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Synthesis and characterization of samarium doped zinc borophosphate glasses

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This paper is focusing on the synthesis and characterization of the optical, mechanical and thermal properties of samarium doped ZnO-rich borophosphate glasses. Two series of samples have been synthesized – non doped with composition: $(68+x)ZnO – 18B_2O_3 – (14–x)P_2O_5$ and doped – $(67.5+x)ZnO – 18B_2O_3 – (14–x)P_2O_5 – 0.5Sm_2O_3$, where x = 0, 2, 4, 6 mol%. The obtained materials have been investigated by powder X-ray diffraction, differential scanning calorimetry, infrared spectroscopy and photoluminescence analysis. Furthermore, the density has been measured and the chemical durability in acid, neutral and alkaline medium has been determined. The obtained samples are amorphous, homogeneous and transparent glasses except for the samples with the highest content of ZnO. Samarium doped samples exhibit strong visible immediate photoluminescence signal under UV light. The synthesized samarium doped ZnO-rich borophosphate glasses may find applications for preparation of energy converters, solar cells, X-ray dosimeters and for protection of valuable documents.

Key words: zinc borophosphate glasses, samarium doping, x-ray powder diffraction, differential scanning calorimetry, photoluminescence.

INTRODUCTION

The developments of industry and technology in recent decades led to the search and application of new technologies and materials in order to meet the ever increasing economic and environmental demands. The phosphate glasses known for their unique properties such as the wide compositional range of glass forming, high thermal expansion, low melting point, high UV transparency are causing growing interest. Introduction of metal oxides improves their properties and expands the scope of their applications [1, 2]. Additional doping with rare earths elements provides the new materials with unique optical and electrical properties and associated fluorescent effects. These materials have high potential application as an active bearer for laser fibres, optical amplifiers, sensors, LEDs, semiconductors and insulators in optoelectronics and others. Such compositions may be prepared either as stoichiometric compounds or as alloys with a polycrystalline, amorphous or amorphous-crystalline structure [3–8].

In this work we present synthesis and characterization studies of samarium doped ZnO-rich borophosphate glasses. Two series of samples have been synthesized: non doped with a composition $(68+x)ZnO – 18B_2O_3 – (14–x)P_2O_5$ and doped – $(67.5+x)ZnO – 18B_2O_3 – (14–x)P_2O_5 – 0.5Sm_2O_3$, where x = 0, 2, 4, 6 mol%.

EXPERIMENTAL

Sample preparation

All samples were prepared by conventional melt-quenching method. The ratio of the main components (ZnO, B_2O_3 and P_2O_5), the content of the dopant rare earth element (Sm as Sm_2O_3) and the conditions of synthesis and analysis were set on the basis of literature data and our previous studies [2, 9, 10]. The reagents were thoroughly mixed, placed in alumina crucibles and heated at 950 °C for 3 hours in a muffle furnace. Samples were quenched out of the melt to room temperatures and annealed at 250 °C for two hours. The obtained materials are predominantly homogeneous, non-hygroscopic, transparent and easily reproducible glasses as seen in Fig. 1.

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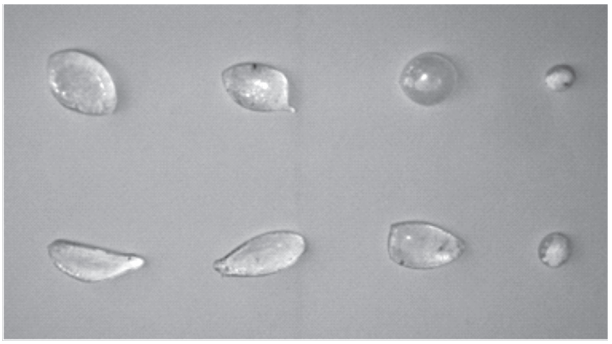

Fig. 1. Photo of the synthesized doped (upper row – samples 5–8) and non doped samples (bottom row – samples 1–4).

