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Structure and properties of ZnO-containing lithium–iron–phosphate glasses

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ABSTRACT

Lithium–iron–phosphate glasses with compositions of $(20-x)Li_2O{\cdot}xZnO{\cdot}30Fe_2O_3{\cdot}50P_2O_5$ ($x = 0$–7.2) have been prepared. The influences of the amount of ZnO on the structure, physical and chemical properties, and crystallization behavior of the glasses were investigated using Fourier transform infrared spectroscopy, differential thermal analysis and X-ray diffraction techniques. The density of glass was measured according to the Archimedes principle. The chemical stability was evaluated based on the weight loss after the glass particles were boiled in water. The results indicate that Zn^{2+} ions cross-linked the phosphate chains by forming P–O–Zn bridges when 2 mol% of ZnO was added. When the amount of ZnO was further increased, $[ZnO_4]$ tetrahedra were formed and ZnO acted as a glass network former, integrating the phosphate glass network. The density, chemical stability and the activation energy of crystallization of the glasses increased with the amount of ZnO, whereas the glass transition temperature decreased. All thermally treated glasses showed surface crystallization with $LiFeP_2O_7$ as the crystalline phase.

1. Introduction

$[PO_4]$ tetrahedron is the basic structural unit in phosphate glasses. It contains three bridging oxygen and one doubly bonded oxygen (P=O). Due to the existence of the P=O bonds, pure or binary phosphate glasses possess layered or chain-like structure, which is susceptible to chemical attacks [1]. With the addition of other oxides, the chemical stability of the phosphate glasses could be greatly improved, because the added cations can connect the layers or interweave the chains in the phosphate glasses, leading to the formation of three-dimensional glass network [2–4]. Phosphate glasses are of great interest as they may find applications in medicine, optics, electronics, etc. [5–7].

ZnO is among the oxides which were used to improve the chemical stability of phosphate glasses [8]. Since Zn^{2+} has a large ion radius and an electronic configuration with 18 outer-shell electrons, ZnO is an intermediate oxide in glass [9]. It can join the glass network by forming $[ZnO_4]$ [10] or cross-link the phosphate chains by forming P–O–Zn bridges [11]. ZnO can also be a glass modifier. In this case, Zn^{2+} occupies interstitial sites in glass network [12]. Due to the complexity of Zn^{2+} in the structure of phosphate glasses [13,14], ZnO has varied influences on the properties of glasses. For example, Takebe et al. [8] reported that the chemical durability of binary ZnO–P_2O_5 glasses with 50–70 mol% of ZnO increased with the concentration of ZnO. In ZnO–Na_2O–P_2O_5 glasses, either as a network modifier or former, the density of glass was found to increase with the increase of ZnO, while the glass transition temperature and durability first increased and then decreased [15]. However, the substitution of CaO with ZnO in the P_2O_5–CaO–Na_2O glasses resulted in a linear increase in the glass density and decrease in the glass transition temperature [16].

The main purpose of this article is to investigate the influences of ZnO on the structure and properties of lithium–iron–phosphate (LIP) glasses. In addition, LIP glasses are precursors to prepare olivine-like $LiFePO_4$ glass–ceramics (a potential cathode material in rechargeable lithium ion batteries) and antiferromagnetic lithium–iron diphosphate [17–19]. Therefore, the crystallization behavior of ZnO-containing LIP glasses is also discussed.

2. Materials and methods

Analytic grade reagents of Li_2CO_3, Fe_2O_3, $NH_4H_2PO_4$ and ZnO were used as starting raw materials to prepare glass batches. Glasses with molar compositions of $(20-x)Li_2O{\cdot}xZnO{\cdot}30Fe_2O_3{\cdot}50P_2O_5$ ($x = 0$, 2.4, 4, 5.6, 7.2 mol%) were prepared by melting the batches in sintered silica crucibles at 1200 °C for 1 h in an electric furnace. The melts were cast in a steel mould and annealed at 350 °C for 1 h. According to the ratio of ZnO in the composition, the glass samples were encoded as Zn0, Zn2.4, Zn4, Zn5.6 and Zn7.2, respectively.

Fourier transform infrared (FTIR) spectra of the glasses were recorded on a Vertex-70 spectrometer (Bruker, Germany) in the range of 400–1600 cm^{-1} with a resolution of 1 cm^{-1}. The glasses were crushed, ground into fine powders, then mixed with KBr and pressed into discs. Differential thermal analysis (DTA) was carried out on an HCT-1 (Henven, China) thermal analyzer with empty

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alumina crucibles as reference. The samples were heated at 5 K/min to 800 °C. The extrapolated onset temperature of the first endothermic peak of the DTA curve was determined as the glass transition temperature (T_g).

