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Fast Li^+ ion conduction in Li_2O–(Al_2O_3 Ga_2O_3)–TiO_2–P_2O_5 glass–ceramics

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Fast lithium ionic conducting glass–ceramics have been obtained by heat-treatment of glasses in the systems Li_2O–M_2O_3–TiO_2–P_2O_5 (M = Al and Ga). The glass–ceramics were mainly composed of $LiTi_2(PO_4)_3$ in which Ti^{4+} ions were partially replaced by M^{3+} ions. Considerable enhancement of the conductivity with the substitution of M^{3+} ions for Ti^{4+} ions was observed. The maximum conductivity obtained at room temperature was 1.3×10^{-3} S cm^{-1} for the aluminium system and 9×10^{-4} S cm^{-1} for the gallium system.

1. Introduction

High lithium ionic conducting solids are potential electrolyte materials for utilization in high energy-density batteries and other electrochemical devices. To date, many conductors have been reported in various systems. Among oxide materials, the solid solutions $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ (M = Al, Sc, In, Y, etc.) exhibit the highest conductivity of over 10^{-4} S cm^{-1} at room temperature, although $LiTi_2(PO_4)_3$ exhibits a poor conductivity [1]. $LiTi_2(PO_4)_3$ consists of both TiO_6 octahedra and PO_4 tetrahedra, which are linked by their corners to form a three-dimensional network structure [2]. This structure results in cavities where lithium ions reside and in bottlenecks in which they pass through. These sintered materials have become attractive for use as solid electrolytes because of their good chemical stability and easy handling. In comparison with the sintered materials, glass-ceramics have a big advantage because they can be easily manufactured into a desired size or shape and have a dense microstructure. It is therefore interesting to explore highly conducting glass–ceramics. In previous work [3], a glass consisting of $14Li_2O$–$9Al_2O_3$–$38TiO_2$–$39P_2O_5$, which can be approximately expressed as a pseudo-binary system $2[Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3]$–$AlPO_4$, was prepared and the effect of heat-treatment conditions on the precipitated phases and the conductivity of the resultant glass–ceramics, was investigated. It was found that the major phase was $LiTi_2(PO_4)_3$ and the maximum conductivity obtained was over 10^{-3} S cm^{-1} at room temperature.

In the present paper, the composition dependence of the conductivity of glass–ceramics in the pseudo-binary systems $2[Li_{1+x}M_xTi_{2-x}(PO_4)_3]$–$MPO_4$ (M = Al and Ga), is reported.

2. Experimental procedure

Glasses were prepared using a conventional melt-quenching method. Reagent-grade chemicals of Li_2CO_3, $Al(OH)_3$, Ga_2O_3, TiO_2 and $NH_4H_2PO_4$ were used as starting materials. The batches were placed in platinum crucibles and melted in an electric furnace. The batches were initially kept at 700 °C for 1 h in order to release volatile products coming from the starting materials. Then, they were heated to 1450 °C and melted at this temperature for 1.5 h. The melts were poured on to preheated stainless steel plates and pressed into plates 1–2 mm thick. The resultant glasses were immediately placed in a furnace at 550 °C for annealing; after holding for 2 h, the furnace was turned off and the glasses were allowed to cool in the furnace.

The glass transition temperature, T_g, and the onset crystallization temperature, T_x, were determined using differential thermal analysis (DTA) at a heating rate of 10 K min^{-1}. Heat-treatment conditions for obtaining maximum conductivity were investigated. Because little difference in the conductivity of the samples prepared in one or two stages was found, a one-stage heat treatment was employed in the present study. The heat treatment was carried out for 12 h at temperatures above T_x. For every glass sample, the heat-treatment temperature was progressively elevated at an interval of 30 °C until the maximum conductivity was reached. Crystalline phases were identified by X-ray diffraction (XRD) analysis at room temperature using CuK_α radiation. In order to determine the lattice constant, the diffraction peak positions (2θ) were precisely measured by scanning between $2\theta = 10°$ and 40° in 0.01° steps and counting for 5 s at each step. High-purity silicon was used as a standard.