Analytical procedures:

Density measurements

Density measurements were carried out according to the Archimedes method using deionized water of density 1g/cm^3 as an immersion liquid.

Chemical durability

The chemical durability was evaluated from the dissolution rate (D_r) of synthesized samples in alkaline, neutral and acidic aqueous solutions at 98 °C for 1, 2 and 3 hours, correspondingly. The following solutions were used for this purpose – 0,1M NaOH + 0,5M Na_2CO_3 (pH = 12.2), deionized water (pH = 7) and 0,1M HCl (pH = 1). The samples were placed for up to three hours in each solution. The change in weight and area of the samples was reported every hour. The dissolution rate D_r of the respective compositions was calculated from the obtained results:

$$D_r = \frac{\Delta W}{t}, [g.cm^{-2}.s^{-1}] \quad (1)$$

where ΔW is the weight loss in relation with the surface area of the immersed sample and t is the time that the sample was immersed in the test solution [11].

Powder X-ray diffraction analysis

Structural characterization was carried out by powder X-ray diffraction (XRD) using a Bruker D8 Advance powder diffractometer with Cu – Kα radiation source (l = 1.5406 nm) and Lynx Eye PSD detector. XRD spectra were recorded at room temperature. Data were collected in the 2θ range from 10° to 80° 2θ with a step of 0.04° 2θ and counting time of 0.2 s/strip (total of 35 s/step). The phase in the XRD patterns was identified using the Diffract Plus EVA v.12 program and ICDD PDF-2 (2009) database – PDF 01-070-8070 (ZnO) [12, 13].

Infrared spectroscopy analysis

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

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.

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.

III. RESULTS AND DISCUSSION

List of the synthesized two series zinc borophosphate compositions with theirs thermal (glass transition temperature) and physical properties (density and molar volume) is presented in Table 1. As can be seen from the results, the values of density of the synthesized materials increase with increasing the content of zinc. Samarium doped samples have higher density. Enhancing the density is probably due to the consolidation of the structure of the compositions.

The results obtained for the chemical durability of the synthesized samples are presented in Table 2. Data about the behaviour of the samples in a neutral aqueous solution are not represented. No change has been observed under these conditions and the dissolution rate is equal to zero. The values for the rate of decomposition in an alkaline medium are in the range of 10^{-8} g.cm^{-2}.s^{-1}, which is comparable with the resistance of the phosphate glass [11, 14]. The most significant changes occur in an acid medium, wherein the samples have been dissolved in

Table 1. Composition, thermal and physical properties of samarium doped zinc borophosphate samples

Sample, №	ZnO, mol%	B_2O_3, mol%	P_2O_5, mol%	Sm_2O_3, mol%	Tg, °C	ρ, g/cm^3	V_m, cm^3
1	68.00	18.00	14.00	–	535.87	2.262	38.798
2	70.00	18.00	12.00	–	541.79	2.727	31.739
3	72.31	18.00	9.69	–	544.57	2.935	28.940
4	74.00	18.00	8.00	–	534.94	2.907	29.011
5	67.50	18.00	14.00	0.50	544.72	3.921	22.726
6	69.50	18.00	12.00	0.50	551.10	4.236	20.749
7	71.81	18.00	9.69	0.50	533.98	4.433	19.510
8	73.50	18.00	8.00	0.50	533.99	4.889	17.482

Table 2. Dissolution rate (D_r) of synthesized samples in alkaline and acidic aqueous solutions at 98 °C for different time

