INFLUENCE OF SAMARIUM DOPING ON ZINC BOROPHOSPHATE GLASSES

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Abstract

The use of rare earth metals as dopant components in oxide glasses is a new research field of inorganic optical functional materials due to the simple preparation process, stable chemical properties and high thermal stability. This study supplements and summarized results we have obtained in recent years. The focus is on samarium doped zinc oxide-rich borophosphate glasses. The obtained glasses were investigated by powder X-ray diffraction, differential scanning calorimetry, infrared spectroscopy and photoluminescence analysis. The synthesized Sm-doped borophosphates are predominantly homogeneous and non-hygroscopic. They are mainly amorphous with the presence of one or more crystalline phases in some of them - $Zn_3(BO_3)(PO_4)$, $Zn_5B_4O_{11}$, $SmPO_4$ and ZnO. They have the typical structure of borophosphate glasses - the presence of PO_4 tetrahedra and BO_4 tetrahedra. The Sm-doped ZnO-rich borophosphate glasses have a potential for practical application in optical devices for engineering, electronics and medicine.

Keywords: Samarium, doped zinc borophosphate glasses, x-ray powder diffraction, differential scanning calorimetry, photoluminescence

1. INTRODUCTION

In recent years, rare earth (RE) metals are used more widely as a dopant components of inorganic luminescent materials (ceramics, phosphors and crystals) due to the development of lighting and illumination technologies, widely applied in many fields – filed emission displays, lasers, optical temperature sensor, solid state lighting, white light emitting diodes, plasma display panels. This interest is driven by RE ions abundant emission colours on the basis of 4*f* – 4*f* or 5*d* – 4*f* transitions. RE ions are shielded by outer 5*s* and 5*p* electrons, and their emission spectra are characterized by narrow lines with high colour purity [1]. The characteristic electronic structure of the rare earth elements gives them unique electronic, optical, luminescent and magnetic properties. Rare earth elements have a wide range of applications due to these properties (synthetic, catalytic, electronic, medical and military) and can be found in computers, cell phones, televisions, automotive catalytic converters, petroleum refining plants, lasers, fuel cells, light-emitting diodes, magnetic-resonance imaging, hybrid electric vehicles, photovoltaics and wind turbines. Their role will increase in the future, expected to be of critical importance in achieving a carbon-free, sustainable, global energy supply [2].

Sm^{3+} ion, as a representative of RE ions, can be successfully used as a doping component in various glass or crystal matrices for intense emissions in the visible region, being an activator with good colour purity and high radiation stability. The Sm^{3+} ion has a strong absorption peak around 402 nm and orange-red or red emission, respectively, due to its ${}^4G_{5/2} \rightarrow {}^6H_J$ (J = 5/2, 7/2, 9/2 and 11/2) transitions obtained from the characteristic internal configuration transitions 4f - 4f. The reddish orange region of emission from Sm doped materials possesses strong luminescence intensity, a large stimulated emission cross section and high quantum efficiency, suitable for laser applications. The study of new samarium doped materials is of great importance to the fundamental research and potential industrial application [1,3].

The rare earth elements included as dopant to the glass matrix improve the melting and some unique properties of the glass [4]. B_2O_3 and P_2O_5 are commonly used as glass network modifiers. B_2O_3 improves the quality of glass with amelioration in transparency, refractive index and solubility of rare earth ions. The phosphate glasses possess low transition temperature, low melting point (compared to silicate glass) and a high coefficient of thermal expansion and biocompatibility. ZnO is known as one of the best glass modifiers. Its presence leads to improved optical and spectral properties, such as their wide direct band gap, large excitation binding energy, and high optical gain at room temperature [3,5,6].