The density of glass was measured based on the Archimedes principle. The chemical stability of the glass was evaluated by comparing the weights of the sample particles (425–250 μm) before and after being boiled in water for 2 h. For both the density and the chemical durability measurements, three parallel tests were performed on each sample and the data were averaged.

To investigate the crystallization behavior of the prepared glasses, different heating rates from 5 to 15 K/min were applied in the DTA analysis on each sample. The heating rate, the crystallization temperature and the activation energy of crystallization are correlated with the following formula.

$$\ln\left(\frac{T_c^2}{\beta}\right) = \left(\frac{E}{RT_c}\right) + C \qquad (1)$$

where, T_c is the temperature of the crystallization peak in the DTA curve; β is the heating rate; R is the gas constant and E is the activation energy of crystallization. As can be seen from Eq. (1), a plot of $\ln(T_c^2/\beta)$ versus $1/T_c$ gives a straight line. The activation energy of crystallization can then be calculated based on the slope, E/R, of the line [20].

The annealed glass samples were cut into small blocks. After being washed and dried, the blocks were thermally treated under different conditions (620 °C/5 h; 680 °C/1 h and 680 °C/5 h). The crystalline phase in the thermally treated samples was identified by X-ray diffraction (XRD) analysis on a D8-Advanced X-ray diffractometer (Bruker, Germany) using Cu Kα radiation.

3. Results and discussion

3.1. Structure of the LIP glasses

The FTIR spectra of the LIP glasses are depicted in Fig. 1. The observed bands from left to right are respectively assigned to (1) the asymmetric stretching vibrations of P=O bonds, supposed with the asymmetric stretching vibrations of PO^{2-} mode in the Q^2 units (at 1206 cm^{-1}) [11,21,22]; (2) the asymmetric stretching vibrations of $P–O^-$ in Q^2 units (at 1084–1103 cm^{-1}) [11,14]; (3) the asymmetric stretching vibrations of P–O–P bonds (at 920–933 cm^{-1}) [11,21,23,24]; (4) the symmetric stretching vibration of P–O–P chains (at 779–752 cm^{-1}) [23]; (5) the bending vibration of O–P–O bonds in Q^3 units (at 540–548 cm^{-1}) [23]; (6) the vibration of Zn–O bonds in [ZnO_4] tetrahedra (at 419 cm^{-1}) [25,26].

Significant spectral differences are observed when the amount of ZnO is increased from 2.4 to 4 mol%. It can be seen the band at 1206 cm^{-1} becomes weaker from sample Zn0 to Zn2.4 and eventually invisible in the spectra of samples Zn4, Zn5.6 and Zn7.2. In contrast, the band at 419 cm^{-1} related to the [ZnO_4] tetrahedra becomes distinguishable with the increase of ZnO. Based on these spectral changes, we suppose that with the initial substitution of Li_2O with ZnO (sample Zn2.4), $P–O^-$ terminals are connected due to the formation P–O–Zn bridges. When ZnO is further increased, the P=O bonds are broken down, accompanied by the formation of [ZnO_4] tetrahedra. ZnO turns to be a glass network former, integrating the phosphate glass network. The enhanced integration of the glass network is also evidenced by the shifts of the bands at 540, 920 and 1084 cm^{-1} to positions at larger wave-numbers. However, one should bear in mind that ZnO would also have negative effects on the glass structure. One the one hand, Zn–O bond has a smaller bonding energy than P–O bond, whereas the [ZnO_4] tetrahedron has a larger volume than the [PO_4] tetrahedron. Moreover, Zn^{2+} ions have an 18 outer-shell electron configuration and will exert a strong polarization on the O ions in the P–O bonds. Therefore, as more [ZnO_4] tetrahedra are formed, the compactness of glass decreases. On the other hand, the increase of 1 mol of Zn^{2+}

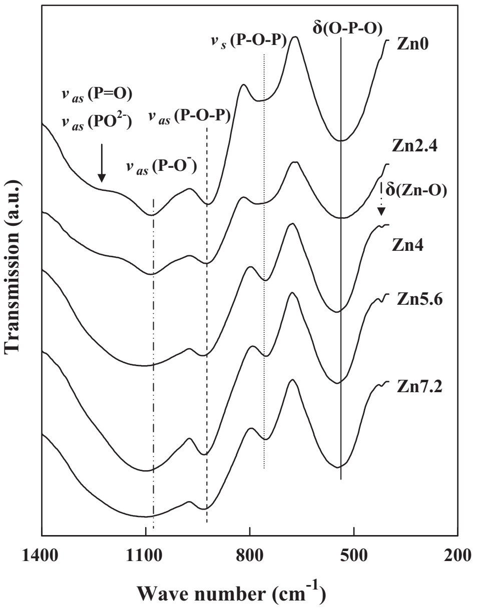

Fig. 1. FTIR spectra of the ZnO-containing LIP glasses.