Sample, №	Alkaline resistance			Acid resistance
	D_{r60}, g.cm^{-2}.s^{-1}	D_{r120}, g.cm^{-2}.s^{-1}	D_{r180}, g.cm^{-2}.s^{-1}	D_{r40}, g.cm^{-2}.s^{-1}
1	$2{,}7778.10^{-8}$	$2{,}7778.10^{-8}$	0	$9{,}9904.10^{-5}$
2	0	0	0	$7{,}8381.10^{-5}$
3	0	0	0	$9{,}2571.10^{-5}$
4	0	$2{,}7778.10^{-8}$	0	$6{,}7524.10^{-5}$
5	0	0	0	$6{,}9208.10^{-5}$
6	0	0	0	$6{,}7.10^{-5}$
7	$2{,}7778.10^{-8}$	$2{,}7778.10^{-8}$	0	$8{,}25.10^{-5}$
8	0	0	0	$7{,}3083.10^{-5}$

less than one hour. It is evident that the synthesized samples are stable both in neutral and in alkaline medium, but are not stable in the acidic medium.

The results obtained from Powder X-ray diffraction analysis show that the samples are predominantly amorphous, except for the samples with the highest content of zinc oxide (Fig. 2). The crystalline phase identified in these samples is indexed as ZnO (PDF 01-070-8070 from ICDD PDF-2 database using DiffractPlus EVA v.12 program (2009)) [12, 13].

Figure 3 presents the infrared spectra of the as-synthesized zinc borophosphate materials – non-doped sample (№1) and doped sample (№8), respectively. The absorption band at about 1250 cm^{-1} is due to the asymmetrical stretching vibration of P = O, the peak around 995 cm^{-1} – vibration of the structural unit BO_4. The absorption band at about 730 cm^{-1} is 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 [2, 9, 15].

DSC analysis of the as-synthesized glass samples in accordance with XRD results are showing

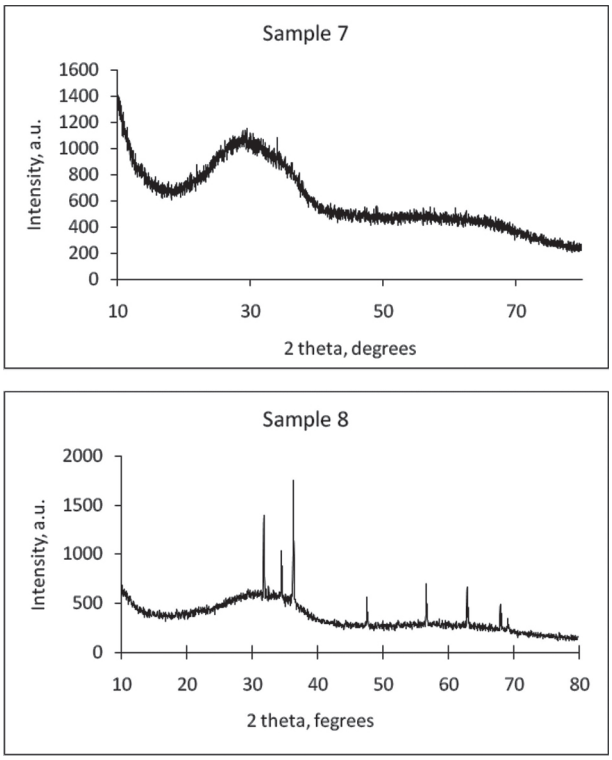

Fig. 2. Powder X-ray diffraction patterns for samples No 7 and No 8.