The present investigations are directed to the synthesis and characterization of Sm doped ZnO-rich borophosphate glasses. Three series of samples have been synthesized: one by varying the ratio of P_2O_5 and B_2O_3 at a constant content of ZnO and Sm_2O_3 - 71.8 ZnO–(27.7-x) B_2O_3–x P_2O_5 :0.5 Sm_2O_3, where x = 9.7, 13.85, 18 mol %; second with varying of ZnO content at the expense of P_2O_5 at a constant content of other components B_2O_3 and Sm_2O_3 - (67.5+y) ZnO–18 B_2O_3– (14-y) P_2O_5:0.5 Sm_2O_3, where y = 0, 2, 4.3, 6 mol % and third with varying the content of the dopant component Sm_2O_3 - (72.3-z) ZnO–18 B_2O_3–9.7 P_2O_5:z Sm_2O_3, where z = 0.25, 0.5, 0.75, 1 mol %.

The synthesized compositions were investigated using a combination of techniques such as powder X-ray diffraction, differential scanning calorimetry (DSC), Raman spectra analysis, infrared spectroscopy and photoluminescence spectroscopy.

2. EXPERIMENTAL

2.1. Sample preparation

All samples were prepared by conventional melt quenching method using ZnO, P_2O_5, B_2O_3 and Sm_2O_3 as starting materials. ZnO-B_2O_3-P_2O_5 ternary system is the most thoroughly investigated from Ji et al [7]. Ten ternary phase regions were determined and no solid-solution composition ranges were found. The small region ZnO-$Zn_3(BO_3)_2$-$Zn_3(PO4)_2$ contains the relatively low-melting compounds $Zn_3(BO_3)_2$, $Zn_3(PO_4)_2$, and Zn_3BPO_7 [7]. Glasses synthesized and studied by us have a composition close to this area.

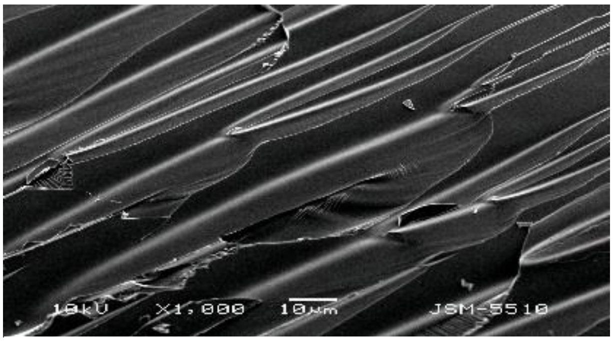

Figure 1 SEM image of the microstructure for sample 72.05 ZnO–18 B_2O_3–9.7 P_2O_5:0.25 Sm_2O_3

The reagents were thoroughly mixed, grinded, placed in alumina crucibles and heated at 950 °C for 3 hours in a muffle furnace. The obtained homogeneous melts were then poured onto a graphite plate. Then the samples were annealed at 250 °C for 2 hours. Synthesized compositions are amorphous (**Figure 1**), mainly homogeneous, non-hygroscopic and predominantly transparent glasses. They are easily reproducible.

2.2. Analytical procedures

Powder X-ray diffraction analysis

Powder X-ray diffraction data were collected on Bruker D8 Advance powder diffractometer with Cu – Kα radiation source (λ = 1.5406 nm) and Lynx Eye PSD detector, in steps of 0.02º over the range of 10º – 80º 2θ, with a time per step of 2.8 sec (32 kW, 15 mA). The phases in the XRD patterns were identified using the Diffract Plus EVA v.12 program and ICDD PDF-2 database [8].

Differential Scanning Calorimetric analysis

DSC measurements were performed using TA Instruments DSC Q100 and DSC 2910 with attached Fast Air Cooling System (FACS) and Refrigerating Cooling System (RCS). The samples (20 – 22 mg) were placed in aluminium hermetic pans. A heating rate of 10 K/min was used to scan all samples.

Infrared spectroscopy analysis

The Infrared spectroscopy studies were conducted using the Perkin Elmer 1750 Infrared Fourier Transform Spectrometer.

Raman spectroscopy analysis

The Raman studies were conducted using the 1064 nm Nd:YAG laser line at a power of 700 mW and a RAM II spectrometer (Bruker Optics) having a resolution of 2 cm^{-1}.

Photoluminescence measurements

The photoluminescence spectra were measured by optical CCD Aventes spectrometer Ave spec - 2048. The set-up consists of a light source, a sample and a detection system. The light source is a combination of a Deuterium and a Halogen lamp, providing a spectrum with the 250 – 1100 nm range for transmission and absorption measurements and semiconductor light emitting diode (LED), emitting at 395 nm to pump directly the sample under study for photoluminescence measurements.

