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Effect of simultaneous addition of aluminum and chromium on the lithium ionic conductivity of $LiGe_2(PO_4)_3$ NASICON-type glass–ceramics

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ABSTRACT

New high lithium ion conductor glass–ceramics with NASICON-type structure ($Li_{1+x+y}Al_xCr_yGe_{2-x-y}(PO_4)_3$, $x + y = 0.5$) were synthesized using melt-quenching method and converted to glass–ceramics through heat treatment. Influence of addition of different concentrations of aluminum and chromium in $LiGe_2(PO_4)_3$ glass-ceramic was investigated. Substitution of Ge^{4+} ions by Al^{3+} and Cr^{3+} ions induced more Li^+ ions in A_2 vacant sites and also changed the unit cell parameters and resulted in ionic conductivity improvement of glass–ceramics. The glass–ceramics were characterized by X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), Energy-Dispersive X-ray spectroscopy (EDX), Differential Scanning Calorimetry (DSC), Complex Impedance Spectroscopy (CIS) and cyclic voltammetry (CV). The highest lithium ion conductivity of 6.65×10^{-3} S/cm was obtained for $x = 0.4$ and $y = 0.1$ ($Li_{1.5}Al_{0.4}Cr_{0.1}Ge_{1.5}(PO_4)_3$) crystallized at 850 °C for 8 h with minimum activation energy of 0.292 eV.

1. Introduction

Safety and high power density are two important challenges in lithium ion batteries (LIBs) production industry. Common LIBs contain organic flammable solvents (such as ethylene carbonate, dimethyl carbonate and ethyl methyl carbonate) and are not appropriate for specific use of transportation industry because charge and discharge processes of batteries in hybrid and electrical vehicles are in high current rate that it can cause explosion in these batteries [1]. Moreover, fabrication costs of batteries, when using organic electrolytes are high. These drawbacks limit their application in large-scale batteries, which require low cost, high safety, and high power density [2]. Recently, aqueous and solid electrolytes as safe, environmentally friendly and cheap electrolytes have been investigated by different researchers [3–6]. All-solid-state and aqueous lithium-air batteries are two new types of LIBs which use these electrolyte and are recently investigated by researchers for safety and power density improvement respectively without common problems of organic solvents. Both of these batteries need solid lithium ion conductors as electrolytes or anode protector [7,8]. Solid electrolytes that are used in these types of batteries must have some properties such as low electron conduction (electronic conductivity), high lithium ion conduction and electrochemical stability in contact with anode and cathode or wide potential window [9–12]. Moreover, these solid electrolytes or lithium ion conductors must have other properties except those that were mentioned above such as stability in contact with lithium metal and no permeability for water and air molecules when used for lithium-air batteries [13]. Perovskite-type, Garnet-type, NASICON-type and LISICON are four main crystalline inorganic lithium ion conductors [14]. NASICON-type has general formula of $LiM_2(PO_4)_3$ where M can be Ti^{4+} or Ge^{4+}. Crystals with Ti^{4+} are unstable in contact with lithium metal because of reduction of Ti^{4+} to Ti^{3+}. Only Ge^{4+} can make a crystalline structure with high lithium ion conduction and all properties that were mentioned above [15–18]. $LiGe_2(PO_4)_3$ NASICON-type crystallizes in 3D network structure (rhombohedral crystal system, space group $R\bar{3}c$) which has appropriate channels for Li ions (Li^+) migration. In this crystal, two types of polyhedrons contain: GeO_6 octahedra and PO_4 tetrahedra which are attached by their corners to form $[Ge(PO_4)]^-$ frame with 3D interconnected channels and two types of interstitial cavities, A_1 and A_2. Li ions migrate in channels of this frame [19]. Li ions can occupy in A_1 and A_2 sites. In $LiGe_2(PO_4)_3$ with no dopant, A_2 sites are vacant when A_1 sites are occupied by Li ions. Partial substitution of Ge^{4+} ions by trivalent cations such as Al^{3+} and Cr^{3+} ions

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increases the unit cell dimensions and residual negative charges are neutralized by additional Li ion that occupy A_2 sites. The change in unit cell dimensions and Li ion concentration in crystal leads to increase of ionic conductivity [19–23].