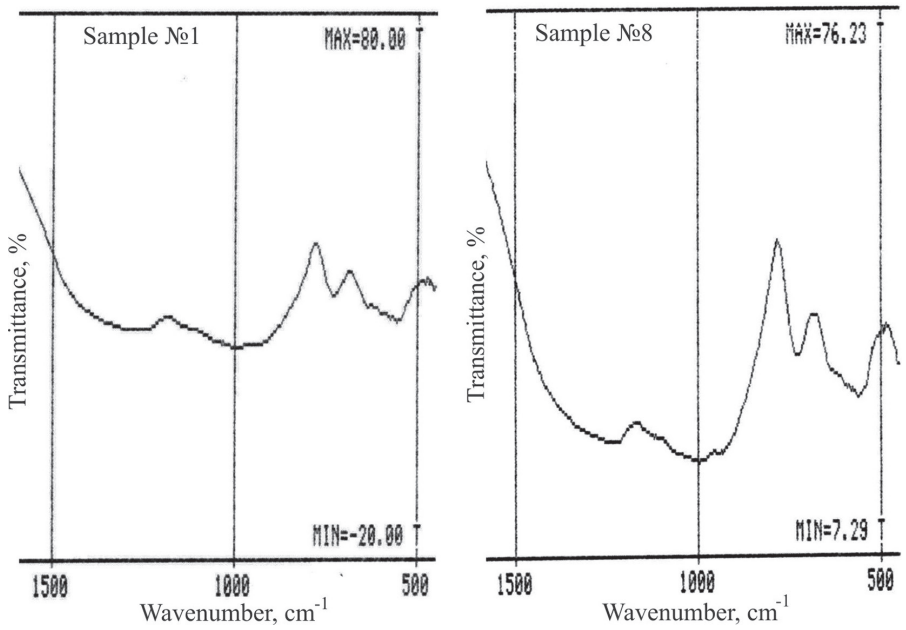

Fig. 3. Infrared spectra of samples №1 and No 8.

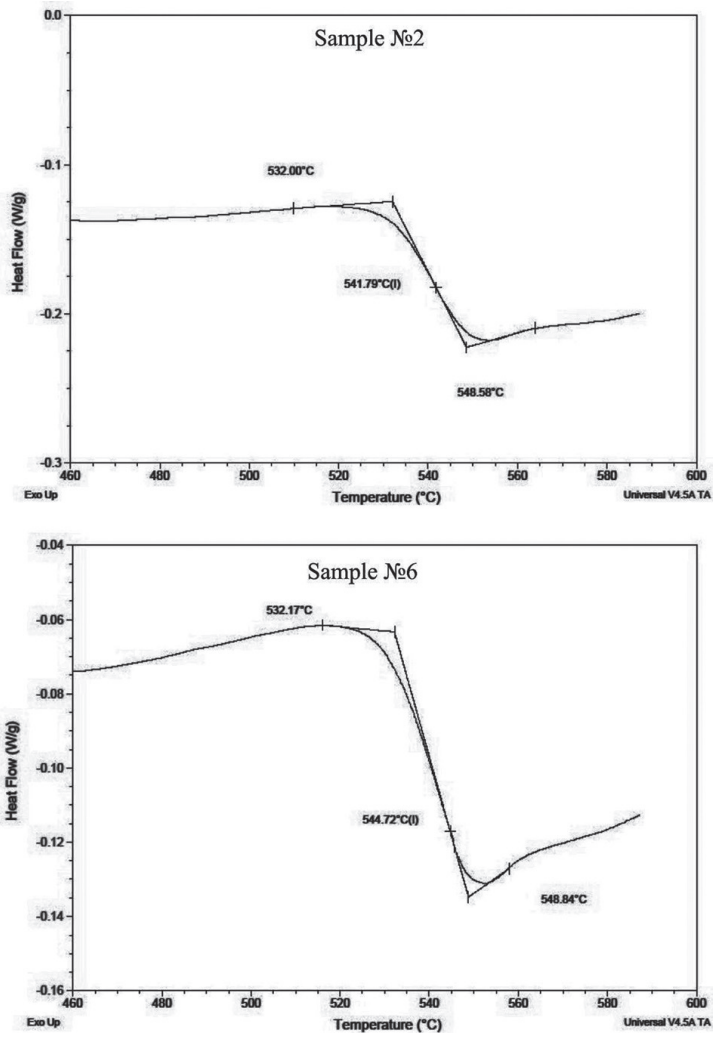

Fig. 4. DSC data of the samples No 2 and No 6.

that partially crystallized samples keep showing an amorphous phase (i.e. it is possible to evaluate glass transition Tg but with reduced relaxation) as shown in Figure 4. The high glass transition temperature is an indication of the stability of the glass (Table 1).

