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La_2O_3-added lithium-ion conducting silicate oxynitride glasses

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ABSTRACT

Lithium-ion conducting silicate oxynitride glasses of $40Li_2O$-xLa_2O_3-$(55\text{-}x)SiO_2$-$5Si_3N_4$ (mol%) were prepared using melt-quenching method under N_2 atmosphere. The doping of La_2O_3 is aim to improve the electrochemical properties of the silicate oxynitride glasses. The thermal behaviors of the silicate oxynitride glasses were studied by dilatometric and DSC methods. The effects of partial substitution of La_2O_3 on the thermal, mechanical, chemical and electrical properties of the silicate oxynitride glasses were investigated. The electrical conductivity is in the range of 0.39–1.81×10^{-6} S·cm^{-1} at room temperature and 3.54–4.21×10^{-3} S·cm^{-1} at 300 °C, respectively. Moreover, the oxynitride glasses had a high chemical stability to water. The addition of La_2O_3 to lithium silicate oxynitride glasses improved the ionic conductivity, which has a potential application as Li^+ glassy solid electrolyte materials.

1. Introduction

Lithium-ion battery technology, widely used in mobile electronic equipment, has significantly improved over the last decades; this is due to their distinctive advantages, such as high energy and power density, low memory effect and environmental friendliness [1–3]. In recent years, applications of lithium-ion batteries have been considered from energy storage devices for mobile equipment such as a portable computer to large energy storage devices such as electric cars [4]. Therefore, many researchers have been working to increase the energy density of lithium-ion batteries by utilizing electrode materials of increased storage capacity. High energy density, all-solid-state rechargeable cells using solid-state electrolyte are expected to be used in next-generation batteries. High ionic conductivity is required for solid electrolytes [5].

With a technological target for practical applications, various types of solid electrolytes have been studied for lithium-ion batteries, sensors, and electrochromic displays, etc. [6–9]. Solid-state ionic conductors exhibiting ionic conductivities of 10^{-3}–10^{-1} S·cm^{-1} are called superionic conductors, in contrast to conventional solid-state materials with conductivities of 10^{-10} S·cm^{-1}. The high ionic conductivity that is comparable with that of liquid electrolytes is achieved by a particular structure that enables easy diffusion of conducting ions [10]. Potential alternatives under consideration include amorphous glass solid electrolytes. The technological advantages of glassy electrolytes can be listed in terms of their nonporous nature, higher strength and simplicity of processing [11–12]. The glassy solid electrolyte structure successfully combines high disordering of the mobile alkali metal ion sublattice and a high concentration of mobile ions that are weakly bound to the anionic framework. As lithium is most electropositive, lithium-ion conducting oxide glasses are one of the promising candidates for lithium-ion battery applications. Ionic conduction in glasses has been studied in depth for decades [13–16]. Solid state lithium-ion batteries employing solid glass electrolytes have been the subject of many investigations.

Lithium silicate glass proves to be a representative system for the study of charge transport in ionic conducting glasses [17–18]. Alkali silicate glasses have been among the most thoroughly studied systems due to their high technological importance. These structural modifications affect the electrical and mechanical behavior of alkali silicate glasses. The presence of conduction pathways has been proposed to understand the dynamics of mobile ions in alkali silicate and other ionic conducting glasses [19–20]. Relevant literature shows that addition of nitrogen to silicate glass improves their thermal stability and chemical stability [21–22]. In oxynitride glasses, the dissolution rate and the thermal expansion coefficient decreased with the increase of nitrogen content [23–24]. Nitrogen is believed to replace the bridge oxygens to increase the crosslinking of the glass network. Lithium phosphorus oxynitride glass has higher ionic conductivity than the corresponding lithium phosphate glass [25–26].

Owing to the high thermo-physical, chemical and mechanical stability of lithium silicate glasses mixed with sesquioxides like La_2O_3 and Y_2O_3, they are considered as excellent materials for integrated optics, photonic and biomedical applications [27–29]. La, one of the rare-earth elements, is frequently used as an additive to improve the properties of

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the different material, such as lithium ionic conductivity of β-eucryptite [30]. We prepared Li-Al-P-O-N glasses containing AlN by melting batches at 1100–1150 °C under N_2 atmosphere. The dissolution rate increases slightly with increasing La_2O_3 content. The modified glass network structures create more conduction paths with low activation energy and give rise to a notable variation of electrochemistry properties as Al_2O_3 is replaced by La_2O_3. However, the chemical stability of the LiPON glass remains to be further improved. The highest ionic conductivity of the investigated LiPON glass with the lowest activation energy of 0.54 eV is up to 1.47×10^{-5} S·cm^{-1} at room temperature. However, this approach has not been applied to a promising LiPON glassy solid electrolyte [31].

In this paper, we investigated the performance improvement of the lithium silicate oxynitride glasses with different lanthanum content, with particular emphasis on the effect of ionic conductivity. This work is focused on the study of the effect of the partial substitution of La_2O_3 for SiO_2 on the properties of lithium silicate glasses for a high Li_2O content, i.e., thermal stability, chemical durability and ionic conductivity.