The effect of Al as dopant on ionic conductivity of $LiGe_2(PO_4)_3$ (LGP) was investigated by researchers and it was proved that highest lithium ion conductivity is obtained when only 25% of Ge^{4+} ions were replaced by Al^{3+} ions in $LiGe_2(PO_4)_3$ crystal structure (x = 0.5 in overall formula of $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$) [24,25]. Other researchers investigated the effect of chromium dopant on lithium conduction improvement of $LiGe_2(PO_4)_3$ [26,27]. Recently, chromium and aluminum co-doped NASICON-type $LiTi_2(PO_4)_3$ (LTP) were synthesized by Zhang et al. and simultaneous replacement of Ti^{4+} ions by aluminum and chromium ions showed good improvement on ionic conduction of LTP glass–ceramics [28].

The NASICON-type lithium ion conductors were prepared by powder sintering route [29,30], Sol–gel method [13,31,32] and glass–ceramic process (melt quenching) [33–35]. Glass–ceramic method produces homogeneous microstructure without porosity with high Li^+ ion conductivity which is better for lithium-air batteries. Therefore, in this research the last method was applied for preparation of lithium ion conductors.

In this research for the first time, the influence of addition of aluminum and chromium as dopants on crystal structure and ionic conductivity of $LiGe_2(PO_4)_3$ NASICON-type glass–ceramics were investigated simultaneously. In this new glass–ceramics ($Li_{1+x+y}Al_xCr_yGe_{2-x-y}(PO_4)_3$, x + y = 0.5,y = 0, 0.1, 0.25, 0.4, 0.5 and x = 0.5, 0.4, 0.25, 0.1, 0) only 25% of Ge^{4+} ions were replaced by different concentrations of aluminum and chromium. These five samples with y = 0, 0.1, 0.25, 0.4 and 0.5 are labeled as #Cr_0, $Cr_{0.1}$, $Cr_{0.25}$, $Cr_{0.4}$ and $Cr_{0.5}$, respectively. In addition crystallization process is an important phenomenon that affects ionic conductivity strongly and recently the effects of crystallization time and temperature have been studied by authors in another work for achievement of maximum ionic conduction in $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass–ceramics (under review). These optimum conditions were used for crystallization of synthesized aluminum and chromium co-doped NASICON-type $LiGe_2(PO_4)_3$.

2. Experimental

2.1. Synthesis

The stoichiometric amounts of Germanium dioxide GeO_2 (Merck), Lithium carbonate Li_2CO_3 (Merck), Aluminum oxide Al_2O_3 (Sigma Aldrich), Chromium(III) oxide Cr_2O_3 (Merck) and Ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ (Merck) were weighted and mixed for 20 min in agate mortar and pestle to prepare ($Li_{1+x+y}Al_xCr_yGe_{2-x-y}(PO_4)_3$, x + y = 0.5, y = 0, 0.1, 0.25, 0.4, 0.5 and x = 0.5, 0.4, 0.25, 0.1, 0) by melt-quenching method. Then they were heated in electrical furnace at 700 °C for 2 h in order to release ammonia, carbon dioxide and water vapor compounds. Then, the puff shape materials were crushed in agate mortar and pestle and were transformed in platinum crucible and heated in electrical furnace at 1450 °C for 1 h. The homogeneous melted glass was pressed and quenched by two preheated (300 °C) stainless steel plates. The transparent thin glass disks were transferred to another furnace and were annealed at 500 °C for 2 h to release the thermal stresses. Then, the annealed thin disks were cut to ~1 × 1 cm specimens and were crystallized at 850 °C for 8 h.

