Study of structures and properties of ZnO–Sb₂O₃–P₂O₅–Na₂O glasses

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The influence of ZnO substitution by 0 – 12 wt.% Na₂O on the properties of ZnO–Sb₂O₃–P₂O₅–Na₂O glasses has been investigated. The structure and properties of the glasses with the composition of (13.86–x)ZnO–57.93Sb₂O₃–28.21P₂O₅–xNa₂O (x = 0 – 12 wt.%) were characterized by infrared spectra (IR), X-ray diffraction and differential thermal analysis (DTA). The results of IR indicated an increase in the intensity of symmetric vibrations of P–O–P bond, which was confirmed by the improvement of water durability with the increasing amount of Na₂O in the range of 0 – 10 wt.%. Substitution of 10 wt.% Na₂O led to the weight loss of the glass to 5.93 mg/cm^{–2} after immersion in deionized water at 50 °C for 24 h. The results of XRD showed that the ability of crystallization decreased, indicating the good thermal stability of the glass. The glass containing 8 wt.% Na₂O had the best properties in every respect and might be an alternative to lead based glasses for the applications, providing further composition improvement.

Keywords: *spectroscopy; X-ray method; chemical properties; antimony phosphate*

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1. Introduction

Lead based low-melting point glasses have been widely used in numerous commercial applications, such as adhesives for glass, ceramics or metal materials, sealing or coating frits for electronic components, conductive or resistive pastes. However, the large amount of lead is deleterious to human health and environment [1–3]. Therefore, the development of lead-free low-melting point glasses with properties, such as adjustable coefficient of thermal expansion (CTE), low T_g , high water durability, high electrical resistance and low cost, has attracted a great interest.

Phosphate glasses show several advantages over silicate and borate ones. These glasses are technologically important materials because they possess some superior physical properties, such as high thermal expansion coefficient, low melting temperature, low transition temperature and high electric conductivity [4–8]. These glasses have a consid-

erable potential for the application in optical data transmission, solid-state batteries, low-melting sealing, sensing and laser technology [4]. However, phosphate glasses typically have a relatively poor chemical durability, which often limits their usefulness. Several studies have shown that the chemical durability of phosphate glasses can be improved by addition of various oxides, such as Al₂O₃, Fe₂O₃, Bi₂O₃, ZrO₂, SiO₂, MnO₂, etc. [1–4, 9]. In addition, phosphate glasses possess higher refractive index than silicate and borate ones. Therefore, the ZnO-containing phosphate glasses with Na⁺ are of interest in connection with optical waveguides based on the ion exchange Na⁺/K⁺ method [4, 6].

The improved water durability of ZnO–P₂O₅ glasses containing SnO and Sb₂O₃ have also been proved [3]. The glasses containing large amount of SnO have lower T_g and excellent water durability. However, the problem of T_g fluctuation in ZnO–P₂O₅ phosphate glasses has not been eliminated completely, which makes them not suitable as a potential alternative to lead glasses. Moreover, the glasses containing Sb₂O₃

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have also low melting and transition temperatures as Sb³⁺ has a lone electron pair. Zhang et al. [5] synthesized Sb₂O₃-containing ZnO–P₂O₅ glasses with low T_g and improved water durability. But the thermal stability decreased with the increasing amount of Sb₂O₃. Therefore, in this work, the influence of ZnO substitution by 0–12 wt.% Na₂O on the properties of ZnO–Sb₂O₃–P₂O₅–Na₂O glasses has been studied.

2. Experimental procedure

The raw materials used in the preparation of (13.86– x)ZnO–57.93Sb₂O₃–28.21P₂O₅– x Na₂O ($x = 0 - 12$ wt.%) glasses were diammonium phosphate ((NH₄)₂HPO₄), antimony trioxide (Sb₂O₃), zinc oxide (ZnO), and sodium carbonate (Na₂CO₃), all of analytical reagents grade. The 100 g batch was well-mixed and pre-tread at 260 °C for 2 hours to avoid the evaporation of P₂O₅ at high temperature, and then melted using a high-purity alumina crucible at 850 to 950 °C for 2 hours. The homogenous melt was cast into a pre-heated mold to form a rectangular block and a club. The block and the club were properly annealed at a temperature 10 °C above the T_g for more than 1 hour, and then slowly cooled to room temperature in a muffle furnace. The samples were cleaned and kept in desiccators before use.

The coefficient of thermal expansion α was measured by a horizontal dilatometer (PCY, Xiangtan Instrument, China). Differential thermal analyzer (WCR-2D, Beijing Photics, China) was used to measure the glasses transition temperature T_g and the crystallization temperature T_x at a heating rate of 10 °C/min. The thermal stability was determined from the temperature difference between T_g and T_x . Water durability of the glasses was evaluated by the weight loss (mg/cm²) of a sample (approximately 20 × 5 × 5 mm³) after inserting it in a volumetric flask with 200 mL deionized water at 50 °C for 24 h. Infrared spectra of the glasses were measured with an infrared spectrophotometer (PE, model spectrum One-B). X-ray diffraction patterns of the glass samples after heating were collected using an X-ray diffractometer (D/Max-3B, Rigaku, Japan).