Polished samples were prepared for ionic conductivity measurements. Gold electrodes were sputtered on both sides of the samples. The measurements were carried out with the complex impedance method using a Solartron 1260 impedance analyser connected to a computer. The frequency range used was 10^{-2}–10^7 Hz. Ionic conductivity, σ, values were calculated with $\sigma = d/AR$, where d is the

sample thickness, A is the area of the electrodes and R is the sample resitivity corresponding to the total of the bulk and the grain-boundary components.

3. Results and discussion

3.1. Glass composition and crystallization

Glass formation in both pseudo-binary systems $2[Li_{1+x}M_xTi_{2-x}(PO_4)_3]$–$MPO_4$ (M = Al and Ga) was first investigated. In the aluminium system, the composition with $x = 0$–0.3 formed glasses under the conditions of this study. The composition of $x = 0.4$ partially crystallized and for $x = 0.5$ the raw materials partially formed a liquid phase but could not be poured out of the crucible. In the gallium system, glasses were obtained easily in the composition range $x = 0$–0.6. For $x = 0.7$ and 0.8 pure glasses could not be formed, but dense glass–ceramics were obtained.

Table I lists the composition and glass transition temperature, T_g, and crystallization temperature, T_x, in each of the systems. Increasing x results in a decrease in T_g. For the same x, the aluminium system exhibits higher T_g than the gallium system. This may be due to the fact that the Al–O bond is stronger than the Ga–O bond and hence leads to stronger mean bonds in the glass network. From Table I it is also seen that the aluminium system has a lower glass forming tendency. This is most likely due to the higher melting temperature of Al_2O_3 (2050 °C) compared with Ga_2O_3 (1740 °C). A higher melting temperature would result in higher liquid temperature and hence require a higher critical cooling rate for glass formation.

Fig. 1 shows the XRD patterns of the glass-ceramics in the aluminium system. The precipitated phases are $LiTi_2(PO_4)_3$ and $AlPO_4$ in all samples, but it is obvious that the former is dominant. Some shift towards higher diffraction angles for $LiTi_2(PO_4)_3$ was observed, indicating the shift to smaller d-spacings. Lattice parameter calculations for $LiTi_2(PO_4)_3$ are shown in Fig. 2. With increasing x, a slight decrease in a-parameter and a large decrease in c-parameter are seen. These results suggest Ti^{4+} ions in the $LiTi_2(PO_4)_3$ are partially replaced by Al^{3+} ions. This suggestion is also supported by the observation that the relative intensity of the $AlPO_4$ peak against the strongest $LiTi_2(PO_4)_3$ peak remains constant, as shown in Fig. 3.

TABLE I Glass transition temperature, T_g, and crystallization temperature, T_x, of the glasses in the pseudo-binary systems $2[Li_{1+x}M_xTi_{2-x}(PO_4)_3]$–$MPO_4$ (M = Al, Ga)

	x	T_g (°C)	T_x (°C)
$2[Li_{1+x}Al_xTi_{2-x}(PO_4)_3]$–$AlPO_4$	0	678	717
	0.1	674	705
	0.2	656	698
	0.3	648	690
$2[Li_{1+x}Ga_xTi_{2-x}(PO_4)_3]$–$GaPO_4$	0	673	703
	0.1	658	688
	0.2	635	678
	0.3	612	660
	0.4	607	648
	0.5	590	631
	0.6	578	620

