Na–Gd PHOSPHATE GLASSES
Preparation, thermal and scintillating properties

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The present paper deals with preparation, thermal properties and radioluminescence of Ce-doped Na–Gd phosphate glasses. Thanks to their high radioluminescence intensity, three times greater than that of BGO, these glasses are promising materials for the detection of neutrons, γ- and X-rays. The glasses with a Gd concentration up to 89 mol% were prepared by a rapid quenching technique in air. Their thermal properties were determined using DSC and temperatures of glass transition were measured in addition using TMA. Temperatures of glass transition, crystallization and melting depend on Gd concentration and they follow the liquidus line in a phase diagram of binary system in which two eutectics and a congruently melting compound exist. High glass-forming ability of this glass system was found evidenced. The glasses containing at least 30 mol% Gd were moisture resistant.

Keywords: *Ce-doped Na–Gd phosphate glasses, DSC, radioluminescence, thermal properties, TMA*

Introduction

Sodium phosphate $NaPO_3$ is an efficient glass former; it is possible to convert it into vitreous state both single and in combination with many other compounds, which alone do not form glasses at all. Phosphate glasses of different compositions are important class of materials attractive for use in optical applications, solid-state batteries, laser technology and immobilisation of radioactive nuclear waste. Very recently our research team developed a new type of phosphate glasses, based on cerium doped sodium gadolinium phosphate, for effective detection of neutrons, γ- and X-rays [1, 2]. A new idea was introduced, namely, by adding gadolinium ions into sodium phosphate to form the gadolinium subsystem which supports resonant energy migration and thus increases luminescence efficiency. This idea was experimentally confirmed and it was found that the radioluminescence intensity of these glasses increased with Gd concentration. The radioluminescence intensity of Ce-doped glasses with a Gd concentration of 20 mol% is as much as 3 times greater than that of only Ce-doped phosphate glass without Gd [2]. However, until now high quality glasses have been prepared only with a Gd concentration between 5 and 40 mol% in the starting batch [3]. The main goal for the technological research is to find an appropriate procedure for the preparation of high quality Na phosphate glasses with a concentration of Gd as high as possible exhibiting maximum radioluminescence intensity.

This contribution deals with the Ce-doped (1 mol%) Na–Gd phosphate glasses and its aim is to present the latest results achieved in preparation and characterisation, including X-ray excited radioluminescence spectra, of these glasses with a gadolinium concentration covering the whole possible concentration range.

Experimental

Cerium doped sodium-gadolinium phosphate glasses were prepared by a rapid quenching technique using reagent-grade Na_2CO_3, P_2O_5, $GdPO_4$ and $CePO_4$. Concentrations of individual cations in molar percentage ranged for Na between 90 and 10 and Gd between 9 and 89 in the starting batch. Concentration of Ce was 1 mol%. The starting materials in the required molar ratios were melted in a quartz crucible in air at 1200°C and homogenised. Then the melt was cast into a graphite mould, which was preheated to a temperature of about 50 K below the expected temperature of glass transition. The mould with the sample was tempered for 2 h at that temperature and then cooled down with a rate of 10 K h^{-1} to room temperature.

Thermal properties of the prepared glass samples, such as the temperatures of glass transition, crystallization and melting of the devitrified phases were determined by differential scanning calorimetry (DSC). DSC was carried out using a Netzsch STA 449C in the temperature range from 20 to 1000°C at heating and

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cooling rates of 10 K min^{-1}. The mass of the charges was approximately 15 mg. Temperatures of glass transition were also determined by thermomechanical analysis (TMA) on samples of about 3×3×2 mm^3 in size. The measurements were carried out using a TA Instruments 990 TMA 943 in a flow of dried nitrogen from room temperature up to the softening of individual tested glasses. The results presented were measured during the second heating of the sample. Radioluminescence characteristics were measured using a procedure described by Nikl *et al*. [2]. The glassy state and composition of the devitrified phases were determined from X-ray diffraction measurements using a Bruker D8 powder diffactometer. The density of glasses was measured by the Archimedes method with toluene as an immersing medium.

Results and discussion

The most important result obtained in our research into phosphate glasses is the preparation of Ce-doped (1 mol%) Na–Gd phosphate glasses with a Gd concentration up to 90 mol%, i.e. considerably higher with respect to previously achieved results (40 mol% in the starting batch) [3]. Prepared samples were transparent, colourless, without any cracks and 1×1×2.5 cm^3 in size. Their glass character was confirmed using X-ray diffraction. This progress in glasses preparation was reached thanks to the detailed study of structure and composition of glassy and devitrified samples. According to it the composition of the starting batch was readjusted and homogenisation temperature, tempering and cooling process were optimised as well. Content of P_2O_5 in the starting batch was increased in order to convert all the compounds into metaphosphates $(PO_3)^-$. Phosphate glasses are generally prepared using ammonium dihydrogen orthophosphate ($NH_4H_2PO_4{\cdot}2H_2O$) [4] but our scintillating glasses cannot be prepared by this procedure because the impurities like $(OH)^-$ originate in the glass and negative influence its optical properties. Consequently, a new preparation method was developed in which P_2O_5 substitutes for ($NH_4H_2PO_4{\cdot}2H_2O$) [2, 3].

