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Influence of the content of samarium on the structure and the optical properties of zinc borophosphate materials

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Glasses, glass ceramics and polycrystalline compositions based on ZnO, P_2O_5 and B_2O_3 have both scientific and technological importance because of their useful applications. Doping with rare earth elements not only leads to a rearrangement in the structure, but also to variation in the optical, magnetic and electrical properties.

We have synthesized samarium doped ZnO-rich borophosphate materials of composition $xSm_2O_3 – (72.31–x)ZnO – 9.69P_2O_5 – 18B_2O_3$, where x = 0, 0.25, 0.5, 0.75, 1 mol%. Samarium doped ZnO-rich borophosphate compositions were annealed with a target to obtain nanocrystalline structures. Materials were characterized by x-ray powder diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and photoluminescence (PL) measurements.

The results obtained show that synthesized materials are predominantly amorphous, with the presence of nano and polycrystalline structures in heat-treated samples. The structure and morphology of the obtained materials were evidenced by powder XRD data, SEM imaging and thermal DSC analysis. All different content Sm doped samples show PL peaks in the range of 550–650 nm belonging to Sm^{3+} ions.

Key words: zinc borophosphates, samarium doping, nanocrystallization, x-ray powder diffraction, differential scanning calorimetry, scanning electron microscopy.

INTRODUCTION

Recently, there is a significant interest in the synthesis and characterization of rare earth doped glasses and glass ceramics. These comparatively novel materials have been developed for a variety of applications. Rare earth ions play an important role in modern technology as active ions in many optical materials due to photoluminescence, X-ray scintillating etc. Glasses doped with rare-earth ions are attracting great interest regarding fibre amplifiers, up conversion lasers and optical devices for three-dimensional displays. Also samarium doped materials are widely used in different optical devices (high-density optical storage, under sea communication, colour display) [1–4].

The functionality of optically active glasses can be modified by appropriate doping and post synthesis thermal processing. Samarium ions fluorescence in glassy materials has attracted a lot of attention. Borate glasses are good candidates as a host matrix material for rare earths ions like ions of samarium since these glasses can offer high optical transparency and are also robust and inexpensive [5–8].

On the other hand the materials with nanocrystals have immense potential for a variety of applications, by virtue of their electrical, magnetic, and optical properties. They are attractive not only for their potential for technological applications, but also the feasibility which they provide to engineer their structures at atomic levels to generate solids with novel properties [2, 5, 9]. It was specially emphasized that optical properties are depending on nano and polycrystalline formation into similar materials especially for high resolution and dosimetric X-ray detectors [10]. With constantly increasing demand for various optical devices, further studies of rare earth doped materials and especially these containing nanocrystals in the glass matrix are becoming more significant.

The purpose of this study is to synthesize stable, transparent samarium doped ZnO-rich borophosphate glassy materials and to form optically active nanocrystalline structures by annealing. We studied the effect of samarium content on the structure and

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the optical properties of Sm doped ZnO-rich borophosphate materials with composition xSm_2O_3 – $(72.31–x)ZnO – 9.69P_2O_5 – 18B_2O_3$, where x = 0, 0.25, 0.5, 0.75, 1 mol%. The obtained compositions were characterized by x-ray powder diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and photoluminescence (PL) measurements.

EXPERIMENTAL

Sample preparation

All samples were prepared by high-temperature melt-quenching method using ZnO, P_2O_5, B_2O_3 and Sm_2O_3 as starting materials. 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. The ratio between the main components – ZnO, P_2O_5, B_2O_3, the amount of dopant – Sm_2O_3 and conditions of the synthesis are based on our previous research in this area [11]. The synthesized compositions were heat-treated at 600 °C for three hours with a target to obtain nanocrystalline structures. We obtained homogeneous, non hygroscopic transparent and easily reproducible glasses. List of the zinc borophosphate compositions is presented in Table 1, where samples 2A–4A and 5A are heat-treated.