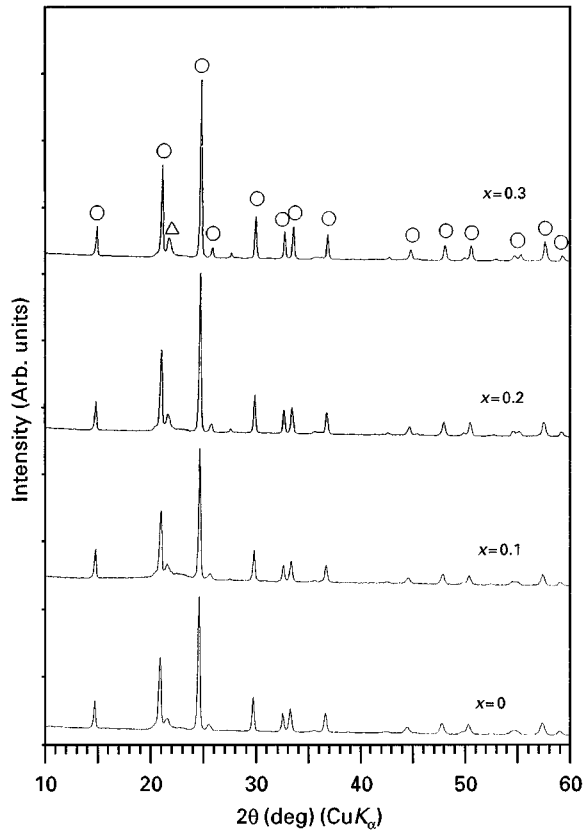

Figure 1 XRD patterns of the glass–ceramics in the pseudo-binary system $2[Li_{1+x}Al_xTi_{2-x}(PO_4)_3]$–$AlPO_4$. (○) $LiTi_2(PO_4)_3$, (△) $AlPO_4$.

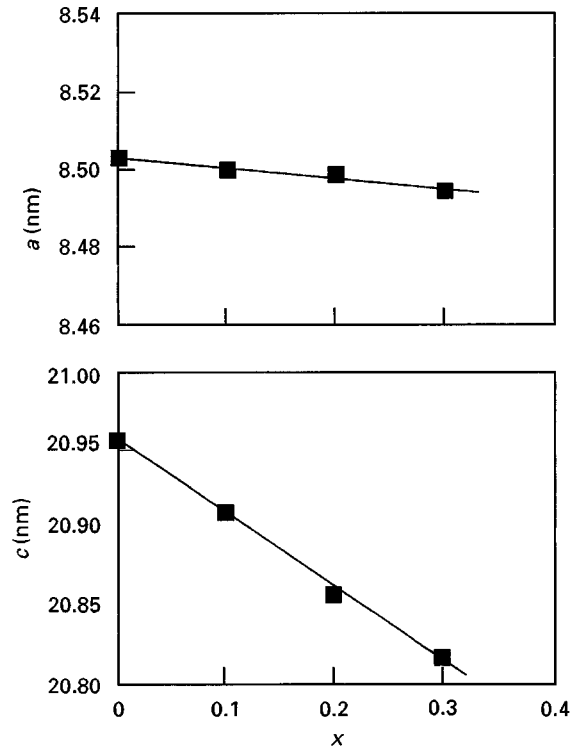

Figure 2 Lattice parameters for $LiTi_2(PO_4)_3$ as a function of x in $2[Li_{1+x}Al_xTi_{2-x}(PO_4)_3]$–$AlPO_4$ glass–ceramics.

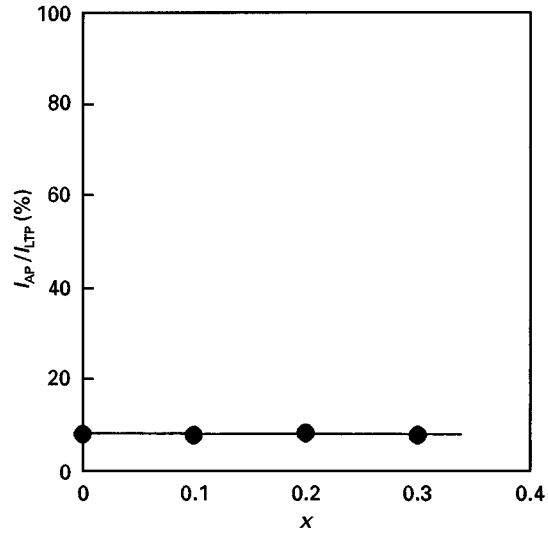

Figure 3 Intensity ratio of the $AlPO_4$ peak, I_{AP}, and the strongest $LiTi_2(PO_4)_3$ peak, I_{LTP}, as a function of x in the $2[Li_{1+x}Al_xTi_{2-x}(PO_4)_3]$–$AlPO_4$ glass–ceramics.

