

Preparation of High Lithium-Ion Conductive Ceramic

Kengo Oda, Satoko Takase, and Youichi Shimizu*

Department of Applied Chemistry, Faculty of Engineering,
1-1 Sensui-cho, Tobata, City of Kitakyushu 804-8550, Japan

* shims@tobata.isc.kyutech.ac.jp

Keywords: solid electrolyte, lithium ionic conductive, NASICON-type, sol-gel method.

Abstract. Lithium ionic conductive solid electrolyte discs based on NASICON-type $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x = 0.1 - 0.9$) were prepared by a wet-chemical route at 1173 - 1273K. Crystalline phase, density, and electrical conductivity of the sintered discs were systematically investigated. Single phase of $\text{LiTi}_2(\text{PO}_4)_3$ systems were obtained at the calcination temperatures above 773K. Maximum conductivity 7.3×10^{-4} S/cm at 303K and activation energy of 0.30eV were obtained for the $\text{Li}_{1.25}\text{Ga}_{0.25}\text{Ti}_{1.75}(\text{PO}_4)_3$ discs sintered at 1223K.

1. Introduction

Recently high energy density and long life batteries using solid electrolytes have been requested. Lithium ion conductors especially are promising as the electrolyte for this purpose [1]. It is well known that NASICON($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$) is a good three-dimensional sodium ion conductor based on the parent compound $\text{Na}_3\text{Zr}_2\text{P}_3\text{O}_{12}$ (NZN) [2]. The usual structure of these compounds is rhombohedra, space group R3c, but in some particular cases they also show a low temperature phase of lower symmetry [3]. In both phases the framework is built up by $\text{M}_2(\text{PO}_4)_3$ units in which two MO_6 octahedral and three PO_4 tetrahedral share oxygen atoms [4]. Lithium analogues of $\text{Na}_3\text{Zr}_2\text{P}_3\text{O}_{12}$ (NZN), exhibits a low ionic conductivity because a Li^+ ion is too small in size to migrate freely in their three-dimension network structure. The ionic conductivity for the system is greatly increased when Zr^{4+} in $\text{LiZr}_2(\text{PO}_4)_3$ is replaced by the smaller Li^+ ion. Since tunnels in $\text{LiTi}_2(\text{PO}_4)_3$ are more suitable size for the lithium ion migration [5]. In general, Li^+ conductivity is higher and activation energy lower in rhombohedra phases. Activation energies for lithium motion decreases when the tetravalent M cations replaced with Ti^{4+} .

In this paper, high lithium ion conductive solid electrolyte discs based on NASICON-type $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x = 0.1 - 0.9$) could be prepared by a wet-chemical route at 1173 - 1273K, and their phase, ionic conductivity, activation energy and density are investigated.

2. Experimental

Compounds with composition $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$, with $x = 0.1 - 0.9$ were synthesized by a sol-gel method as shown in Fig.1. Aqueous solutions of LiNO_3 , $\text{TiO}(\text{OCCH}_3\text{CHCOCH}_3)_2$, $\text{Ga}(\text{NO}_3)_3 \cdot 8\text{H}_2\text{O}$, TiO_2 (rutile), $\text{Li}_3(\text{PO}_4)$ and $(\text{NH}_4)\text{H}_2\text{PO}_4$ in stoichiometric ratios were mixed together to form a sol, which was dehydrated at 348K for about 3h to form a viscous gel [6]. The gel was then dried at 393K for 12h to form a fine dry xerogel powder, which was then ground and calcined at

773K for 3h. The calcined material was ground again and ball milled for 4h. The powder was pressed into sample discs under 520MPa, and finally sintered at 1173 - 1273K for 6h in air. They were characterized by means of thermogravimetry differential thermal analysis (TG-DTA) (Rigaku TG8120), X-ray diffraction (XRD) (XD-D1, Shimadzu Ltd), field emission scanning electron microscopy (FE-SEM) (JIR-5500, Jeol Ltd), and AC complex impedance techniques(HIOKI 3521 Z), and so on.

3. Results and Discussion

3.1 X-ray diffraction analysis

Figure 2 shows XRD patterns of $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x = 0.1 - 0.9$) sintered at 1173 - 1273K for 6h in air. All diffraction lines were indexed based on a rhombohedral structure with a space group of R3c. When the discs were sintered at 1173K, the single phase solid electrolyte was formed between $x = 0$ and $x = 0.4$, while the impurity phases of LiTiPO_5 and GaPO_4 (hexagonal) [7] appeared at the higher content ratio of $x > 0.5$. While, for the discs sintered at 1223K, the single phase solid electrolyte was formed between $x = 0.25$ and 0.35 . On the other hand, when the discs were sintered at 1273K, the single phase solid electrolyte was formed up to $x = 0.2$, while the impurity phases of LiTiPO_5 and GaPO_4 (orthorhombic) appeared for $x > 0.4$.

