Structure and crystallization kinetics of Li$_2$O modified sodium-phosphate glasses

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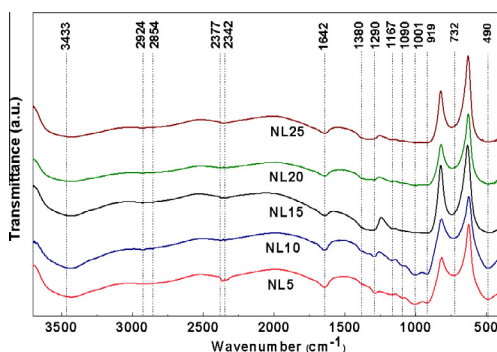
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GRAPHICAL ABSTRACT

FTIR spectra of the 5, 10, 15, 20 and 25 mol% Li$_2$O glasses.

ABSTRACT

Glasses of $55P_2O_5$—$(45 - x)Na_2O$—xLi_2O; $(5 \leqslant x \leqslant 25)$ are synthesized by melt-quench technique. The amorphous nature of the as-quenched sample is confirmed by X-ray powder diffraction (XRD). The glass transition (T_g) and crystallization temperatures (T_c) are evaluated under non-isothermal conditions using the differential thermal analyzer (DTA). Crystallization kinetic of present glasses is studied using Kissinger's and Augis–Benett models. The activation energies for glass transition (E_g) and crystallization (E_c) increases up to 15 mol% of Li$_2$O and after that decreases. 15 mol% Li$_2$O contained glass exhibits minimum crystallization frequency, which indicates its higher thermodynamic and kinetic stability than other glasses. FTIR and Raman analysis confirmed the higher polymerization of phosphate groups in 15 mol% Li$_2$O glass as compared to other glasses.

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Introduction

Sodium and lithium phosphate glasses/glass–ceramics are being used as solid electrolytes for battery applications [1–3]. During battery operation, the electrolyte degrades due to inter and intra diffusion with different components of battery. In this process, some undesirable crystalline phases are formed. The formation of these crystalline phases depends on the time, temperature and glass constituents. These crystalline phases get segregated in the glass matrix causing residual, thermal and mechanical stresses and changes the overall properties of electrolyte. In addition to this, P$_2$O$_5$ contained glasses exhibit poor thermal stability and are easily converted into glass–ceramics with undesirable crystalline phases. Higher thermal stability with lesser tendency to form undesirable crystalline phases can be achieved by proper selection of glass constituents without compromising the ionic conductivity of these glasses. However, the multi-component

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based glasses exhibit the complex crystallization process as compared to binary glasses. Moreover, the modifiers used in glasses can also help in increasing the thermal stability of glasses by delaying the crystallization process due to competition between different cations to form crystalline phases. In other words, it will increase the thermal stability without compromising the ionic conductivity of the glasses. For glasses, non-isothermal heat treatment has gained wide attention to study the effect of temperature on crystallization and stability of glasses [4,5]. Several theoretical models and mathematical functions are also proposed to explain the crystallization kinetics and thermal stability of the glasses [6,7]. Cheng [8], Money and Hariharan [9] studied the non-isothermal method and investigated the crystallization kinetics for Li_2O—SiO_2 and Li_2O—P_2O_5 systems, respectively. The activation energy observed for crystallization is higher for lithium silicate glasses ($\sim$269 kJ/mol) as compared to lithium phosphate glasses ($\sim$122 kJ/mol). It indicates that phosphate glasses can exhibit glass transition and crystallization at lower temperatures. Arora et al. [10] investigated the crystallization kinetics for borosilicate glasses and reported the formation of spherulitic crystalline phases with passage of time. They reported that spherulitic structure further transformed to equilibrium structure at a higher temperature. The above phenomenon designates that crystallization kinetics of glass depends on the processing conditions and their compositions. Crystallization of glasses is defined as a heterogeneous process where molecular and atomic diffusion leads to bulk crystallization at the phase boundary through an interface [11]. Sodium phosphate glasses are in great demand because of their strong glass forming nature, low crystallization and melting temperatures. It is expected that the replacement of Na_2O by Li_2O in P_2O_5 based glasses exhibit better ionic conductivity due to smaller size of Li^+ (0.76 Å) as compared to Na^+ (1.02 Å). On the other hand, the smaller size of Li^+ (0.76 Å) leads more rigorous interfacial reaction with electrodes and may form some undesirable crystalline phases with time and temperature. Therefore, it is worthwhile to study the effect of two modifiers (Na_2O and Li_2O) on the thermal stability and crystallization of glass. In the present study, glasses of composition $55P_2O_5$—$(45 - x)Na_2O$—xLi_2O; $(5 \leqslant x \leqslant 25)$ are synthesized by the conventional melt-quench technique. The mixed modifier effect on crystallization and their thermal stability in phosphate glasses are studied systematically. The obtained experimental data were fitted in different models to calculate the activation energy and also to propose the crystallization mechanism of the prepared glasses.