The TMA and DSC traces of sample 60/39/1 are shown in Fig. 1 (the samples are noted as X/Y/Z, where the letters denote the molar concentrations of Na, Gd and Ce in the starting batch). The TMA curve shows only the effect of glass transition and softening. DSC trace exhibited except the intense endothermic feature characterising glass transition further weak peaks, both exothermic and endothermic. It was very difficult to assign them to thermal effects of crystallization and melting. To identify them, the samples were annealed above their melting point and slowly cooled down. The DSC curves of the same

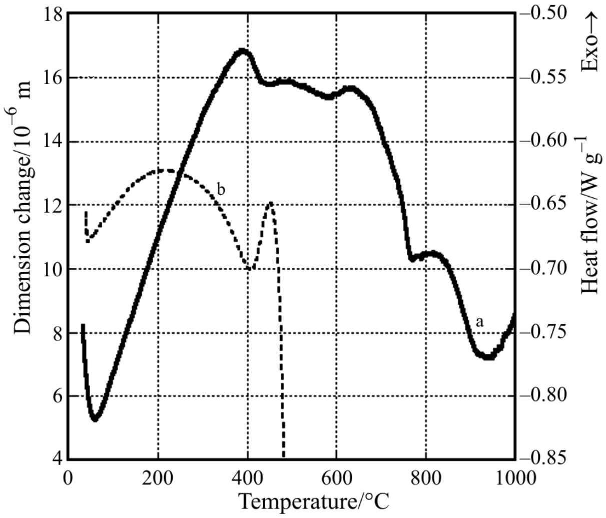

Fig. 1 Thermal analysis of sample 60/39/1: a – DSC, b – TMA

glass samples, before and after annealing were compared. The effects occurring at the same temperatures were analysed and we tried to assign them to the individual effects.

The compositions of glasses prepared, their thermal properties such as glass transition, crystallization and melting temperatures and numerical measures of glass forming tendency K_{gl} are summarised in Table 1. Glass transition temperatures determined using both DSC and TMA are presented and their values for individual glass samples agree very well. The temperature range between 300 and 600°C guarantees good temperature stability in application. Temperatures of glass transition, crystallization and melting change with glass composition – the dependence of glass transition temperatures on Gd concentration in glass is shown in Fig. 2. They vary with Gd concentration

Table 1 The composition of glasses and their thermal properties

Sample	Transition temperature/°C				K_{gl}
	TMA	DSC			
Na/Gd/Ce	T_g	T_g	T_c	T_m	
90/9/1	338	335	451	608	0.739
83/16/1	345				
80/19/1	313	321	460	695	0.591
70/29/1	377	390	547	680	1.081
60/39/1	412	409	598	747	1.268
50/49/1	432	441	642	790	1.358
40/59/1	426	425	557	810	2.491
30/69/1	386				
24/75/1	453				
20/79/1	497	493	686	814	1.508
10/59/1	522	519	593	809	0.343

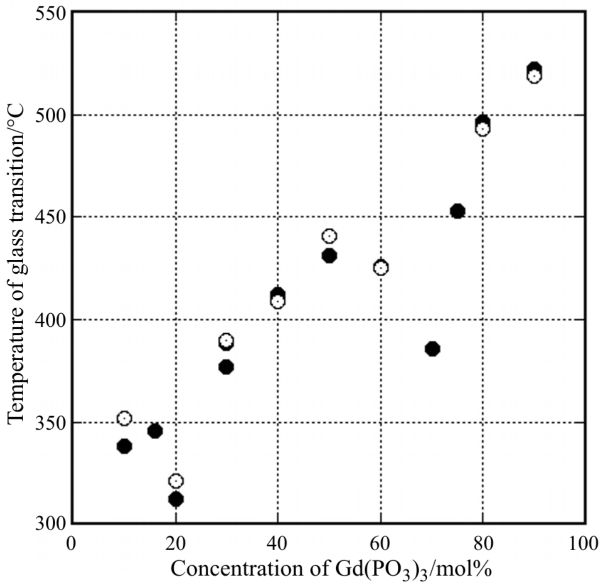

Fig. 2 The dependence of glass transition temperature on glass composition; ● – TMA, ○ – DSC

and follow the liquidus line in a phase diagram of binary system in which two eutectics and a congruently melting compound exist. The minimal temperature of glass transitions of 313 and 386°C were found using TMA for Gd concentrations of about 20 and 70 mol%, respectively. As intermediate compound, $NaGd(PO_3)_4$ was determined by X-ray diffraction in devitrified samples. The dependencies of crystallization and melting temperatures exhibit similar traces as glass transition temperature. However, because they were not determined reliably, further research is necessary to plot these dependencies or even to construct the phase diagram of this system.

