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Preparation method and thermal properties of samarium and europium-doped alumino-phosphate glasses

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ABSTRACT

The present work investigates alumino-phosphate glasses from Li_2O–BaO–Al_2O_3–La_2O_3–P_2O_5 system containing Sm^{3+} and Eu^{3+} ions, prepared by two different ways: a wet raw materials mixing route followed by evaporation and melt-quenching, and by remelting of shards. The linear thermal expansion coefficient measured by dilatometry is identical for both rare-earth-doped phosphate glasses. Comparatively to undoped phosphate glass the linear thermal expansion coefficient increases with 2×10^{-7} K^{-1} when dopants are added. The characteristic temperatures very slowly decrease but can be considered constant with atomic weight, atomic number and f electrons number of the doping ions in the case of T_g (vitreous transition temperature) and T_{sr} (high annealing temperature) but slowly increase in the case of T_{ir} (low annealing temperature–strain point) and very slowly increase, being practically constant in the case of T_D (dilatometric softening temperature). Comparatively to undoped phosphate glass the characteristic temperatures of Sm and Eu-doped glasses present lower values. The higher values of electrical conductance for both doped glasses, comparatively to usual soda-lime-silicate glass, indicate a slightly reduced stability against water. The viscosity measurements, showed a quasi-linear variation with temperature the mean square deviation (R^2) being ranged between 0.872% and 0.996%. The viscosity of doped glasses comparatively to the undoped one is lower at the same temperature. Thermogravimetric analysis did not show notable mass change for any of doped samples. DSC curves for both rare-earth-doped phosphate glasses, as bulk and powdered samples, showed T_g values in the range 435–450 °C. Bulk samples exhibited a very weak exothermic peak at about 685 °C, while powdered samples showed two weak exothermic peaks at about 555 °C and 685 °C due to devitrification of the glasses. Using designed melting and annealing programs, the doped glasses were improved regarding bubbles and cords content and strain elimination.

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1. Introduction

Several studies on optical glasses doped with rare-earth ions were made since 1980th [1]. The interaction between UV laser radiation and phosphate/silicate glasses doped with Ce^{3+} and Sm^{3+} ions generates luminescence in visible domain with direct applications as scintillation materials for X-ray detection [2]. Vitreous active laser media are phosphate or silicate glasses doped with rare earth ions, such as Nd^{3+}, Tb^{3+}, Ho^{3+}, Er^{3+}, Yb^{3+}, Pr^{3+}, Gd^{3+}, Tm^{3+} [3].

The researches on amplifiers based on fiber glass doped with Er^{3+} ions generated a profound impact on the evolution of optical communication systems [4]. Second degree optical non-linearity was recently induced in doped phosphate glasses, with applications in laser sources as frequency conversion guides [5]. Laser fibers based on phosphate glasses doped with Er^{3+}/Yb^{3+}, having high power and fluorescence present a lot of utilizations in commercial and military domains [6]. Comparatively to silicate glasses the phosphate matrix can include rare-earth ions (erbium and ytterbium) in higher concentrations and the energy of emitted radiation increases without increasing of upper conversion speed [7]. A new class of laser phosphate glasses doped with Er^{3+}/Yb^{3+}/Nd^{3+}/Pr^{3+}, adnoted QX which will bring a quantic vault in laser fibers technology was developed [8]. Recently channel wave guide lines, based on phosphate glasses doped with erbium, obtained by selective Na–Ag ionic exchange process was reported [9–13]. Recent work

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of the authors are related to phosphate glasses doped with transition and rare-earth ions, as bulk and thin films and their complex characterization [14–18].

The most part of papers on phosphate glasses doped with rare-earth ions are related to laser useful properties, such as fluorescence or light transmittance at specific wavelengths. Thermo-mechanical properties, such as expansion and viscosity as well as density, solubility at different temperatures, evolution of glass in time at different temperatures are scarcely investigated.

For this reason the purpose of this study is to investigate the thermo-mechanical properties of phosphate glasses from Li_2O–BaO–Al_2O_3–La_2O_3–P_2O_5 system, doped with rare-earth ions such as samarium and europium oxides. The novelty of this paper consists of evaluating the working limits of new Eu and Sm doped phosphate glasses, namely the working temperatures domain where no crystalline phases appear. Dilatometric and thermal characterization of these new glasses and the melting and annealing established and improved programs for their obtaining with quality are also elements of novelty. The correlation between the characteristic temperatures and atomic features of Eu and Sm as dopants aims at increasing the knowledge data base in the field of rare-earth-doped glasses. This study is useful to better understand the influence of the thermal treatments on the thermo-mechanical properties of the doped-glasses and aims at improving the quality and thermal behavior of these materials. Other novelty of this study is the improvement of Sm and Eu-doped glass synthesis parameters and the establishment of effective working limits for these vitreous materials. These doped-phosphate glasses have new applications in optical sensors for measuring the mechanical displacement of different moving parts of engines from automotive and energy industry, based on the fluorescence properties of the dopants embedded in the phosphate matrix. The quality of the doped-phosphate glass is correlated to its practical uses. Thus, the thermal treatments of these glasses can be designed using previously measured thermal properties.