Experimental procedure

Glasses of $55P_2O_5$—$(45 - x)Na_2O$—xLi_2O; $(5 \leqslant x \leqslant 25)$ were prepared by melt quenching technique. Reagent grade of P_2O_5 (Sigma Aldrich, 99.99%), Na_2CO_3 (Sigma Aldrich, 99.99%) and Li_2CO_3 (Sigma Aldrich, 99%) were used as starting materials for the preparation of glasses. As per stoichiometry ratio for each glass, required amount of chemicals, were hand ground for 20 min in the benzene medium using an agate mortar pestle. Mixtures of these ground powders were transferred to alumina crucible and preheated for 4 h to ensure the removal of CO_2 and water and then melted at 1000 °C with heating rate of 5°/min. After holding the molten mass at 1000 °C for 30 min, it was splat-quenched between copper plates to obtain transparent glass. For all characterization, prepared glasses were hand ground for 2 h to obtain homogenous and fine powder. The amorphous nature of synthesized glass samples was confirmed by X-ray diffraction (PANalytical X'Pert PRO) using Cu Kα radiation of wavelength 1.541 Å with Ni-filter at room temperature. During measurement, voltage, current and scan speed were selected as 40 kV, 45 mA and 0.013°/min, respectively.

Continuous XRD patterns were recorded from 10° to 80° for all the samples. The synthesized samples containing 5, 10, 15, 20 and 25 mol% of Li_2O are labeled as NL5, NL10, NL15, NL20 and NL25, respectively, as have been given in Table 1. To know about the T_g (Glass transition temperature), T_x (Onset crystallization temperature) and T_c (Crystallization temperature), Differential thermal analysis (DTA) was done using Perkin Elmer (Model: Diamond Pyris) equipment. The DTA equipment was calibrated for temperature as explained by Krishnan and Nagarajan [12], where the accuracy of temperature measurement was ±1 °C. High purity (99.9%) alumina powder was used as a reference material. The experiments were performed under Argon atmosphere with flow rate of 180 ml/min for all the samples. The experiments were performed at different heating rates (10, 20, 30 and 40 °C/min) using 8 mg (±3 µg) of glass powder in a Pt crucible in the temperature range (200–800 °C). Archimedes principle was used to measure the density of the quenched samples using microbalance having least count (0.01 mg). Xylene was used an immersion liquid at room temperature. The well known equation used for density calculation is given below:

$$\rho_{Sample} = \frac{w_a}{w_a - w_x} \rho_x \tag{1}$$

where ρ_{Sample} stand for density of sample, w_a is the weight of sample in air, w_x is the weight of sample in xylene and ρ_x is the standard density of xylene ($\rho = 0.863$ g/cm³). The tabulated density values are the average of at least four independently measured values. Moreover, the molar volume of the synthesized samples was also calculated with the help of following equation:

$$V_M = \frac{M}{\rho} \tag{2}$$

where V_M is the molar volume, ρ is the density and M is the molar mass of the sample. FTIR spectra were collected at room temperature using Agilent (Model No. Carry-600) FTIR spectrometer. Mid-IR spectra were recorded using KBr beam splitter in the range of 2000–400 cm⁻¹. Two milligrams of each glass sample were ground with 100 mg of KBr into a fine powder and pressed into pellets for IR study. The changes in phosphate structural units in all glasses were examined by Raman spectroscopy. The data were collected using Renishaw in via Raman spectrometer. For data collection 514.5 nm line of Ar⁺ laser alongwith 20 mW power was used. The calibration was done with the help of silicon as a reference at 520 cm⁻¹ within ±1 cm⁻¹. For Raman spectra, the powder sample was loaded in a plastic sample holder, and surface was made smooth by compressing the powder. At different locations, spectra was taken to check the homogeneity in the glasses.

Results and discussion

Structural and thermal analysis

Fig. 1 shows the X-ray powder diffraction patterns of the as-quenched samples (NL5, NL10, NL15, NL20 and NL25) at room

Table 1
Glass compositions, theoretical density, experimental density and molar mass (V_M) for all glass samples.

Sample name	P_2O_5	Na_2O	Li_2O	Theoretical density (g/cm³)	Experimental density (g/cm³)	Molar mass (V_M)
NL5	55	40	5	2.32	2.37	183.24
NL10	55	35	10	2.31	2.40	180.77
NL15	55	30	15	2.29	2.44	179.17
NL20	55	25	20	2.28	2.41	177.57
NL25	55	20	25	2.27	2.36	175.96