Powder X-ray diffraction analysis

Powder X-ray diffraction data were collected on Bruker diffractometer operating with a CuKα radiation source (λ = 1.5406 nm), in steps of 0.02° over the range of 10–80° 2θ, with a time per step of 2.8 sec. The crystalline phases were identified using the powder diffraction files PDF 01-083-0655 ($SmPO_4$ – Monazite-(Sm)) from ICSD using POWD – 12++ (2004) [12], PDF 19-1455 (α-$Zn_5B_4O_{11}$ – Zinc Borate) and PDF 86-2017 ($Zn_3(BO_3)(PO_4)$ – Zinc Borate Phosphate) from database JCPDS – International Centre for Diffraction Data PCPDFWIN v.2.2 (2001) [13, 14].

Differential Scanning Calorimetry

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

Scanning electron microscopy analysis

Scanning electron microscopy (SEM) was performed using a JEOL scanning microscope JSM-5510 operating at 10 kV with magnification of 1000, 5000 and 10000. The surfaces of the samples were gold sputtered using a JEOL fine coater JFC-1200.

Photoluminescence measurements

The photoluminescence spectra were measured by optical CCD Avantes spectrometer Avaspec 2048, operating at 25 MW in the range 250–1100 nm at room temperature. The light source was a semiconductor light emitting diode, emitting at 395 nm wavelength to pump directly the sample under study for photoluminescence measurements.

RESULTS AND DISCUSSION

The X-ray diffraction pattern of the synthesized and heat-treated Sm^{3+}-doped Zn-B-phosphate glasses are presented in Fig. 1. No diffraction peak appears for the Sm^{3+}-doped samples (2–5) which indicate that these materials are amorphous (glass structure). The main crystallization phases that are indexed in some areas of nondoped sample 1 are zinc borate phosphate $Zn_3(BO_3)(PO_4)$ (JCPDS file 86-2017 – [13]) and zinc borate α-$Zn_5B_4O_{11}$ (JCPDS file 19-1455 – [14]). These XRD results were presented in our previous investigations [11].

Table 1. List of the samarium doped zinc borophosphate samples

Sample, No	ZnO, mol%	B_2O_3, mol%	P_2O_5, mol%	Sm_2O_3, mol%
1	72.31	18.00	9.69	–
2, 2A	72.06	18.00	9.69	0.25
3, 3A	71.81	18.00	9.69	0.50
4, 4A	71.56	18.00	9.69	0.75
5, 5A	71.31	18.00	9.69	1.00