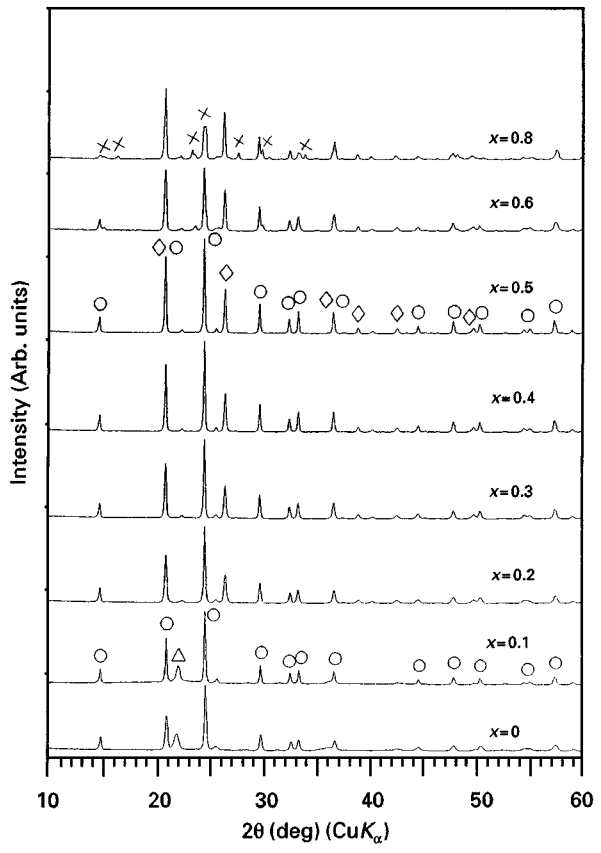

Figure 4 XRD patterns of the glass–ceramics in the pseudo-binary system $2[Li_{1+x}Ga_xTi_{2-x}(PO_4)_3]$–$GaPO_4$. (○) $LiTi_2(PO_4)_3$, (△) $GaPO_4$ (orthorhombic), (◇) $GaPO_4$ (hexagonal), (X) unknown phases.

Fig. 4 shows the XRD patterns of the glass-ceramics in the gallium system. The $LiTi_2(PO_4)_3$ phase is precipitated in all specimens. Secondary-phase $GaPO_4$ with orthorhombic structure is produced at $x < 0.2$ and it is transformed into hexagonal structure with further increases in x. In addition, unknown phases begin to appear at $x = 0.6$ and grow thereafter. Nevertheless, $LiTi_2(PO_4)_3$ is the major crystalline

