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Thermal, optical and structural properties of Tb doped zinc aluminum phosphate glasses

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Abstract

Zinc aluminum phosphate (ZAP) glasses and Tb^{3+} ions doped zinc aluminum phosphate (Tb doped ZAP) glasses have been prepared by melt quenching method. The effects of the ZnO and Tb_2O_3 content on the thermal, optical and structural properties of the ZAP, $(90-x)$ P_2O_5–$10Al_2O_3$–xZnO ($x=30$, 35, 40 mol%), and the Tb doped ZAP, $(90-x)$ZAP xTb_2O_3, vitreous systems were investigated. It was found that the glass transition temperature (T_g) and glass dilatometric softening temperature (T_d) were lowered as ZnO content increased. The addition of Tb^{3+} ions also increases the T_g and T_d, and the coefficient of thermal expansion (CTE) is reduced to less than 5×10^{-6}/°C under higher Tb_2O_3 content. Higher refractive index ($n\sim1.55$) is achieved for Tb doped ZAP under higher ZnO and Tb_2O_3 content. Besides, the Tb doped ZAP shows greater chemical durability with the dissolution rate as low as 3×10^{-7} g/cm^2-min. Analyses from FTIR, Raman and NMR spectroscopies are discussed in comparison with the quantitative results of bridging oxygen (BO) and non-bridging oxygen (NBO) by O1s-XPS. It was found that the metaphosphate (Q^2) dominates the ZAP glasses; however, the pyrophosphate (Q^1) becomes significant for the Tb doped ZAP under addition of higher Tb_2O_3 content, leading the enhanced glass network. Highest Tb^{3+}/Tb^{4+} ratio with value of 2.33 is observed for $(90-x)(50P_2O_5$–$10Al_2O_3$–$40ZnO)$–xTb_2O_3 ($x=3$), which exhibits much enhanced emission band at 545 nm. Also, the sensitized effect of ZnO on the emission band is verified. The enhanced emission properties suggest that the Tb doped ZAP glass is a promising material for the application in green LED device by modulation of Tb composition.

Keywords: Zinc aluminum phosphate glasses; Tb^{3+} doped; Glass properties; Infrared spectroscopy; Emission properties

1. Introduction

The zinc phosphate glasses are becoming more and more attractive because they can be prepared and easily modified with ZnO to obtain the depolymerized phosphate structures by exceeding the pyrophosphate composition limit. When zinc was further incorporated into the binary phosphate systems such as BeO. P_2O_5 and MgO. P_2O_5, the composition of metaphosphate (Q^2) chain and zinc coordination changes become complicated and show anomalous composition/properties behavior [1]. The binary zinc ultraphosphate glass, xZnO. $(1-x)P_2O_5$ with $0\leqq x\leqq0.5$ and zinc polyphosphate glass, xZnO. $(1-x)P_2O_5$ with $0.5\leqq x\leqq0.71$, have been prepared by Brow et al. [1] and Meyer [2], respectively, and the structure and the distribution of Q^i-phosphate sites were investigated by Raman and NMR spectroscopy. Their results show that the addition of low ZnO content leads to the increase in Q^2-phosphate sites [1,2], and as $x>0.6$, Q^0 tetrahedra is formed, i.e., chain phosphate unit dominates the glass structure at lower ZnO content, and pyrophosphate (Q^1) and orthophosphate (Q^0) units become dominant in the glass network at higher ZnO composition [1]. A series of xZnO. $(1-x)P_2O_5$ with $0.5\leqq x\leqq0.71$ exhibit refractive index (n) ranged from 1.52 to 1.64, and the n values increase monotonically with increasing ZnO content [1]. The bond strengths of the non-bridging P–O^- bonds in the orthophosphate, pyrophosphate and metaphosphate (Q^2) chain

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structures were calculated to be 1.25 vu, 1.33 vu and 1.5 vu [1], respectively, and could be assigned to characteristic Raman peaks to investigate the effect of ZnO on the structural transition.