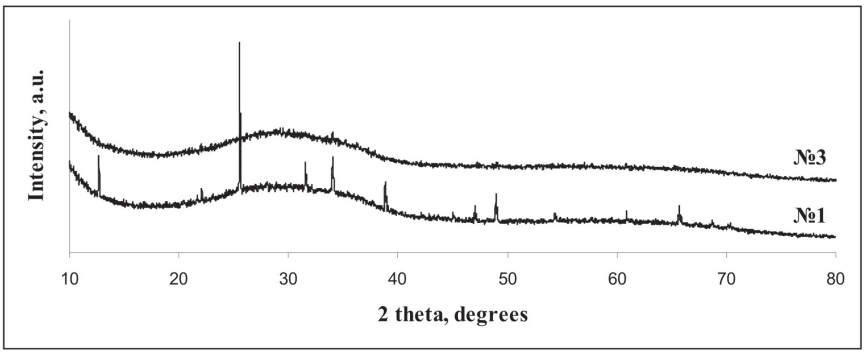


Fig. 1a. Powder X-ray diffraction patterns for samples № 1, 3

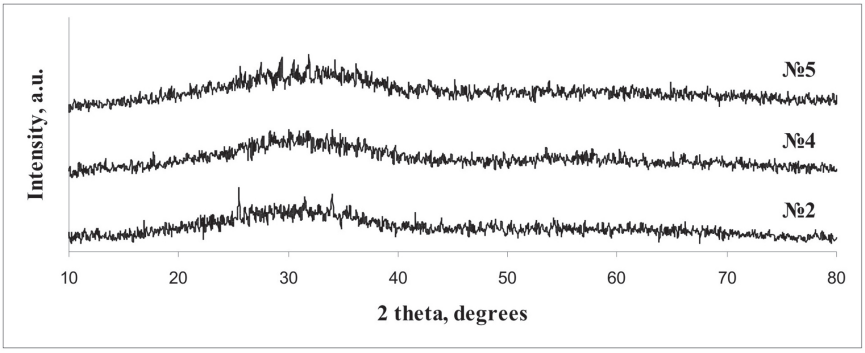


Fig. 1b. Powder X-ray diffraction patterns for samples № 2, 4, 5

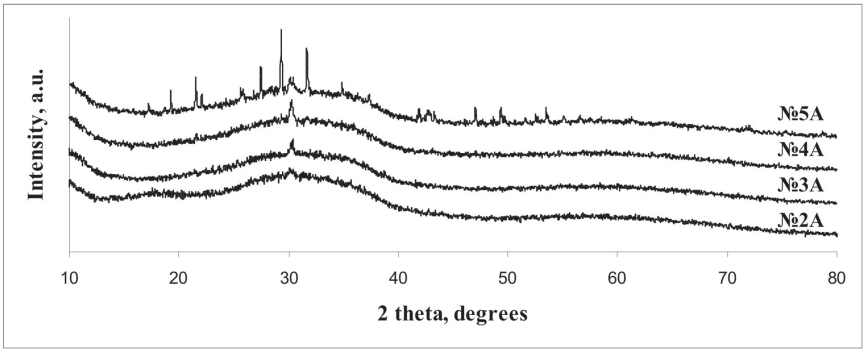


Fig. 1c. Powder X-ray diffraction patterns for heat-treated samples № 2A, 3A, 4A, 5A

Fig. 1. Powder X-ray diffraction patterns for the synthesized and heat-treated samples

Looking at XRD figure of heat-treated samples it is possible to observe nano crystallization in samples 2A, 3A, 4A (0.25, 0.5 and 0.75 mol% Sm). Only sample 5A (1% Sm) is showing an evidence of nano and poly crystallization mixed structure. Crystalline phase identified in all heat-treated samples is indexed as samarium phosphate $SmPO_4$ – Monazite-(Sm) (ICSD file 01-083-0655 – [12, 15]). The appearance of phosphate in the crystallization products shows the important role of PO_4 structural units in the structural network of borophosphate glasses.

The average crystallite size (diameter, d) is calculated by using the Scherer's equation [16]:

$$d = \frac{0.89\lambda}{\beta \cos\theta}, \qquad (1)$$

where λ is the wavelength of X-ray radiation, β is the full width at half maximum of the diffraction peak and θ is the diffraction angle. The average calculated crystallite size of $SmPO_4$ nanocrystals was found to be in the range 80–120 nm.

DSC analysis of annealed and non-annealed glass samples are in accordance with XRD results. The presented thermograms show 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 the Figure 2. However in Figure 3 almost full crystallization can be observed after annealing. It is not possible to observe Tg and there is no any other transitions that could be evaluated. This result is confirmed by XRD data. The sample 5A is also opaque (non transparent).

