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Influence of B_2O_3 addition on the ionic conductivity of $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ glass ceramics

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HIGHLIGHTS

- B_2O_3 added LAGP glass ceramics were prepared by melt-quenching method.
- Effect of B_2O_3 addition on ionic conductivity of LAGP glass ceramics was studied.
- Stability of B_2O_3 added LAGP glass ceramics in aqueous electrolytes was studied.

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ABSTRACT

The effects of B_2O_3 addition on the properties of the $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) glass ceramic have been studied. The crystallization temperature of the LAGP decreases with the addition of B_2O_3. The glasses are crystallized at different temperatures and characterized for microstructure and ionic conductivity. The highest total conductivity of the glass ceramic material, 6.9×10^{-4} S cm^{-1} at 25 °C is achieved by crystallizing the glass at 825 °C for 5 h with the addition of 0.05 wt% B_2O_3. Non-linearity in Arrhenius plot is observed due to the characteristics of $AlPO_4$ dielectric phase. In addition, the B_2O_3 added LAGP glass ceramic is stable in weak acidic and neutral solutions, but highly corroded in strong acidic and basic solutions.

1. Introduction

Rechargeable Li-ion batteries are key components in our current, information-rich world [1]. They have been used as energy sources for a variety of electronic devices used daily for communication and tasks because of their high energy densities. However, to drive an electric vehicle over a long distance in a single charge, the energy density of state-of-the-art Li-ion technology is insufficient. On the other hand, Li-air batteries have 3–5 times higher gravimetric energy density than conventional Li-ion batteries, so if commercialized, they would dramatically improve the driving distance of electric vehicles (EV) [2]. The high energy densities of both battery systems have been resulted from a high operation voltage. Hence, flammable organic solvents have been exclusively used in these batteries as electrolytes, because they can tolerate such high voltages. In some cases, organic electrolytes have caused serious safety problems in Li-ion batteries such as fire hazards and electrolyte leakage, calling for the need to replace currently used organic carbonate liquid solutions with safer and more reliable electrolytes [3]. In order to overcome the safety issues, researchers have employed polymers [4,5], and ceramics [6–8] as electrolytes for rechargeable Li-ion batteries. In particular, all solid state batteries with ceramic solid electrolytes have been recognized as ultimate safe batteries. However, to make solid-state Li-ion batteries of efficient design and high performance, a solid lithium ion conductor with a total conductivity above 10^{-3} S cm^{-1} is desirable [9].

Some crystalline glass ceramics, known as LISICON (Lithium super ionic conductor), exhibit ionic conductivity comparable to those of liquid electrolytes. These are the Lithium-analogues of NASICON type glass ceramics like lithium-aluminium-titanium-phosphate (LATP) [10] and lithium-aluminium-germanium-phosphate (LAGP) [11], and they are good candidate as

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electrolytes for all solid state lithium-ion batteries. In addition to the ionic conductivity, the surface of a solid electrolyte should be stable in contact with other components for longer lifetime of battery. The solid electrolyte should be stable in contact with lithium, water and electrolytes containing Li-salts if it is to be used as a protective layer in all solid state batteries.

The LAGP glass ceramic has been reported to exhibit superior stability in contact with lithium metal [12], but lower ionic conductivity than that of a liquid electrolyte (~ 10^{-3} at room temperature) [13,14]. Therefore, the insufficient conductivity of the LAGP needs to be improved. There have been reports on the preparation of LAGP by melt-quenching [15], solid solution [16] and sol–gel [17] methods. For the LAGP made by melt-quenching processes, the temperature and duration of time required for crystallization were reported to be 850 °C and 12 h respectively [12,15]. One way to decrease the crystallization temperature is to add sintering aids that have low melting points and make liquid phases at comparatively lower temperatures. In addition, the liquid phases promote densification and coarsening at lower temperatures. Low temperature crystallization with sintering aids reduces dielectric properties, because the dielectric constants of the sintering aids are lower than that of the ceramic. Furthermore, the reaction between the sintering aid and ceramic causes the formation of a secondary phase with a low dielectric constant [18]. However, some sintering aids improve dielectric properties as they incorporate into the ceramic grain and suppress the formation of the secondary phase [19].

The present study investigates the effects of B_2O_3 as sintering aid on the thermal properties, crystallization behaviour, microstructure and ionic conductivity of the LAGP glass ceramic. Since B_2O_3 has a flat 6-numbered ring structure formed of boron and oxygen, its structure is more open than the open tetrahedron structure of quartz glass, and it is favourable for ion conductivity [20].