The most efficient LED for pumping the glasses is the one at 395 nm according to our previous research [16]. Representative emission spectra for synthesized samples are illustrated in Fig. 5. 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 the others. These four peaks are characteristic of Sm^{3+} ions and correspond to transitions [17]:

560 nm – $^4G_{5/2} \rightarrow {}^6H_{5/2}$
600 nm – $^4G_{5/2} \rightarrow {}^6H_{7/2}$
645 nm – $^4G_{5/2} \rightarrow {}^6H_{9/2}$
704 nm – $^4G_{5/2} \rightarrow {}^6H_{11/2}$

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

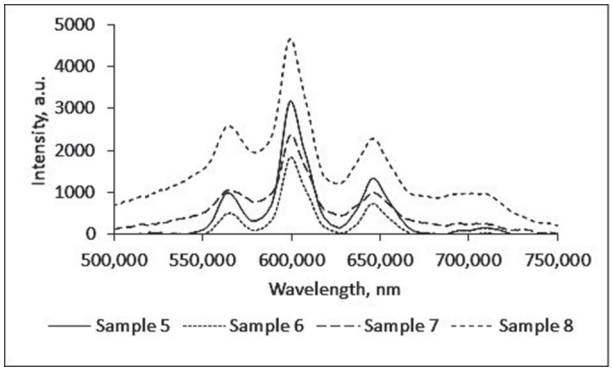

Fig. 5. Photoluminescence spectra for doped samples at an excitation wavelength 395 nm.

CONCLUSIONS

Samarium doped ZnO-rich borophosphate glasses with varying content of ZnO have been synthesized and investigated by powder X-ray diffraction, IR spectral analysis, differential scanning calorimetry (DSC) and photoluminescence spectroscopy.

The obtained samples are amorphous, homogeneous and transparent glasses except for those ones with the highest content of ZnO. The data from the IR spectral analysis and the DSC confirmed the results obtained from the XRD analysis.

Samarium doped samples exhibit strong visible (orange to red) immediate photoluminescence (scintillation) signal under UV light.

The content of zinc and doping of materials play an important role in the structural and thermal properties of glass, as evidenced from the presented here results.

The synthesized samarium doped ZnO-rich borophosphate glasses may successfully be applied for preparation of energy converters for solar cells, X-ray dosimeters and for protection of valuable documents.

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СИНТЕЗ И ХАРАКТЕРИСТИКА НА ЦИНК БОРОФОСФАТНИ СТЪКЛА, ДОТИРАНИ СЪС САМАРИЙ

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(Резюме)

Статията насочва вниманието върху синтеза и охарактеризирането на оптичните, механичните и термичните свойства на богати на ZnO борофосфатни стъкла, дотирани със самарий. Синтезирани са две серии проби – недотирани със състав: $(68+x)ZnO – 18B_2O_3 – (14–x)P_2O_5$ и дотирани – $(67,5+x)ZnO – 18B_2O_3 – (14–x)P_2O_5 – 0,5Sm_2O_3$, където x = 0, 2, 4, 6 mol%. Получените материали са изследвани чрез рентгенодифракционен анализ, диференциална сканираща калориметрия, инфрачервена спектроскопия и фотолуминесцентен анализ. Освен това е измерена плътността и определена химическата устойчивост в кисела, неутрална и алкална среда. Получените проби са аморфни, хомогенни и прозрачни стъкла с изключение на тези с най-високо съдържание на ZnO. Дотираните със самарий проби показват силен видим непосредствен фотолуминесцентен сигнал под ултравиолетова светлина. Синтезираните богати на ZnO борофосфатни стъкла, дотирани със самарий, могат да намерят приложение при изготвяне на енергийни преобразуватели, соларни клетки, рентгенови дозиметри и за защита на ценни документи.