Solid-state NMR studies of local structure and lithium mobility $Li_{1+x}Al_xSn_yGe_{2-(x+y)}(PO_4)_3$ glass to ceramic materials

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Introduction

Since the significant development of lithium-ion battery technologies, they have been widely used in various applications ranging from electronic devices to increasing numbers of electric vehicles and large-scale energy storage equipment [1]. NASICON (Na Super Ionic Conductor)-type framework reported to be a fast ionic conductor [2]. The glass ceramics have high ionic conductivity at room temperature and good electrochemical stability. The structural aspects of the glass-to-crystal transition in the technologically important ion conducting glass ceramic system of $Li_{1+x}Al_xSn_yGe_{2-(x+y)}(PO_4)_3$ have been examined by complementary multinuclear solid state NMR single ande double-resonance experiments. In the crystalline state, the materials form solid solutions in NASICON structure.

Results and Discussion

Table 1: Sample compositions, Glass transition (Tg) and SS ^{27}Al NMR Lineshape parameters extracted for the individual Al coordination states from TQMAS-NMR data obtained on glassy of $Li_{1+x}Al_xSn_yGe_{2-(x+y)}(PO_4)_3$

Compositions	*Tg* (^oC)	*Al* (δ_{iso}) *±0.5, ppm*	*SOQE ±0.2 (MHz)*
x=0 y=0 G	520	-	-
x=0 y=0.5 G	528	-	-
x=0.25 y=0.25 G	538	46.1/9.8/ -12.5	4.5/2.3/2.0
x=0.25 y=0.45 G	536	44.6/11.3/ -15.6	4.7/3.6/2.3
x=0.25 y=0.25 C	-	-13.8	2.0
x=0.25 y=0.45 C	-	-14.0	2.3

The glass composition obtained and glass transition temperature (Tg) shown in Tab. 1. There is no significant temperature increase in Tg with substitution of germanium by aliovalente ions of Al^{3+} and Sn^{4+} in the network. The ^{31}P MAS NMR spectra of glass and crystalline $Li_{1+x}Sn_yAl_xGe_{2-(x+y)}(PO_4)_3$ samples. For the glass samples, broad gaussian-shaped curves are obtained and crystalized samples observed with three distinct compositions sites. The spectra are consistent with the XRD results, suggesting the formation of single-phase materials and small amounts of $LiGe_2(PO_4)_3$ and GeO_2. In the region between −20 and −40 ppm, multiple signals are observed, whose intensity distribution depends on the aluminum and tin content.

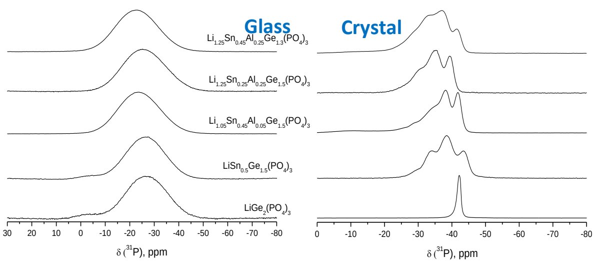

Figure 1: ^{31}P - MAS NMR spectra.

The ^{27}Al-MAS NMR spectra obtained for the present glasses. They indicate the presence of four-, five-, and six-coordinated aluminum when the samples are crystallized. All Al resonance at an isotropic chemical shift near -13ppm correspond aluminum six-coordinated.

$^{27}Al\{^{31}P\}$ REDOR data is to indicate that the second coordination sphere of both aluminum species is dominated by phosphorus.

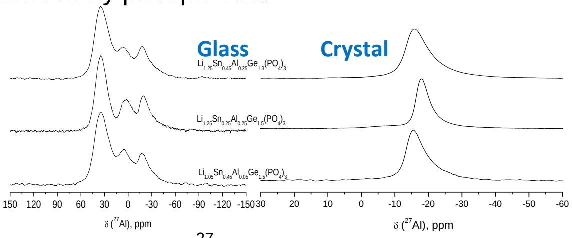

Figure 2: ^{27}Al-MAS NMR spectra.

Concluson

- The glasses have different structures of glass ceramics;.
- ^{27}Al–MAS NMR data for glass samples shows Al-IV Al-V and Al-V coordination;
- In glass ceramics, the conversion of Al-IV and Al-V to Al-VI occurred, confirming the data observed by XRD and ^{31}P-NMR data, ie the crystallization of NASICON-type structure.

Acknowledgement

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[1] <u>*J. Mater. Chem. A*</u>, 2014, **2**, 5358-5362.
[2] <u>*Adv. Funct. Mater*</u>., 2013, **23**, 947–985.