3. RESULTS AND DISCUSSION

List of the three synthesized series of Sm doped ZnO-rich borophosphate glasses with theirs thermal properties (glass transition temperature) is presented in **Table 1**.

Table 1 Composition and glass transition temperature of samarium doped zinc borophosphate samples

First series			**Second series**			**Third series**		
№	**Composition, mol%**	***Tg*** (°C)	**№**	**Composition, mol%**	***Tg*** (°C)	**№**	**Composition, mol%**	***Tg*** (°C)
1	71.8 ZnO–18 B_2O_3–9.7 P_2O_5:0.5 Sm_2O_3	532.60	4	67.5 ZnO–18 B_2O_3–14 P_2O_5:0.5 Sm_2O_3	544.72	7	72.05 ZnO–18B_2O_3–9.7 P_2O_5:0.2 5Sm_2O_3	526.28
2	71.8 ZnO–13.85 B_2O_3–13.85 P_2O_5:0.5 Sm_2O_3	551.94	5	69.5 ZnO–18 B_2O_3–12 P_2O_5:0.5 Sm_2O_3	551.10	1	71.8 ZnO–18 B_2O_3–9.7 P_2O_5:0.5 Sm_2O_3	532.60
3	71.8 ZnO–9.7 B_2O_3 – 18 P_2O_5:0.5 Sm_2O_3	533.30	1	71.8 ZnO–18 B_2O_3–9.7 P_2O_5:0.5 Sm_2O_3	532.60	8	71.55 ZnO–18 B_2O_3–9.7 P_2O_5:0.75 Sm_2O_3	525.36
			6	73.5 ZnO–18 B_2O_3 – 8 P_2O_5:0.5 Sm_2O_3	533.99	9	71.3 ZnO–18 B_2O_3–9.7 P_2O_5:1 Sm_2O_3	539.17

The results obtained from Powder X-ray diffraction analysis show that the samples are predominantly amorphous, with the presence of crystalline phases in some of them (**Figure 2**).The main crystalline phases identified in these samples are indexed as $Zn_3(BO_3)(PO_4)$ (sample 2 - powder diffraction file PDF 86-2017 Zinc Borate Phosphate), α-$Zn_5B_4O_{11}$ (sample 2 - PDF 19-1455 Zinc Borate), ZnO (sample 6 - PDF 01-070-8070 Zinc Oxide) and $SmPO_4$ (sample 9 - PDF 01-083-0655 Monazite-(Sm), syn)[8]. The appearance of borate and phosphate in the crystallization products shows the important role of PO_4 and BO_4 structural units in the structural network of borophosphate glasses. It is possible to suggest based on other authors' studies that these borophosphate glasses contain B–O–P linkages within their structural network [3,5].

DSC analysis of the as-synthesized glass samples in accordance with XRD results are showing that partially crystallized samples keep showing an amorphous phase (i.e. it is possible to evaluate glass transition *Tg* but with reduced relaxation). The high glass transition temperature is an indication of the stability of the glass (**Table 1**).

The first series of synthesized glass samples was investigated by Raman spectroscopy and the other two series - via infrared spectroscopy. Raman spectra contain a vibrational band at 968 cm^{-1} ascribed to the vibrations of isolated PO_4 units in the structural network of borophosphate glasses at the B_2O_3 - rich side. The Infrared spectra contain an absorption band at about 1250 cm^{-1} due to the asymmetrical stretching vibration of P = O and peak around 995 cm^{-1} - vibration of the structural unit BO_4. The absorption band at about 730 cm^{-1} was determined by the symmetrical vibration P-O-P, those about 560 cm^{-1} - by stretching vibration P-O- and peaks about 500 cm^{-1} - from the structural unit PO_4. The results are in agreement with the existing literature data on the structure of borophosphate glasses [4,9,10].