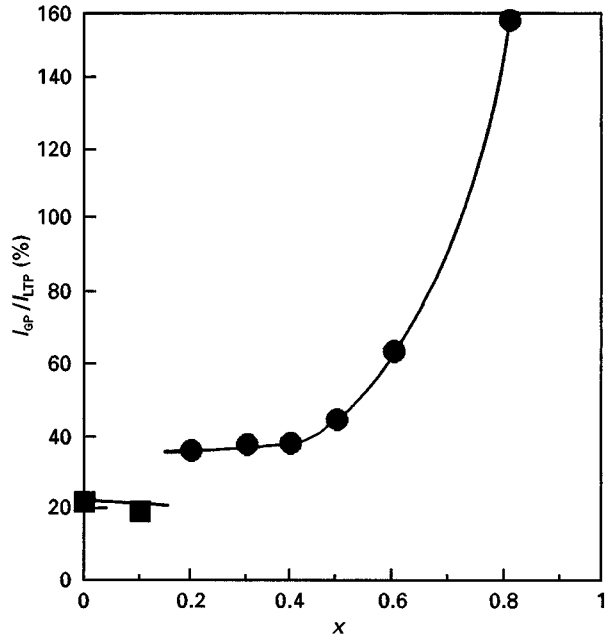

Figure 5 Intensity ratio of the strongest $GaPO_4$ peak, I_{GP}, and the strongest $LiTi_2(PO_4)_3$ peak, I_{LTP}, as a function of x in the $2[Li_{1+x}Ga_xTi_{2-x}(PO_4)_3]$–$GaPO_4$ glass–ceramics. (■) Orthorhombic $GaPO_4$, (●) hexagonal $GaPO_4$.

phase until $x = 0.6$. A change in lattice constant with the substitution of Ga^{3+} ions for Ti^{4+} ions is not expected because of their closely matching ionic radii (0.062 nm for Ga^{3+} ion and 0.0605 nm for Ti^{4+} ion). The intensity ratio of the strongest $GaPO_4$ peak and the strongest $LiTi_2(PO_4)_3$ peak is shown in Fig. 5. For the orthorhombic $GaPO_4$, the ratio remains almost unchanged. For the hexagonal $GaPO_4$, the ratio also remains almost unchanged until $x = 4$, but it rapidly increases with further increasing x. These results hence suggest that the substitution of Ga^{3+} ions for Ti^{4+} ions takes place in the $LiTi_2(PO_4)_3$ and reaches a maximum substitution into the structure at $x = 0.4$. For greater x the non-substituting Ga^{3+} ions form $GaPO_4$ and/or unknown phases (Fig. 4).

3.2. Conductivity of the glass–ceramics

Fig. 6 shows the temperature dependence of conductivity of the glass–ceramics in both systems. For all compositions the conductivity obeys an Arrhenius-type equation. The conductivity at room temperature for both systems is presented in Fig. 7. Conductivity enhancement of more than three orders of magnitude in both systems is observed. For the aluminium system, increasing x from 0 to 0.3 increases the conductivity from $5 \times 10^{-7}\,cm^{-1}$ to $1.3 \times 10^{-3}\,S\,cm^{-1}$. Above $x > 0.3$, the conductivity is not given because the samples for measurements could not be obtained. Perhaps conductivity attains an almost saturation value around $x = 0.3$ because no large difference in conductivity between $x = 0.2$ and 0.3 was observed. For the gallium-containing system, on the other hand, the conductivity increases from $1.2 \times 10^{-7}\,S\,cm^{-1}$ to $9 \times 10^{-4}\,S\,cm^{-1}$ as x increases from 0 to 0.4 and it decreases with further increase in