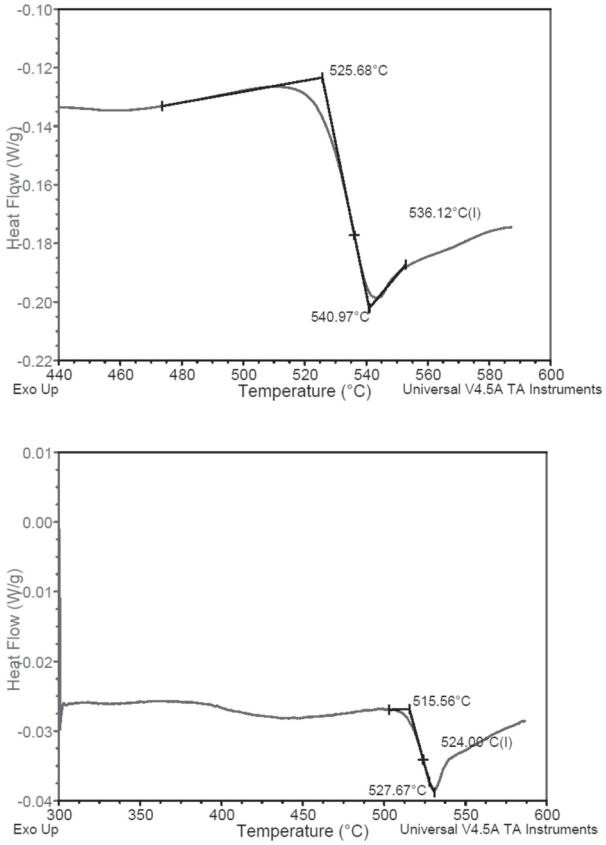


Fig. 2. DSC data of the samples No 2 and No 2A (0.25% Sm)

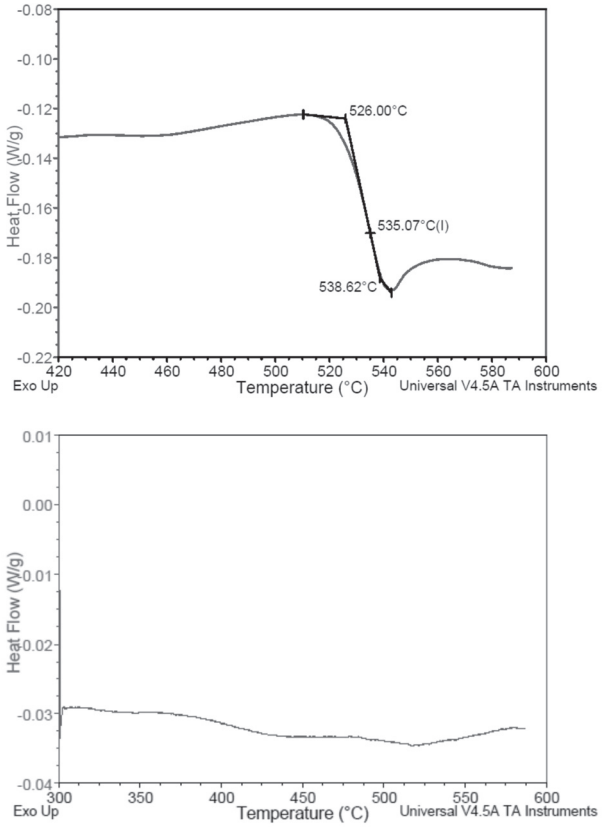
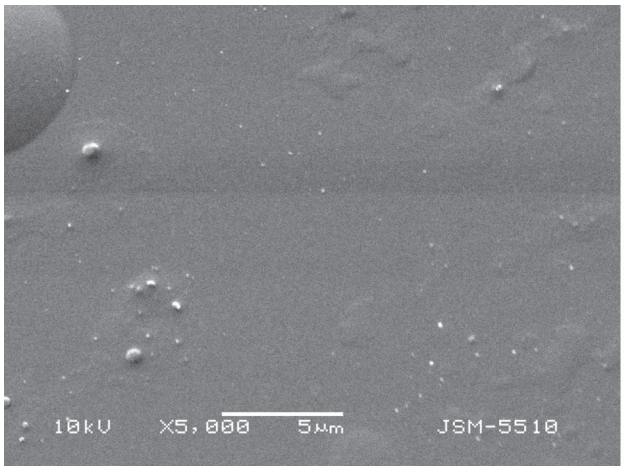


Fig. 3. DSC data of the samples No 5 and No 5A (1% Sm)



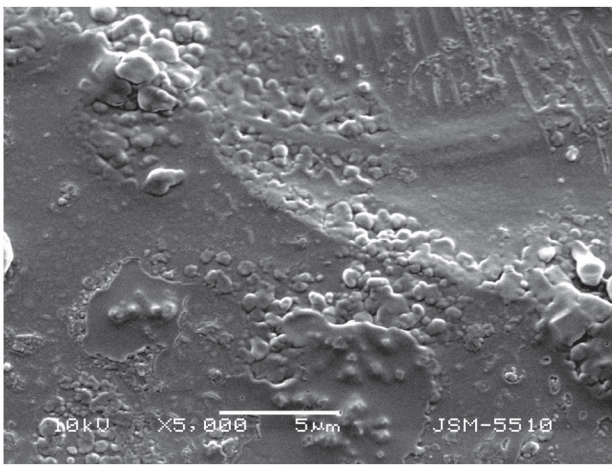


Fig. 4. SEM images of the microstructure for the samples No 2 and 2A (0.25% Sm)

