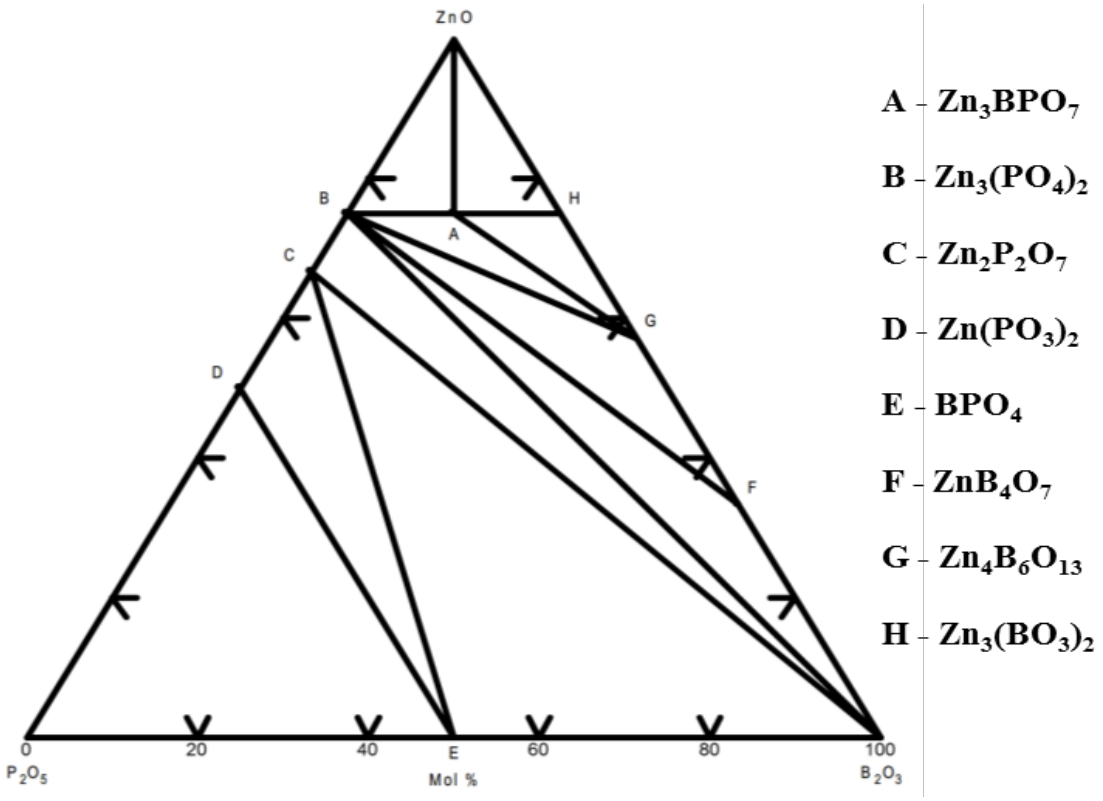

Figure 2-3: Ternary subsolidus phase diagram of ZnO-P_2O_5-B_2O_3 system (L. N. Ji 2008).