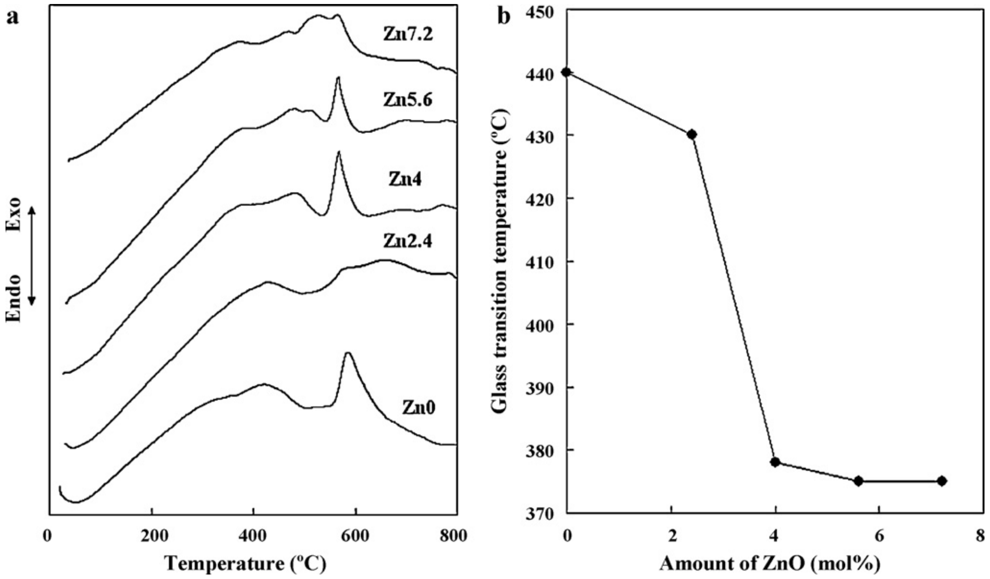

Fig. 2. DTA curves (a) and T_g values (b) of the ZnO-containing LIP glasses.

ions is at the expense of 2 mol of Li^+, the aggregation effect that Li^+ ions played on the glass network is decreased, resulting in a locally looser glass structure. When a large amount of ZnO is added, these negative effects become to manifest. As a result, the band at 779 cm^{-1} in the IR spectra of samples Zn0 and Zn2.4 shifts to positions at smaller wave-numbers for samples Zn4 ~ Zn7.2.

Fig. 2a shows the DTA curves of the glass samples. Differences are among the glass transition temperature (T_g), the shape and position of the main crystallization peaks. The T_g value almost monotonously decreases with the amount of ZnO (Fig. 2b). When the amount of ZnO increases from 2.4 to 4 mol% (samples Zn2.4 and Zn4), the largest decrease in T_g is observed. This trend is in very good agreement with the FTIR results, in which the spectrum of sample Zn2.4 differs significantly from that of sample Zn4.The decrease in the T_g value indicates that the viscosity of the LIP glass is reduced when Li_2O is replaced by ZnO. The strong polarizability of Zn^{2+} ions, the smaller bonding energy of Zn–O bonds and the larger volume of [ZnO_4] are responsible for the decrease in the viscosity of the LIP glasses with the additions of ZnO.

3.2. Density and chemical durability of the LIP glasses

Fig. 3 shows the densities and weight losses of the ZnO-containing LIP glasses. It can be seen that the density monotonically increases, while the weight loss decreases with the amount of ZnO. Sharp changes in the density and the weight loss are also shown for sample Zn2.4 relative to sample Zn4.

The density of glass is mainly influenced by the molecular weight of glass components, the integration and the compactness of the glass network. When Li_2O is substituted by ZnO, the larger molecular weight of ZnO contributes to the increase in the density. Moreover, the formation of [ZnO_4] improves the integration of the network of the LIP glass and consequently increases the density. However, the afore-mentioned negative effects of ZnO may manifest and partially offset the positive contributions of ZnO to the glass density. Therefore, the density only slightly increases when the amounts of ZnO increases from 4 to 5.6 and 7.2 mol% (samples Zn5.6 and Zn7.2).

Three-stage variations of the weight losses are shown for the glass samples (Fig. 3). Since the pH values of the testing solutions in which the LIP glasses were boiled are all acidic, the weight losses of the LIP glasses were caused not only by the leaching of metal ions, but also the dissolution of the phosphate network. The overall decrease in the weight loss with the increase of ZnO is due to the decrease in the concentration of Li^+ and the enhanced integration of the glass structure.