Scanning electron microscopy analysis was performed to study the particles size, shape and morphology of Sm-doped Zn-B-phosphate glasses. SEM images of the fractured surface of synthesized and heat-treated samples are presented in Fig. 4 (samples 2 and 2A – 0.25% Sm) and Fig. 5 (sample 5A with highest content of Sm – 1%). The SEM micrographs are clearly showing that the synthesized non annealed samples are homogeneous. A spontaneous formation of defined crystallites takes place in all annealed samples. The nanocrystallites are spherical in shapes and joined each other to form clusters. The size of these clusters increases with an increase of samarium content. The size of nanocristallites is over 100 nm and corresponds to results obtained from the XRD data as presented above. A polycrystalline material for the sample with highest content of Sm (Fig. 5) is formed.

According to our previous research [17] the most efficient LED for pumping the glasses is the one at 395 nm. In all of the presented spectra, we can observe three peaks at correspondingly 560, 600 and 645 nm. The band at 600 nm, which corresponds to orange emission, is the most intense [18]. In addition, a fourth peak at 704 nm is observed which is considerably weaker than the former. These peaks are characteristic for Sm^{3+}. The photoluminescence spectra of synthesized samples are illustrated in Fig. 6.

CONCLUSIONS

ZnO-rich borophosphate compositions doped with different content of Sm (0.25, 0.5, 0.75 and 1.0 mol%) were synthesized, annealed and inves-

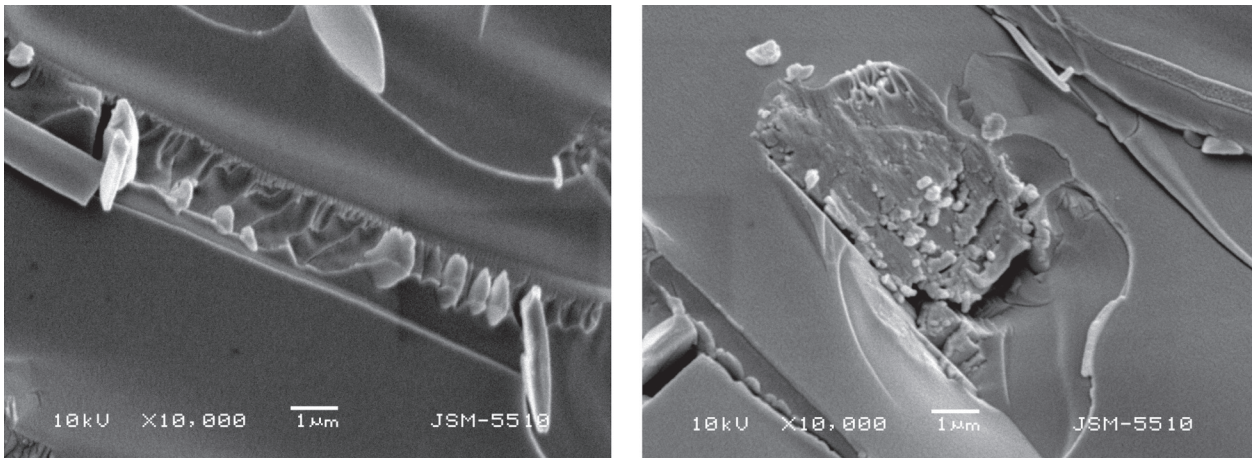


Fig. 5. SEM images of the microstructure for heat-treated sample No 5A (1% Sm)