Aluminum is one of the most widely used oxides which could play an intermediate role between glass former and glass modifier in the glass structure due to three different coordination numbers [3]. The formation of P–O–Al chains in $Al(OP)_4$ plays as the glass former, while excess Al^{3+} ions lead to $Al(OP)_6$ and play as the glass modifier. Several phosphate glasses such as P_2O_5–Al_2O_3–K_2O–BaO have been made for analysis of UV absorption and fluorescence dynamics [4]. Al_2O_3 also shows high solubility with rare earth ions, thus zinc–aluminoborosilicate (ZABS) glasses, SiO_2–Al_2O_3–B_2O_3–ZnO–Li_2O–BaO, and europium (Eu)/dysprosium (Dy) co-doped ZABS glasses have been fabricated for the application of white LED [5]. The ZABS host glass shows high glass transition temperature ($T_g \sim 658$ °C) and high optical transmission in the visible range. By adjusting the concentration ratio between Eu and Dy ions, the color of luminescence between blue and white could be tuned. Zhu et al. [6] have also made a complex P_2O_5–SrO–BaO–B_2O_3–Ce_2O_3–Tb_2O_3–Eu_2O_3 glass system to achieve full-color luminescence; however, the structural characteristics were not discussed in their work. In addition, it has been shown that the addition of Al_2O_3 and ZnO mixed in the phosphate glasses may produce $Al(OP)_4$ and $Zn(OP)_4$ in the glass network to increase the number of the bridging oxygen (BO), thus the chemical durability can be enhanced [7,8]. Our former work has prepared new Li_2O–SrO–Nb_2O_5–P_2O_5 glasses, where the addition of Nb ions efficiently increases the glass density and the refractive index. Meanwhile, the glass structure is dominated by tetrahedral NbO_4 unit and the whole network can be enhanced as well [9]. However, for Nb_2O_5 content higher than 20 mol%, blue color is appeared and accompanied by the reduced optical transmittance [10]. More recently, several rare earth ions such as Dy [5], Ce [6], Eu [5,6], Tb [6,11], Tm [11] and Sm [11] have been utilized to dope with phosphor materials or various glasses [12], and these luminescence glasses can be used as an alternative to LED [11]. Verma et al. [12] has prepared MO–Al_2O_3:Tb phosphor materials, and showed that the ratio of Tb^{3+} to Tb^{4+} states is varied under different calcination temperatures and can affect the luminescence intensity. However, the effects of these rare earth ions on the structural properties have yet to be quantitatively investigated.

In the present work, a series of zinc aluminum phosphate (ZAP) glasses and Tb doped ZAP have been prepared. The effects of ZnO and Tb composition on the thermal, optical, chemical durability and structural properties of the ZAP glass system were investigated respectively. In addition, the structural bonding transition from bridging oxygen and non-bridging oxygen was examined by FTIR and Raman analysis. O1s-XPS and ^{31}P–NMR spectroscopies provide quantitative information about Q^i tetrahedral distributions in the glass structure with addition of Tb_2O_3 contents. Tb 4d-XPS analyses provide quantitative results of Tb^{3+}/Tb^{4+} ratio; the energy transfer mechanism of Tb^{3+} transition from $^7F_6 \rightarrow {}^5D_j$ ($j=1$, 2, 3 and 4) was described according to the UV absorption spectra. The sensitized effect of ZnO on the Tb doped ZAP glass was verified from the enhanced green emission (545 nm).

2. Experimental procedures

2.1. Glass preparation

Targeting glasses have the nominal molar compositions $(90-x)P_2O_5$–$10Al_2O_3$–xZnO (ZAP), where x was varied between 30 and 40 mol%. All raw materials are reagent-grade including $NH_4H_2PO_4$ (99.0% purity, Hayashi Pure Chemical Industries, Ltd.), Al_2O_3 (98.0% purity, Riedel-de Haen) and ZnO (99.0% purity, Hayashi Pure Chemical Industries, Ltd.). The above constituents in given proportions were melted in an aluminum crucible furnace to obtain the host ZAP glasses. Tb_4O_7 (99.9% purity, Alfa Aesar) was used as a dopant oxide to prepare a series of Tb doped ZAP glasses, $(100-x)$ZAP $x Tb_2O_3$, with nominal Tb_2O_3 contents between 0 and 3 mol%. The batches were first preheated to 600 °C to remove NH_3, NO_3 and H_2O with a heating rate of 10 °C/min. The above materials were then melted for 1 h in air ambient at temperatures between 1200 °C and 1400 °C depending on the glass compositions. Melts were quenched onto stainless steel plates to form rectangular samples with dimension of 25 mm × 20 mm × 1 mm followed by thermal annealing at 400–500 °C in air for 6 h.

2.2. Characterization of glass properties

Density, ρ, was measured by the Archimedes method at room temperature using deionized water as the immersion fluid. The experimental uncertainty is ± 0.001 g/cm^3. Molar volumes (V_m) were then calculated from density (ρ) and the molecular weight (W_m) of the nominal glass composition ($V_m = W_m/\rho$). Refractive index (n) was measured by a Digital Abbe Refractometer (ATAGO DR-A1, λ: 589 nm); the estimated uncertainty is ± 0.1% relative.

Thermal properties of glasses were measured by a thermo-mechanical analyzer (Perkin Elmer TMA7 Analyzer). The sample thickness is 5 mm. The experimental uncertainty was about 0.1 °C. Aqueous durability was measured by immersing a sample glass (size: 5 mm × 5 mm × 1 mm) in de-ionized water (100 ml, 70 °C) for 72 h. Since the weight loss of each glass was linear with time, the chemical durability expressed as the dissolution rate (in g/cm^2-min) can be obtained from the slope of the curve given by

$$DR\ (\text{dissolution rate}) = \frac{W_i - W_f}{A \times t} \quad (1)$$

where W_i and W_f is the initial and remaining weight (g) of sample glass, respectively. A is surface area (cm^2) of the sample and t is the immersion time in minutes.

2.3. Structural analyses by spectroscopy

The infrared spectra of the ZAP glasses were collected with a Fourier-transformed infrared spectrometer (FTIR, Jasco 300E) was used to obtain information about the glass structure. Glasses