3. Results and discussion

3.1. IR spectra and XRD analysis

Infrared spectra of the glasses are shown in Fig. 1. The spectrum of Na0 glass reveals some indirect structural information: the absorption peaks at 926 cm^{−1} and 718 cm^{−1} can be ascribed to the asymmetric and symmetric vibrations of P–O–P bonds, respectively [4–6]. The band around 538 cm^{−1} is the absorption peak of bending vibration of P–O bonds, δ (P–O), of Q⁰ tetrahedra [5, 8, 13]. The absorption peak around 628 cm^{−1} is assigned to the stretching vibration of P–O–Sb linkages [5]. The absorption peak at 463 cm^{−1} is the asymmetric stretching vibration of Sb–O bond (O_{NB}) [9, 12]. Some significant differences in the line shapes of the FT-IR spectra have appeared with the increase of Na₂O content. Bond of Sb–O asymmetric stretching mode moves to higher frequency with the increase of Na₂O content. The intensity of absorption peak at 718 cm^{−1} increases, which indicates that the structure of PO₄ tetrahedron is strengthened when Na₂O replaces ZnO because of the increasing number of P–O–P bridges [9]. This change also proves the improvement of water durability (Fig. 4). Meanwhile, the bond around 538 cm^{−1}, which is due to the bending vibration of P–O bonds of Q⁰ tetrahedra, decreases in intensity. This change leads to the lower crystallization ability, according to XRD patterns and DTA curves. A new absorption peak at 1083 cm^{−1} occurs, which is affirmed to be the PO₂ symmetric stretching vibration bond (ν_s PO₂). It is obvious that the intensity of vibration of P–O[−] groups at 1163 cm^{−1} increases gradually as ZnO is replaced by Na₂O. The phenomenon demonstrates that excessive Na⁺ ions tend to form more end groups in the phosphate chain structure [14].

Portions of glasses containing 0, 2, 8 wt.% Na₂O were crystallized by heating for 3 h at 550, 538, and 580 °C, respectively, which correspond to the temperature of crystallization peak in the DTA curves (Fig. 3). The XRD patterns shown in Fig. 2 indicate that SbPO₄ (PDF#35-0829) is the major crystalline phase. It is obvious that the intensity of crystallization peaks becomes weaker from Na0 to

Na8, which denotes that the thermal stability of the glass systems is systematically improving [9].

Fig. 1. Infrared spectra of the glass samples with different amounts of Na₂O.

Fig. 2. X-ray diffraction patterns of Na0, Na2, Na8 glasses after heating for 3 h.

3.2. DTA and CTE measurements

The differential thermal analysis (DTA) curves of the glasses are shown in Fig. 3. The thermal stability is confirmed with an approximate method by measuring the difference between T_x and T_g , $\Delta T = T_x - T_g$ [1, 5, 10]. Glass transition temperature T_g and the first crystallization temperature T_x are shown in Table 1. ΔT increases gradually from 117 °C for Na0 to 172 °C for Na8, indicating the

increase in thermal stability. From Fig. 3 it is clear that there are no peaks from Na10 and Na12, which suggests excellent thermal stability with the increasing amount of Na₂O. This phenomenon can be explained on the basis of XRD patterns, which show that the ability of crystallization declines. The CTE (α) data show an increasing tendency from $104 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ for Na0 to $158 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$ for Na12, according to Table 1.

Fig. 3. DTA curves of the glasses with different amounts of Na₂O.

3.3. Water durability

In order to investigate the chemical stability of phosphate glasses containing different amounts of Na₂O, water durability was measured for the samples immersed in deionized water at 50 °C for 24 h. The curve of weight loss in Fig. 4 shows that the values clearly vary with the Na₂O content, firstly decreasing from $9.0 \pm 0.05 \text{ mg/cm}^2$ for Na0 glass, to $5.9 \pm 0.03 \text{ mg/cm}^2$ for Na10 glasses and then increasing to $9.40 \pm 0.03 \text{ mg/cm}^2$ for Na12.

It is well known that the poor water durability of phosphate glasses is attributed to the breaking of phosphate chains and their dissolution into water [7, 11, 14]. According to the literature [5, 15] it can be seen that the P–O–Sb bonds are corrosion resistant because of their high polarizing power. The results of FT-IR spectra indicate an increase in intensity of the P–O–Sb linkages and explain the improvement of water durability from

Table 1. Temperature of initial crystallization T_x , $T_x - T_g$ and α of the synthesized glasses.

Sample	Na ₂ O content (wt.%)	T_g (± 2 °C)	T_x (± 2 °C)	$\Delta T = T_x - T_g$ (± 2 °C)	$\alpha/10^{-7}$ °C ⁻¹
Na0	0	398	515	117	104
Na2	2	362	488	126	113
Na6	6	356	501	145	140
Na8	8	350	522	172	138
Na10	10	347	No peak	–	157
Na12	12	328	No peak	–	158

Fig. 4. Weight loss of the glass samples containing different amounts of Na₂O after immersion in deionized water at 50 °C for 24 h. (The error is estimated as ± 5 %).

Na0 to Na10. In addition, the increase of P–O–P bond also can explain the phenomenon. But an excess of Na₂O in glasses could break down the network structure by providing a large number of free O²⁻ anions and increase the amount of end groups (P–O⁻) in the phosphate chain structure, which has been verified by the FT-IR spectra.

4. Conclusions

The structures and properties of the glasses with the composition (13.86– x)ZnO–57.93Sb₂O₃–28.21P₂O₅– x Na₂O ($x = 0 - 12$ wt.%) have been investigated. The ZnO substitution by Na₂O resulted in a decrease in glass thermal stability and an im-

provement of water durability. Meanwhile, Sb₂O₃ played an important role in improving water durability as the glass network former connected with [PO₄] tetrahedra with increasing Na₂O content [5].

The variations in chemical and thermal properties of the glass systems seem to be related to the variation of glass structures. FT-IR indicates an increase in the intensity of asymmetric stretching vibration of Sb–O bond and symmetric vibrations of P–O–P bond. This is confirmed by the improvement of water durability. Meanwhile, XRD and DTA showed the improved thermal stability and glass forming ability, which can be explained by the decrease of bending vibration of P–O bonds of Q⁰ tetrahedra. In addition, the glass containing 8 wt.% Na₂O could be an alternative to optical waveguides providing its further improvement.

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