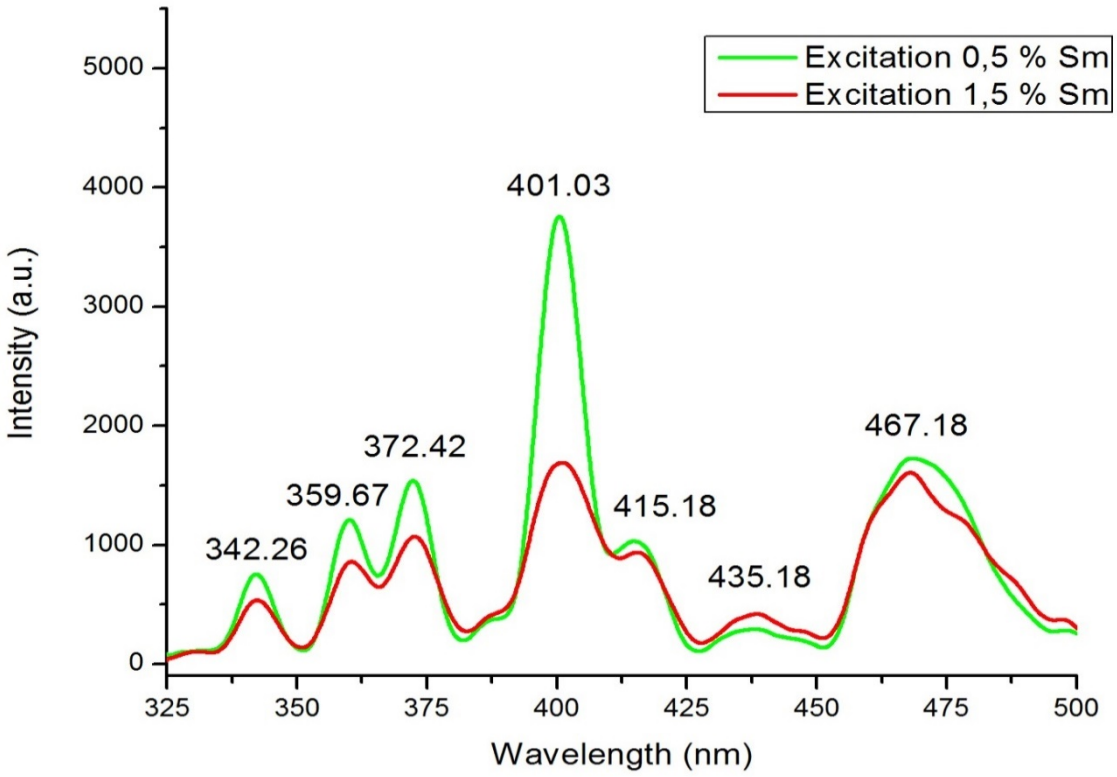

Figure 3-4: Excitation spectra of samples 1 (0.5% Sm) and 2 (1.5% Sm).

3 RESULTS AND DISCUSSIONS

3.1 Fluorescence spectroscopy

The obtained two glass samples have been object of optical characterization by Fluorescence spectroscopy. The fluorescence spectra were taken on a Perkin Elmer LS 45 fluorescence spectrophotometer.

Figure 3-1 shows the excitation spectrum of samples with index 1 (0.5% Sm) and index 2 (1.5% Sm). The excitation in the UV region is well expressed. In this context, higher intensity is registered at 345, 360, 375 and 400 nm wavelengths and also in the visible region at 467 nm, illustrating that all of them undoubtedly emit light.

Figure 3-2 and Figure 3-3 show the behavior of the fluorescent spectra of Sm containing samples from the ZnO-B_2O_3-P_2O_5 system at different Sm ratio in the glass matrix (Sample 1 - 0.5% Sm and Sample 2 - 1.5% Sm). The characteristic fluorescence emission of Sm is observed with three strong peaks corresponding to transitions as follows:

$$564 \text{ nm} \leftrightarrow {}^4G_{5/2} \rightarrow {}^6H_{5/2}$$

$$600 \text{ nm} \leftrightarrow {}^4G_{5/2} \rightarrow {}^6H_{7/2}$$

$$645 \text{ nm} \leftrightarrow {}^4G_{5/2} \rightarrow {}^6H_{9/2}$$

For all samples, the most intensive fluorescence spectrum is obtained with excitation source at 400 nm wavelength (Figure 3-1). Figure 3-2 and Figure 3-3 show that with increasing of the excitation wavelength an increase of the fluorescence intensity at the both studied samples was registered.