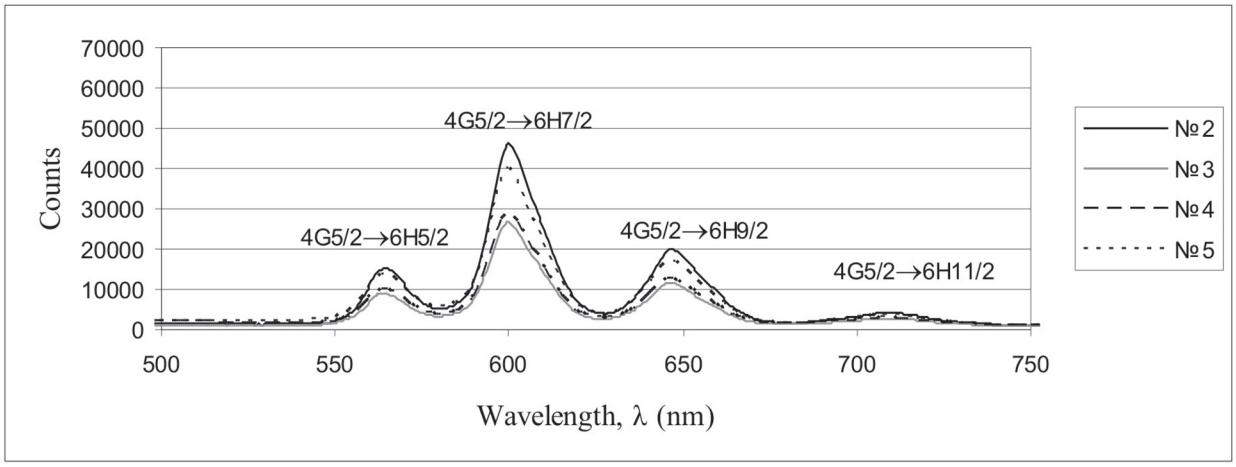


Fig. 6. Photoluminescence spectra for samples No 2–5 at an excitation wavelength 395 nm

tigated by powder X-ray diffraction, SEM analysis, differential scanning calorimetry (DSC) and photoluminescence spectroscopy.

The results show that synthesized samples are predominantly amorphous, with the presence of nano (samples % 2–4) and polycrystalline structures (sample % 5) in heat-treated samples. The crystalline phase identified in all heat-treated samples is indexed as samarium phosphate $SmPO_4$. The average XRD calculated crystallite size of $SmPO_4$ nanocrystals is in the range of 80–120 nm. This result is confirmed by SEM images.

Thermal analysis (DSC) is showing that obtained materials are stable (T_g is over 500 °C) and materials transformations are in accordance to XRD and SEM data.

All doped samples with different content of Sm are optically active with a photoluminescence signal out of Sm^{3+} ions.

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ВЛИЯНИЕ НА СЪДЪРЖАНИЕТО НА САМАРИЙ ВЪРХУ СТРУКТУРАТА И ОПТИЧНИТЕ СВОЙСТВА НА ЦИНК-БОР-ФОСФАТНИ МАТЕРИАЛИ

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(Резюме)

Материалите на основата на ZnO, P_2O_5 и B_2O_3 (стъкла, стъклокерамики и полокристални композиции) имат важно значение, както от научна, така и от технологична гледна точка поради техните полезни приложения. Дотирането с редкоземни елементи води не само до промяна в структурата, но и до вариране на оптичните, магнитните и електричните им свойства.

Настоящото изследване представя синтез и характеристика на богати на ZnO борфасфатни материали, дотирани със Sm със състав $xSm_2O_3 – (72{,}31–x)ZnO – 9{,}69P_2O_5 – 18B_2O_3$, където x = 0, 0,25, 0,5, 0,75, 1 mol%. Синтезираните композиции са отгрети с цел получаване на нанокристална структура. Материалите са охарактеризирани чрез рентгеноструктурен анализ, диференциално сканираща калориметрия, сканираща електронна микроскопия и фотолуминесцентни измервания.

Получените резултати показват**,** че синтезираните материали са основно аморфни с присъствие на нано- и поликристална структура в отгретите проби. Всички дотирани с различно съдържание на Sm проби дават фотолуминесцентни пикове в интервала 550–650 nm отнасящи се за Sm^{3+} йони.