2. Experimental

2.1. Glass preparation

Laboratory reagent-grade Li_2CO_3 (99.9%), SiO_2 (99.9%), α-Si_3N_4 (99.0%) and 4 N grade La_2O_3 (99.99%) powders were chosen as the raw materials. Glasses in the lithium silicate oxynitride system were melted; the chemical compositions of all samples used were presented in Table 1. Dried powders were weighed and performed by mechanical agitation, mixed in isopropyl alcohol for 24 h, and then dried again. These dried powders were placed in a molybdenum crucible which was introduced into a preheated furnace at 450 °C to allow for removal of H_2O and CO_2 gas then followed by melting at the temperature range of 1350–1400 °C for 1.0–1.5 h. These lithium silicate oxynitride glasses were prepared by the melt-quenching technique in a glove box in an atmosphere of high purity nitrogen gas. Then the melted glass was then poured into a pre-heated graphite mold to relieve internal stress. The samples were then annealed at the appropriate temperature, determined by differential thermal analysis (T_g-50 °C). Final nitrogen contents of the glasses were determined by a nitrogen/oxygen determinator (TC-436 model, LECO Corp, USA). Nitrogen analysis results for all the obtained glasses showed that N losses were minimal, with glass compositions having nitrogen contents of within 3 wt% N of the starting composition. For further characterization and analysis, glass bars or glass plates were cut and polished.

2.2. Glass characterization

The amorphous nature of the samples was verified by an X-ray diffractometer (D/max 2500 model, Japan) with Cu-K$_\alpha$ radiation. Voltage and current were selected as 40 kV and 50 mA, respectively. Data were collected from 2θ = 20° to 80° at a scanning rate of 8°/min.

The density (ρ) of glasses was measured by the pycnometric method. Samples were ground into powder to avoid bubble effect. Results were averaged on 10 measurements. The experimental error on the measured value was ± 0.001 g/cm^3. The molar volume (V_m) was calculated using the relation $V_m = \Sigma(X_i \cdot M_i) / \rho$, where X_i is the molar fraction, M_i is the total molecular weight of the ith component.

The glass transition temperatures (T_g), crystalline phase formation temperatures (T_c), and melting temperatures (T_m) were determined using differential scanning calorimetry (DSC) methods. A part of each glass was ground to fine powders for differential scanning calorimetry. Differential scanning calorimetry (model Netzsch 404PC) of 50 mg powder of the glass was performed in a dry nitrogen atmosphere at a heating rate of 10 °C/min from room temperature to 1200 °C.

Dilatometric measurements were performed using a Netzsch DIL 402C dilatometer under flowing high purity argon environment, with samples in the form of bars of 20 mm length. Experimental error was ± 5 °C for the glass transition temperature and $\pm 0.01 \times 10^{-6}$ °C^{-1} for thermal expansion coefficients, respectively.

Vickers hardness was measured using a Matsuzawa micro-hardness tester Model MXT-a 1 with a pyramid-shaped diamond indenter. A load of 1000 g was applied on polished glass samples. At least 10 indentations were made on each sample, using the average indentation diagonal length to calculate hardness values in GPa.

The chemical durability of the glasses was measured in a beaker at 95 °C, using 0.1 L of deionized water. Weight loss measurements of the specimens after 60 min exposure to the solution were used to determine relative hydrolysis behavior. The dissolution rate (*D.R.*) was calculated from the weight loss normalized to the glass surface area and corrosion time. Experimental error was $\pm 0.1 \times 10^{-6}$ g·cm^{-2}·min^{-1} for the dissolution rate.

Ionic conductivity measurements were performed by electrochemical impedance spectroscopy in a Zahner Im6ex impedance analyzer (10–10^6 Hz). The samples were cut into discs of 1–2 mm in thickness and 10–20 mm in diameter, and platinum electrodes were sputtered on both faces as contacts for electrical measurements. The electrical conductivity (σ) is determined by the resistance value (R) read at the low-frequency intersection of the semicircle with the X-axis in the Nyquist plots using the sample geometric factor (l/A; l = thickness, A = electrode area) following $\sigma = l / (R \cdot A)$ formula. Conductivity measurements were performed in the temperature range of 298–573 K. Experimental error was $\pm 0.01 \times 10^{-6}$ S·cm^{-1} for the ionic conductivity.

The Raman spectra the glass samples were recorded on a Horiba Jobin Yvon LabRAM HR-800 spectrometer using a He-Ne laser (633 nm) and 8 mW of power before the entrance optics. The measurements were performed on bulk samples and made in the range 50–1400 cm^{-1} at room temperature.

3. Results and discussion

3.1. Glass formation

Lithium silicate oxynitride glasses having different compositions

Table 1
Chemical compositions (mol%), the theoretical and experimental nitrogen contents (wt%), and X-ray analysis of the lithium silicate oxynitride glasses doped with La_2O_3.

Samples no.	Compositions (mol%)				N (wt%) The.	N (wt%) Exp.	X-ray analysis
	Li_2O	Si_3N_4	SiO_2	La_2O_3			
G0	40	5	55	0	5.39	5.28 ± 0.01	Amorphous
G1	40	5	54	1	5.04	4.92 ± 0.01	Amorphous
G2	40	5	53	2	4.73	4.69 ± 0.01	Amorphous
G3	40	5	52	3	4.46	4.35 ± 0.01	Amorphous
G4	40	5	51	4	4.22	4.11 ± 0.01	Amorphous
G5	40	5	50	5	4.00	3.88 ± 0.01	Crystal