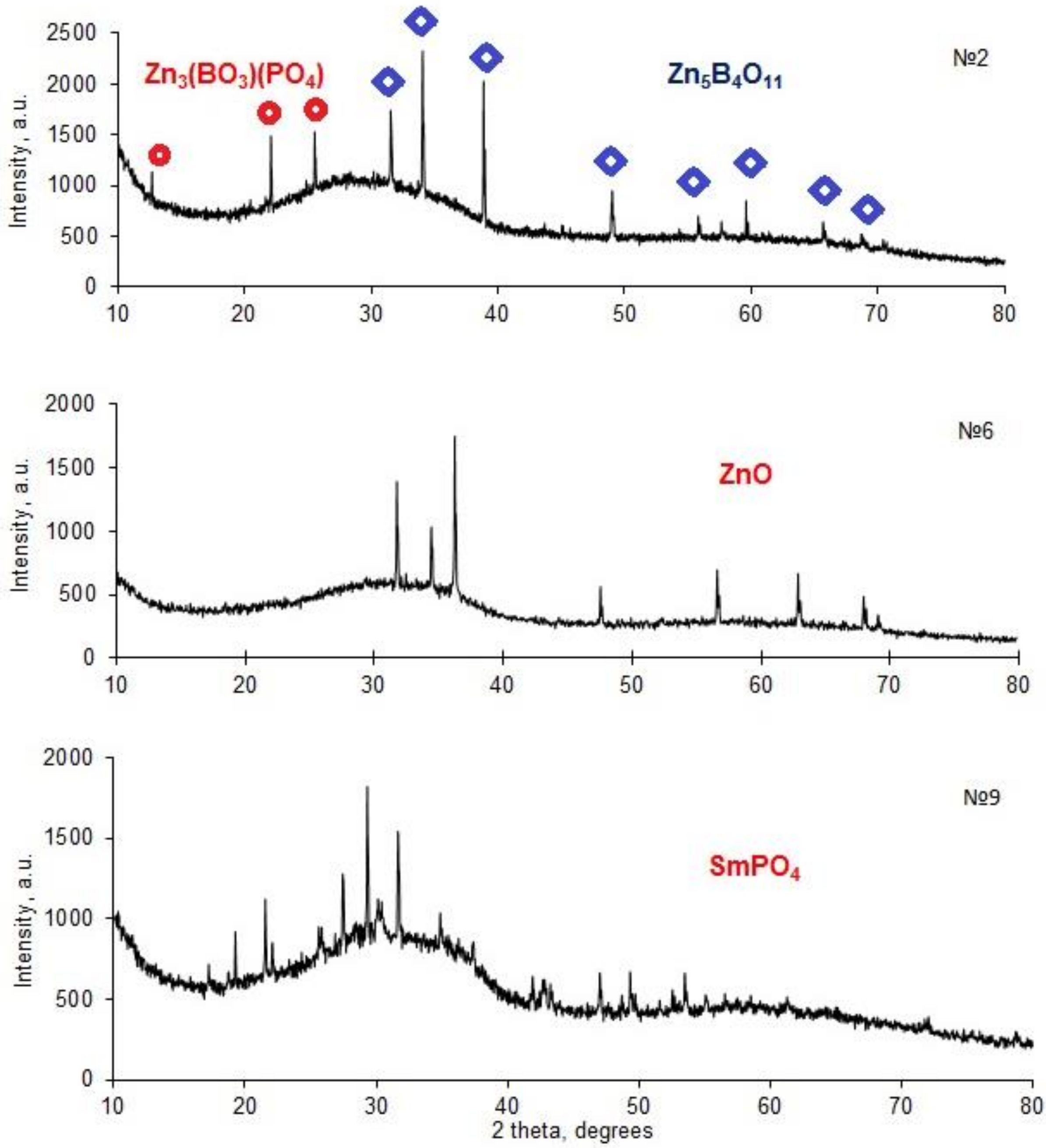

Figure 2 Powder X-ray diffraction patterns for samples 2, 4, 5 and 6

The most efficient LED for pumping the glasses is the one at 395 nm according to our previous research [11]. All samarium doped samples were optically active with a photoluminescence signal out of Sm^{3+} ions. Energy level diagram of Sm^{3+} doped zinc borophosphate glass is presented in **Figure 3**, representative emission spectra for synthesized samples are illustrated in **Figure 4.** The observed spectra depict three pronounced peaks at wavelengths of 560 nm, 600 nm and 645 nm, respectively. There is a fourth peak at 704 nm, which is much less intense than others. These four peaks are characteristic of Sm^{3+} ions and correspond to transitions: 560 nm – $^4G_{5/2}\rightarrow{}^6H_{5/2}$, 600 nm – $^4G_{5/2}\rightarrow{}^6H_{7/2}$, 645 nm – $^4G_{5/2}\rightarrow{}^6H_{9/2}$ and 704 nm – $^4G_{5/2}\rightarrow{}^6H_{11/2}$. The band at 600 nm, which corresponds to orange emission, is the most intense [11].

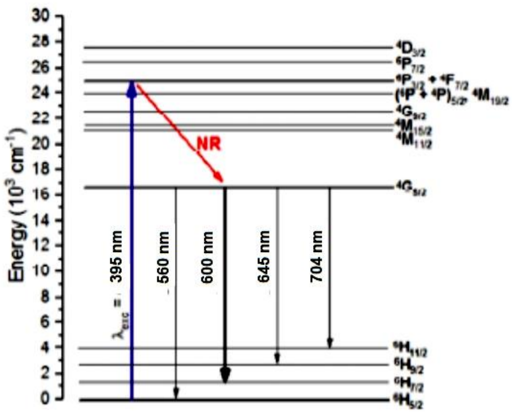

Figure 2 Energy level diagram of Sm^{3+} doped zinc borophosphate glass [6]

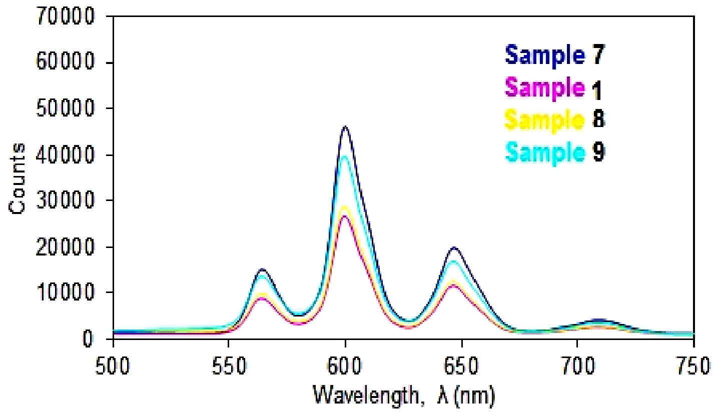

Figure 2 Emission spectra recorded at 395 nm excitation

Therefore, samarium ions effectively activated the zinc borophosphate matrix. This evidences the opportunity to use the as-synthesized samarium doped zinc borophosphate glasses for application in optical devices.

The samarium doping of materials play an important role in the structural, thermal and optical properties of glasses, as evidenced from the presented results.

4. CONCLUSIONS

Zinc oxide rich borophosphate glasses doped with samarium have been synthesized and investigated by powder X-ray diffraction, Raman spectroscopy analysis, IR spectral analysis, differential scanning calorimetry and photoluminescence spectroscopy.

The obtained materials were homogeneous, non-hygroscopic and transparent glasses. The high glass transition temperature was an indication of the stability of the glasses obtained. They were amorphous, with the presence of crystalline phases in some of them. The synthesized compositions had the typical structure of borophosphate glasses - the presence of PO_4 tetrahedra and BO_4 tetrahedra. The main crystalline phases observed were Zinc Borate Phosphate $Zn_3(BO_3)(PO_4)$, Zinc Borate α-$Zn_5B_4O_{11}$, Zinc Oxide ZnO and Samarium Phosphate $SmPO_4$.

The content of samarium and doping of materials play an important role in the structural and optical properties of compositions. Samarium doped samples exhibit strong fluorescence for different doping ions.

The synthesized Sm doped ZnO-rich borophosphate glasses have a potential for practical application in optical devices.

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