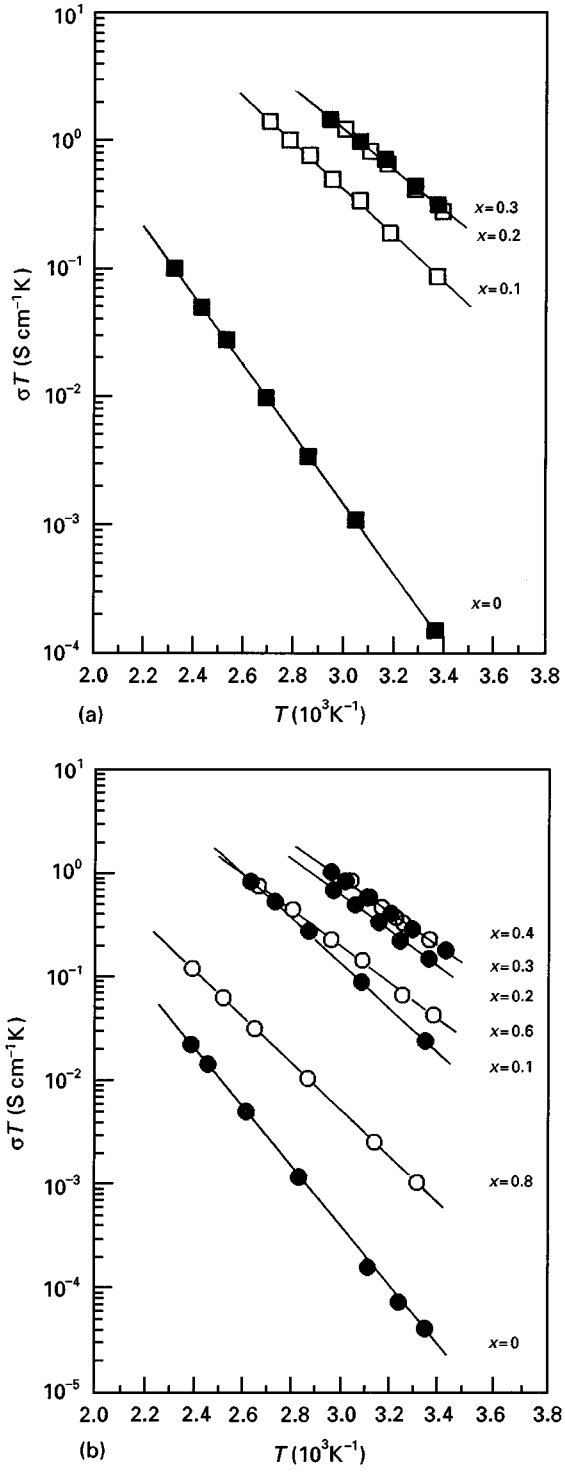

Figure 6 Temperature dependence of conductivity for the glass–ceramics in the pseudo-binary systems (a) $2[Li_{1+x}Al_xTi_{2-x}(PO_4)_3]$–$AlPO_4$ and (b) $2[Li_{1+x}Ga_xTi_{2-x}(PO_4)_3]$–$GaPO_4$.

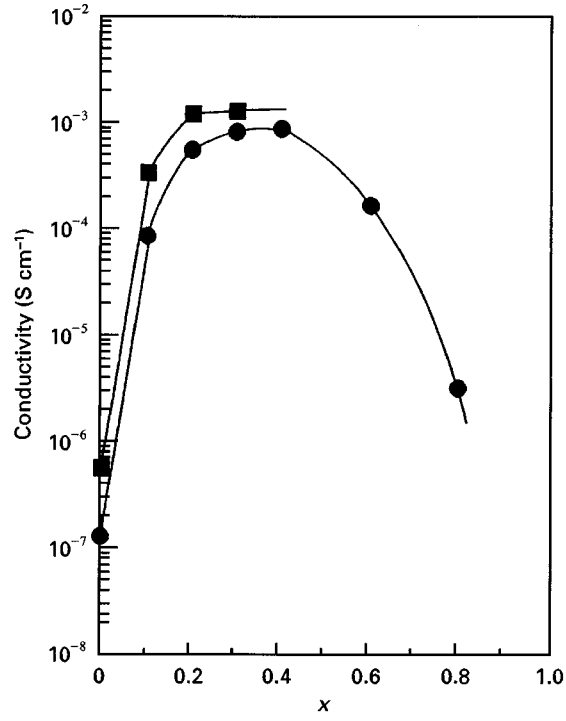

Figure 7 Electrical conductivity at room temperature of the glass–ceramics in the pseudo-binary systems $2[Li_{1+x}M_xTi_{2-x}(PO_4)_3]$–$MPO_4$(M = (■) Al, (●) Ga) as a function of x.

x. Fig. 8 shows the composition dependence of activation energy, E_a, for both systems. In the aluminium system, E_a decreases rapidly with increase in x. In the gallium system, E_a also decreases rapidly, reaching a maximum at around $x = 0.4$ and then increases. These changes in E_a correspond to that in the conductivity, indicating the conductivity is determined by the E_a.