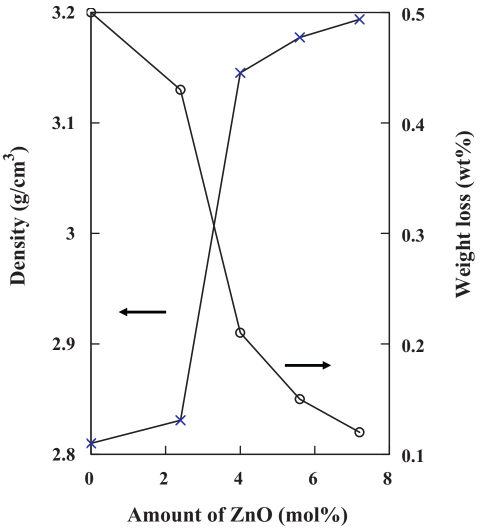

Fig. 3. Densities (○) and weight losses (×) of the LIP glasses with different amounts of ZnO.

3.3. Crystallization of the LIP glasses

The activation energy of crystallization, *E*, of the LIP glasses are shown in Fig. 4a. It can be seen that *E* increases with the amount of ZnO, suggesting that the substitutions of Li_2O with ZnO benefit the formation of more stable glasses.

After the glasses were heat-treated under different conditions, all the samples showed features of surface crystallization. However, the thickness of the crystallized layer increases with the temperature and soaking time applied in the treatments. Fig. 4b shows the XRD patterns of the glasses treated at 680 °C for 5 h. All the patterns can be indexed to the monoclinic $LiFeP_2O_7$ phase, indicating that the addition of ZnO does not influence the crystalline phase in the heat-treated samples. In addition, it can be seen that under the same conditions, the intensity of the diffraction peaks in

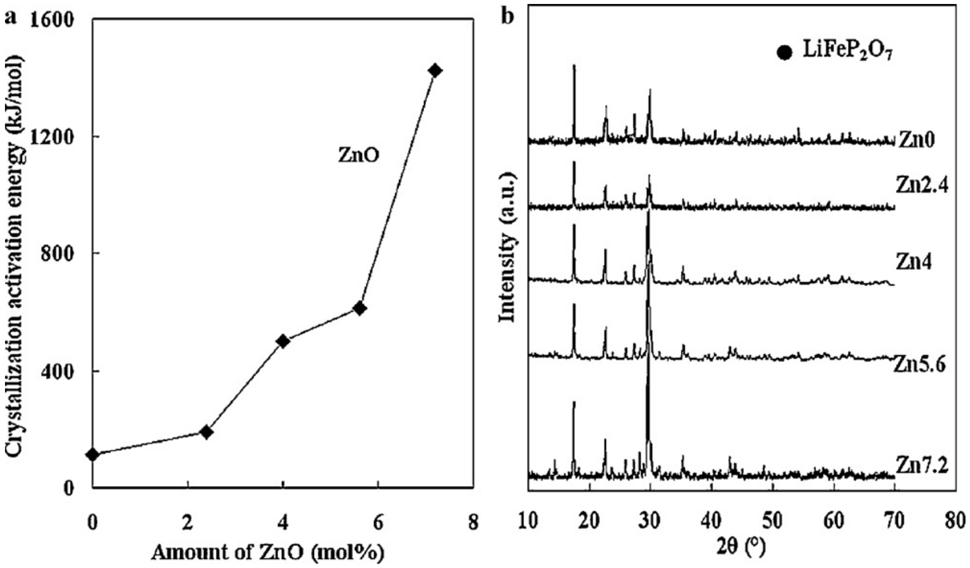

Fig. 4. Activation energy of crystallization (a) and XRD patterns of the ZnO-containing LIP glasses.

the patterns of Zn0 is higher than that of Zn2.4, indicating that the initial addition of ZnO retards the crystallization of LIP glass. However, comparison of the XRD patterns of the four ZnO-containing LIP glasses suggests that the crystallization is improved with increasing ZnO.

4. Conclusions

The structure, transition temperature, density, chemical durability and crystallization behavior of lithium–iron–phosphate glasses with different amounts of ZnO have been investigated. It was shown that the ZnO integrated the phosphate glass network by forming P–O–Zn bridges and $[ZnO_4]$ tetrahedra. When the amount of ZnO was increased, the glass density and chemical durability was increased, while the transition temperature was decreased. The activation energy of crystallization of the lithium–iron–phosphate glasses increased with the addition of ZnO. All the heat-treated samples had $LiFeP_2O_7$ as the crystalline phase.

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