The glass-forming ability was evaluated according to the relation

$$K_{gl}=(T_c-T_g)/(T_m-T_c) \quad (1)$$

where K_{gl} is the numerical measure of glass forming tendency, T_g, T_c and T_m are the temperatures of glass transition, crystallization and melting [5]. For our estimation the data reading-off the DSC traces were used (Table 1). If the K_{gl} is greater than 0.5 the glass-forming tendency is high, what means that sodium phosphate with Gd concentrations between 9 and 79 mol% creates easily the glass.

Test of chemical resistance of glasses against water steam presented in [3] showed that the glass samples with Gd concentration lower than 30 mol% were slightly hygroscopic. Increasing Gd concentration improves chemical resistance and the glasses with Gd content greater than 30 mol% are quite stable.

The density of tested samples is shown in Fig. 3. It depends first of all on the Gd concentration and ranges from 2.68 for glass with a Gd concentration

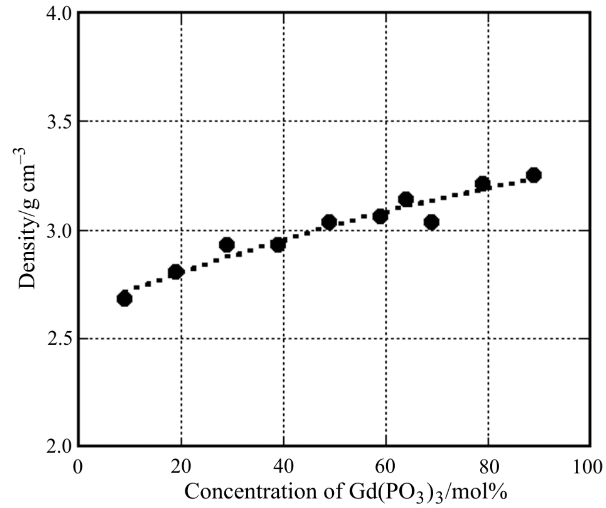

Fig. 3 Glass density *vs*. Gd concentration

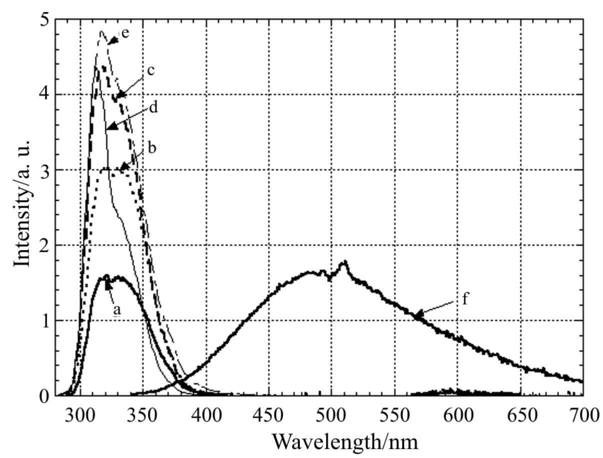

Fig. 4 The X-ray excited radioluminescence spectra (28 kV, Mo cathode) of glasses with compositions a – 90/9/1, b – 70/29/1, c – 50/49/1, d – 30/69/1, e – 10/89/1 and f – BGO

of 9 mol% to 3.25 g cm^{-3} for glass containing up to 89 mol% Gd in the starting batch.

Because of importance of these glasses for scintillator application the X-ray excited radioluminescence spectra were measured on a set of prepared glass samples and compared with that of BGO – $Bi_4Ge_3O_{12}$ (a scintillator standard). Figure 4 shows X-ray excited radioluminescence spectra of five selected samples with various Gd concentration. The radioluminescence efficiency increased sharply with Gd concentration. While for the Gd concentration of 9 mol% (90/9/1) it is comparable to that of BGO, for concentration of 89 mol% (10/89/1) it is almost threefold.

Conclusions

Na–Gd phosphate glasses of high quality with Gd concentration between 9 and 89 mol% and doped by 1 mol% of Ce in the starting batch were prepared by a rapid quenching technique in air. The prepared glassy samples were transparent, colourless, without any cracks and 1×1×2.5 cm in size. The thermal properties such as temperatures of glass transition, crystallization and melting of all the prepared samples were determined using DSC. Temperature of glass transition were also measured using TMA. The measured temperatures vary with Gd concentration and follow the liquidus line in a phase diagram of binary system in which two eutectics and a congruently melting compound – $NaGd(PO_3)_4$ – exist. All the prepared samples exhibited glass transitions above 300°C, what guarantees glass stability in a sufficiently broad temperature range. The glasses with Gd concentration greater than 30 mol% are very stable and moisture resistant what is very attractive for their employment as components in detectors or in other optical applications. The glass forming ability for samples with Gd concentration between 9 and 79 mol% was evaluated as high what is important from the production point of view. Radioluminescence efficiency of Ce doped glasses increased sharply with Gd concentration and for a glass with a Gd concentration of 89 mol% it is almost threefold in comparison with BGO.

Acknowledgements

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