Aono *et al.* [1] reported a great enhancement in conductivity of the $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ (M = Al, Sc, In, Y, etc.) ceramics. They analysed the activation energy of electrical conduction for bulk and grain-boundary contributions, and found that the activation energy for the bulk remained constant while that for the grain boundary appreciably decreased with the substitution of M^{3+} ions for Ti^{4+} ions. From these results, they suggested that the enhanced conductivity by the M^{3+} ion substitution was due to the decrease in the activation energy of the grain-boundary component [4]. Amatucci *et al.* [5] studied the conductivity and activation energy of the $Li_3Sc_{2-x}M_x(PO_4)_3$ (M = Al and Y) ceramics and showed that the increased conductivity with the substitution of M^{3+} ions for Sc^{3+} ions resulted from the decrease of both bulk and grain-boundary activation energies.

In the present glass-ceramics, the bulk component in the impedance plots (Cole–Cole plot) was observable only at low temperature, below −10 °C [3] and separation of the bulk and the grain-boundary component was not made. At present, therefore, the reason for the enhanced conductivity by the substitution of M^{3+} ions for Ti^{4+} ions cannot be accounted for clearly. Work on this aspect is now in progress.

A comparison of the conductivity of the aluminium and gallium systems with the same x reveals a higher value for the aluminium system (Fig. 7). If the grain-boundary states are the same for the same x, it is considered that the difference in conductivity would result from the bulk structure. Because the Al–O bond is stronger than the Ga–O bond, a stronger covalent network is formed in the aluminium system. This would result in a weaker bond between the network and Li^+ ions. Hence, the Li^+ ions in the aluminium system become more mobile, and higher conductivity is observed for the same x. Such effects of chemical-

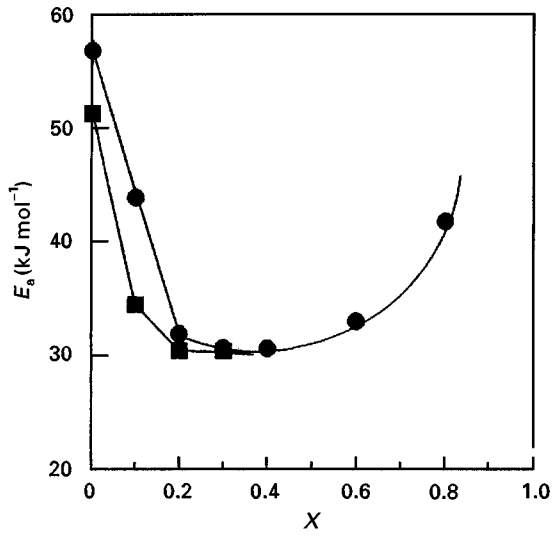

Figure 8 Activation energy for electrical conduction of the glass–ceramics in the pseudo-binary systems $2[Li_{1+x}M_xTi_{2-x}(PO_4)_3]$–$MPO_4$(M = (■) Al, (●) Ga) as a function of x.

bonding compensation have been shown, for instance, in the solid solutions $Na_{1+x}Zr_{2-x/2}Mg_{x/2}(PO_4)_3$, $Na_{1+x}Zr_{2-x}In_x(PO_4)_3$ [6] and $K_xAl_xTi_{8-x}O_{16}$ [7].

The decrease in conductivity of the gallium system for $x > 0.4$ might be due to the increasing amount of $GaPO_4$ and unknown phases (Fig. 4). These phases have an insulative effect and hence hamper the mobility of the lithium ions between the grains.

4. Conclusion

High-lithium ionic conducting glass-ceramics containing $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ as their major crystalline phase have been successfully prepared in the systems Li_2O–M_2O_3–TiO_2–P_2O_5 (M = Al and Ga). The composition dependence of conductivity shows that substitution of M^{3+} ions for Ti^{4+} ions results in a considerable enhancement in conductivity. The maximum conductivity obtained at room temperature is 1.3×10^{-3} S cm^{-1} for the aluminium system and 9×10^{-4} S cm^{-1} for the gallium system. The high conductivities of the present glass-ceramics make them appealing candidates for use as solid electrolytes.

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