2.2. Characterizations

Thermal behavior of the glass (glass transition temperature T_g and crystallization temperature T_C) was analyzed by Differential Scanning Calorimetry (DSC, NETZSCH 404 F1 Pegasus-High Temperature DSC, Germany) on the fine powdered glass and heating rate of 5 °C/min. Determination of phase formation during heat treatment process were done by X-ray diffraction (XRD, Xmd300 Unisantis, Germany) using Cu Kα radiation in 2θ range from 0 to 70°. Crystallized specimens were fractured and microstructure of glass–ceramics specimens were investigated from fractured section by Field Emission Scanning Electron Microscopy (FESEM, Sigma-vp Zeiss, Germany), elemental analysis of phases were done by Energy-Dispersive X-ray spectroscopy (EDX), ionic conductivity of polished and silver painted specimens were determined using Complex Impedance Spectroscopy (CIS, Metrohm Autolab PGST302, Netherlands) in frequency range of 1–10^6 Hz. Furthermore, electrochemical stability of specimens in contact with lithium metal foil for corrosion investigation was determined using cyclic voltammetry method (CV, Metrohm Autolab PGST302, Netherlands) at scanning rate of 0.5 mV/s between −0.6 and 7 V. silver paint and lithium foil on specimen faces, were counter and working electrodes, respectively. The test was done in argon filled glovebox.

3. Results and discussion

Fig. 1 shows the crystallization temperature (T_C) graph of fine glass powder for Cr_0, $Cr_{0.1}$, $Cr_{0.25}$, $Cr_{0.4}$ and $Cr_{0.5}$ (heating rate of 5 °C/min). As seen in the figure, increasing the chromium concentration increases the T_C (Comparison between Cr_0 and $Cr_{0.5}$) but for specimen with no aluminum ($Cr_{0.5}$), T_C is increased sharply and is around 787 °C. The glass transition and strong exothermic crystallization peak are appeared at around 533 and 628 °C, respectively for specimen with no chromium dopant (Cr_0). Crystallization at temperature above the T_C ensures the perfect and homogeneous crystallization [34].

Fig. 2 shows the XRD patterns of specimens crystallized at 850 °C for 8 h. In all samples, the main peaks are related to NASICON-type structure $LiGe_2(PO_4)_3$ space group ($R\bar{3}c$) according to JCPDS 80-1924 index file. There is no Al^{3+} or Cr^{3+} ions in $LiGe_2(PO_4)_3$ structure but the aluminum and chromium make a solid solution with this structure and Ge^{4+} ions were partially replaced by Al^{3+} and Cr^{3+} ions because the radii of these ions are close to each other [20] (Ge^{4+} = 0.53 A°, Al^{3+} = 0.54 A° and Cr^{3+} = 0.61 A°) solid solution forms and NASICON-type was retained as main phase in XRD pattern. Moreover these substitutions induce more lithium ions in NASICON-type structure in A_2 vacant sites and increase the cell volume. Increasing the chromium concentration in crystal structure leads to forming secondary $CrPO_4$ phase in grain boundary during the crystallization process that it prevents from lithium ions migration between grains. Only in XRD pattern of $Cr_{0.1}$ sample, peaks are related to $LiGe_2(PO_4)_3$ structure with no $CrPO_4$ phase and minimum peak intensity of GeO_2. Addition of more chromium in crystal structure leads to formation of higher $CrPO_4$ and GeO_2 in grain boundaries. Diffraction peaks due to $CrPO_4$ and GeO_2 phases in the XRD pattern of $Cr_{0.5}$ show highest intensity among other specimens.

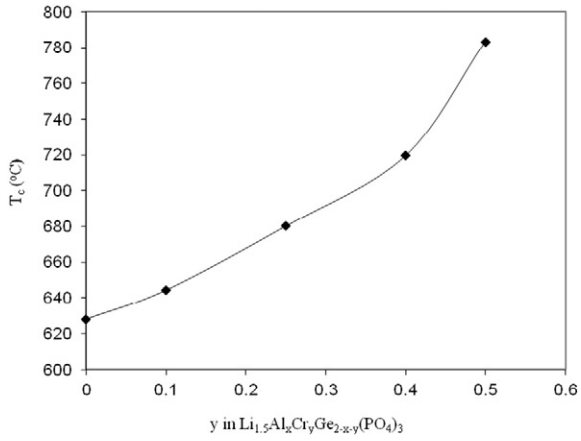

Fig. 1. Composition dependence of T_C for synthesized glasses of $Li_{1.5}Al_xCr_yGe_{2-x-y}(PO_4)_3$.