2. Experimental

Phosphate glasses doped with samarium and europium trivalent ions (rare-earth phosphate glasses – REPG) have been obtained by a wet non-conventional melting-quenching method, using analytical grade reagents: Li_2CO_3, $BaCO_3$, Al_2O_3, La_2O_3, H_3PO_4, Sm_2O_3 and Eu_2O_3 [16,19,20]. This method is termed as wet method because all the reagents are introduced in a H_3PO_4 solution followed by evaporation and homogenization of all components by mechanical stirring. In contrast with this method, the conventional method consists of mixing and grinding of all dry powder reagents followed by melting the batch.

The doped phosphate glass compositions correspond to the following molar formula:

$$REPG1 : 56.66LiPO_3 \cdot 28.33Al(PO_3)_3 \cdot 10Ba(PO_3)_2 \cdot 2La_2O_3 \cdot 3Sm_2O_3;$$

$$REPG2 : 56.66LiPO_3 \cdot 28.33Al(PO_3)_3 \cdot 10Ba(PO_3)_2 \cdot 2La_2O_3 \cdot 3Eu_2O_3.$$

In order to study the influence of rare-earth oxides on the thermal properties of the doped glasses, a vitreous material having a similar composition, without Sm or Eu was prepared, denoted as base glass, with the molar formula $58.42LiPO_3 \cdot 29.21Al(PO_3)_3 \cdot 10.31Ba(PO_3)_2 \cdot 2.07La_2O_3$.

Taking into account that P_2O_5 is volatilized from phosphoric acid in initial stage of preparation and from phosphates in latest stage of melting and refining process in amount of over 8%, as resulted from previous work [21], a supplement of phosphoric acid was introduced to compensate the loss of phosphorus pentoxide. The oxide compositions (weight %) of the doped-phosphate glass, taking into account the above-mentioned addition, are presented in Table 1.

Oxide composition corresponds to initial reagents mixture which is processed in order to obtain doped-phosphate glasses, and it is calculated taking into account both the molar formula of each sample of glass as well as the type of the used reagents, providing the vitreous oxide network after melting and pouring of the glass.

The preparation method includes the following steps: (i) homogenization and evaporation of the water from the raw materials (in quartz crucibles provided with flexible electric stirrer, on a hotplate), up to 100–120 °C; (ii) drying at 180–200 °C (in electric oven); preliminary heat treatment carried out between 200 and 800 °C; (iii) melting and refining of the glass at 1000–1200 °C; (iv) molding of the glass and (v) annealing of the molded glass. This laboratory method is used to prepare both the undoped alumino-phosphate and the doped-alumino-phosphate glasses containing rare-earth oxides. The main chemical reactions occurring in the course of glass preparation are the next ones:

$$Li_2CO_3 + 2H_3PO_4 \rightarrow 2LiPO_3 + CO_2 + 3H_2O \quad (1)$$

$$Al_2O_3 + 6H_3PO_4 \rightarrow 2Al(PO_3)_3 + 9H_2O \quad (2)$$

$$BaCO_3 + 2H_3PO_4 \rightarrow Ba(PO_3)_2 + CO_2 + 3H_2O \quad (3)$$

The wet method applied to prepare phosphate glasses offers the advantage of a best homogenization of the raw materials even in the early phases of processing and also allows to initiate metaphosphates forming even in the first stages of the preliminary heat treatment. This process reduces the duration of melting and refining and provides a high optical uniformity of the obtained phosphate glasses.

Rare-earth oxides are mixed together with the other reagents during the initial stage of the preparation process, that aims at performing the homogenization of the dopant in the glass batch.

For the improvement of the quality as regard the bubbles, cords and strains elimination from the alumino-phosphate glass, several attempts were done of re-melting the shards of as-above obtained glass.

2.1. *Melting of REPG*

2.1.1. *Melting from raw materials*

The alumina crucible with the mixture of raw materials was introduced into the oven for the implementation of the REPG melting–forming–conditioning–refining–cooling program. The oven has the following technical features: maximum working temperature: 1400 °C; heating elements: bars of silite.

The obtained glasses have been cast in preheated square molds made of pure spectral graphite.

2.1.2. *Melting from shards of glass*

In order to increase the quality of the obtained glass, as regards the content of bubbles and cords, the method of melting from shards has been tested. Shards of samples have been used together with a mixture of raw materials. Shards were previously grinded in an agate mortar to a grain size which is characterized by integral passing on the sieve of less than 0.8 mm.

2.2. *Annealing of REPG*

The annealing of the glass samples was made in an oven equipped with kanthal heating wires. Technical characteristics of oven are: maximum working temperature: 1100 °C; heating elements: kanthal wires.

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