2. Experimental

The melt-quenching method was used to prepare the LAGP and B_2O_3-added LAGP ceramics. B_2O_3 of 0.05, 0.1, 0.2 and 0.4 wt% was added to pristine LAGP ($Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$), respectively. The starting precursor materials viz. Li_2CO_3, Al_2O_3, GeO_2, B_2O_3 and $NH_4H_2PO_4$ were mixed in mortar and then ball milled further for 1 h for homogenization. The milled batch was transferred to the electric furnace for melting. Initially, the furnace was heated to 350 °C at a rate of 1 °C min^{-1} and held at that temperature for 1 h to release volatile components. Then, the furnace was heated to 1250 °C at the same rate and held for another 2 h. A clear, homogeneous and viscous melt was poured onto a preheated (150 °C) stainless steel plate and quickly pressed by another steel plate to yield transparent glass. Furthermore, the obtained transparent glass was annealed for 2 h at 500 °C to release the thermal stresses and then cooled to room temperature. After the heat treatment, the annealed glass specimens were crystallized for 5 h at various temperatures from 800 to 850 °C. The LAGP glass ceramics, in which various B_2O_3 concentrations of 0 wt%, 0.05 wt%, 0.1 wt%, 0.2 wt% and 0.4 wt% were added, were named as B_0, $B_{0.05}$, $B_{0.1}$, $B_{0.2}$ and $B_{0.4}$ respectively.

Differential thermal analysis (DTA) was conducted to investigate the effect of B_2O_3 addition on the crystallization temperature of LAGP. The content of Li, Al, Ge, P and B in the specimen was measured by using inductively coupled plasma atomic emission spectroscopy (ICP-AES). X-ray diffraction (XRD) patterns of all specimens were obtained using the Rigaku-D/MAX-Ultima III-600 X-ray diffractometer operated at voltage of 40 kV and current of 40 mA with Cu Kα radiation in the 2θ range from 2° to 80° with a 0.02° step size and step scan of 0.3s. Crystalline phases were identified by comparing the observed data with the standards from International Center for Diffraction Data. Scanning electron microscope (SEM) images were obtained using Hitachi S-4700 FE-SEM. The AC impedance measurements of all the crystallized samples were carried out using the ZIVE SP2 instrument in the 1 Hz to 1 MHz frequency range at voltage amplitude of 100 mV. Samples for AC impedance measurement were polished to obtain uniform thickness and flat surfaces. Further, the opposite faces were coated with Ag paint for good electrical contact. Ag paint was dried at room temperature in dry atmosphere for several hours. The good electrical conductivity of coated surface was ensured before loading the samples in the setup for conductivity measurements. The Ag coated specimens were assembled into a cell using stainless steel (SS) blocking electrode in a cell fixture. The fixture containing the SS/Ag/glass ceramic/Ag/SS cell was subsequently placed in a stable fixture holder with attached electrical connection leading to the impedance spectrometer. The conductivity of specimens was computed from the ac impedance spectra. *Z* plot and Z view software was employed for impedance data acquisitions analysis. The impedance spectra show normally one semicircle at room temperature (25 °C). The diameter of the semicircle was further normalized with respect to the thickness and cross-sectional area of the specimens to obtain the total conductivity of the specimens.

3. Result and discussion

Fig. 1(a) shows the DTA curves obtained for LAGP and B_2O_3 added LAGP glasses in the temperature range of 200–700 °C at the heating rate of 10 °C min^{-1}. The glass crystallization temperature

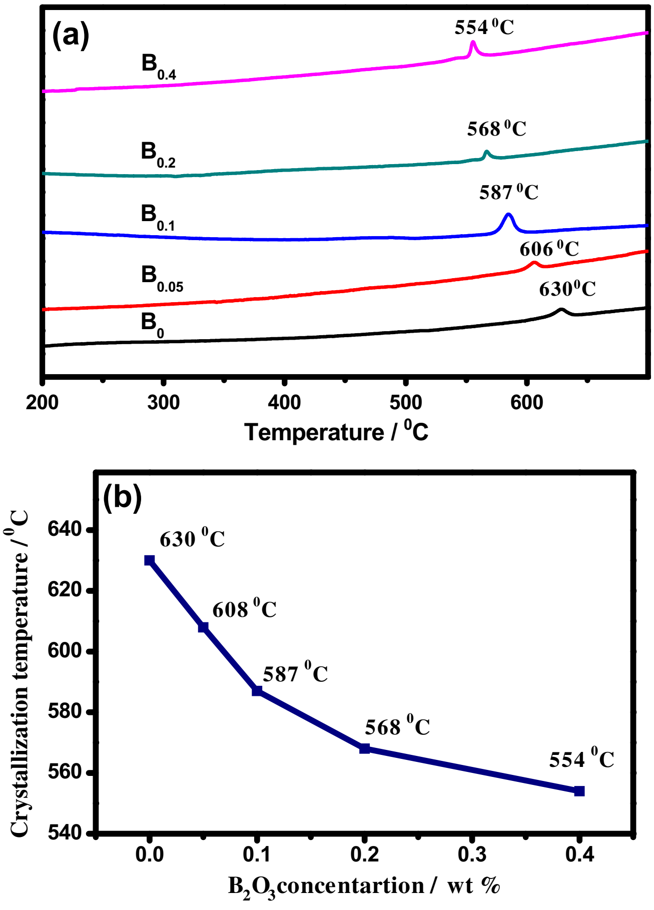

Fig. 1. (a) DTA plot for B_0 (0 wt% B_2O_3), $B_{0.05}$ (0.05 wt% B_2O_3), $B_{0.1}$ (0.1 wt% of B_2O_3), $B_{0.2}$ (0.2 wt% of B_2O_3) and $B_{0.4}$ (0.4 wt% of B_2O_3) samples. (b) The variation of crystallization temperature with the different B_2O_3 addition.