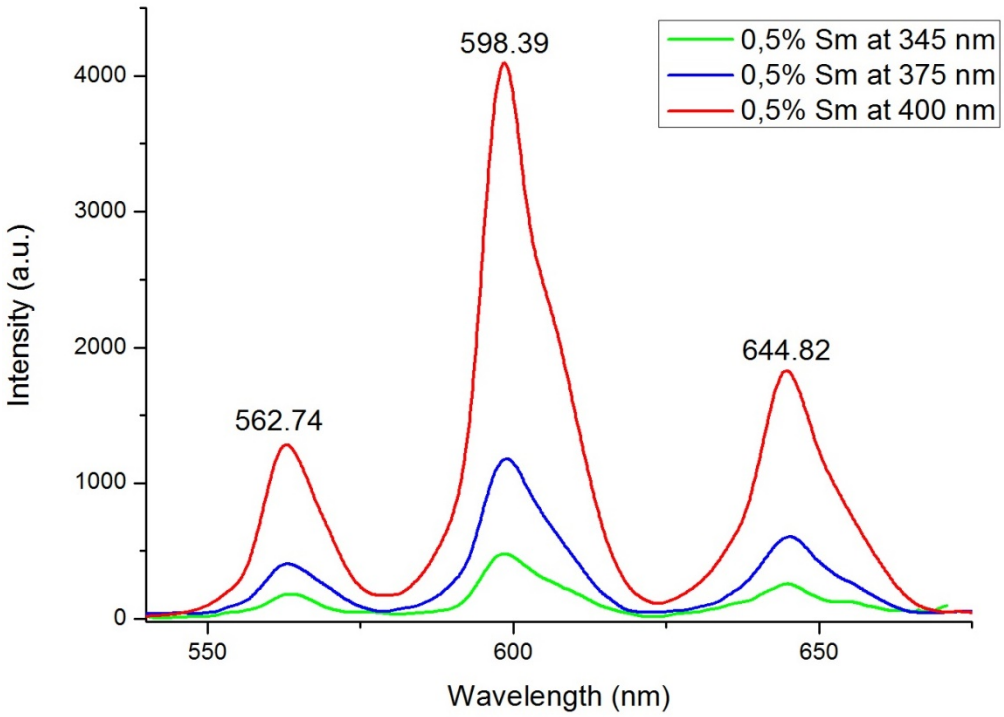

Figure 3-1: Dependence of fluorescent spectra of samples 1 (0.5% Sm) at different wavelengths excitation process.

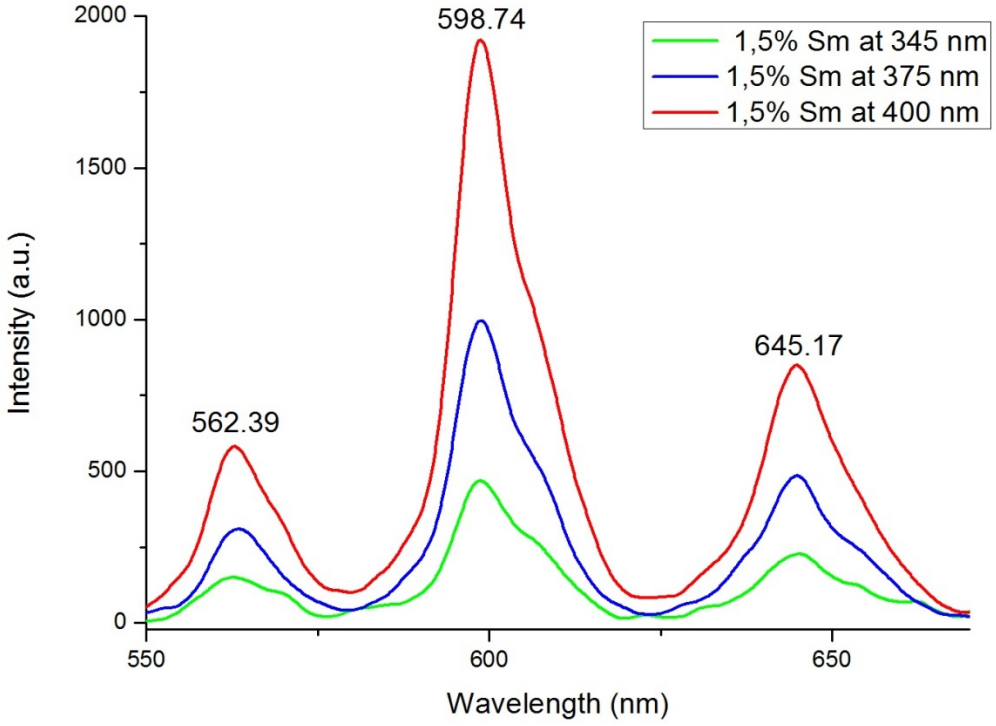

Figure 3-2: Dependence of fluorescent spectra of samples 2 (1.5% Sm) at different wavelengths excitation process.

4 CONCLUSIONS

The synthesized Sm- doped boron phosphate glasses showed a strong effect of luminescence. From the experiments it can be concluded that the optimum amount of rare earth oxide in boron phosphate glass is 0.5 mole%. Increasing the concentration above this value results in a decrease of emission.

Fluorescence properties studied, indicates that both compositions possess strong photoluminescence signals. Both samples clearly show the positive effect of Sm which is expressed in good optical energy absorption in 250–450 nm spectral range and emission in the wavelength range between 550 and 675 nm.

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