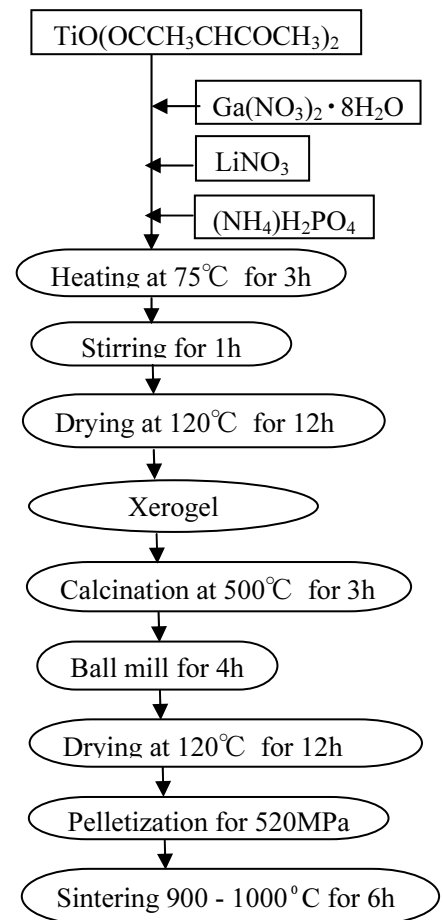


Fig.1 Preparation process of $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ sintering disc.

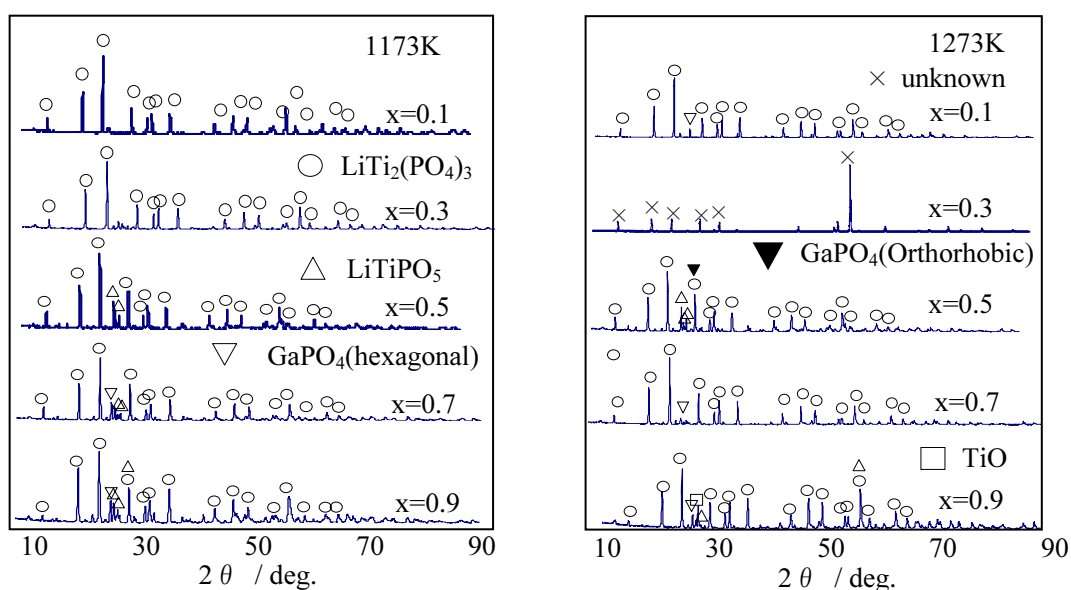


Fig. 2 XRD patterns of the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($x=0.1 - 0.9$) discs sintered at 1173K and 1273K.

3.2 TG-DTA analysis

Figure 3 shows the TG-DTA curves of the $\text{Li}_{1.2}\text{Ga}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$ xerogel powder before heat

treatment at 773K. The sample showed weight loss in the examined temperature range between 373 and 673K. The TG curve was due to the separated organics. In contrast, DTA peak was appeared at around 873 - 973K. The DTA curves were due to be crystallized. All the other samples of TG-DTA curves were similar in shape for $\text{Li}_{1.2}\text{Ga}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$.

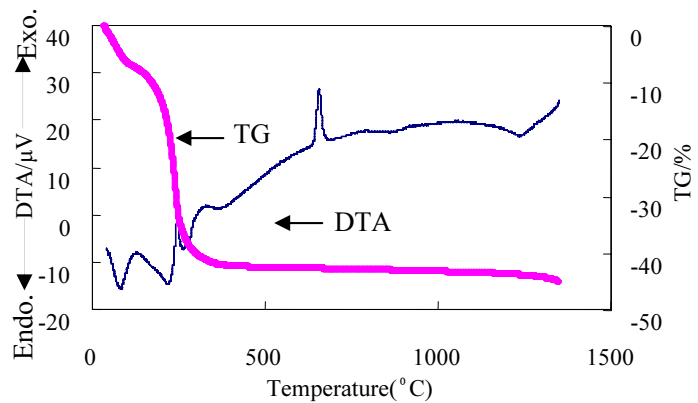


Fig. 3 TG-DTA curves of $\text{Li}_{1.2}\text{Ga}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$.

3.3 FE-SEM, Density and Lattice constant

Figure 4 shows the SEM image of the surface of the $\text{Li}_{1.3}\text{Ga}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ sintered at 1173K. Similar sized particles with a mean particle size of about $1\mu\text{m}$ were shown. The particle size was increased by increasing the sintering temperature and content of Ga^{3+} , but similarly sized particles were not observed. Fig. 5 shows the relation between the relative density of the sintered discs and the x value for the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ systems. Relative density of $\text{LiTi}_2(\text{PO}_4)_3$ ($x=0$) was as low as 55%. Relative density was increased until formed up to $x = 0.3$, while relative density was decreased for $x > 0.4$, as impurity phases appeared for $x > 0.4$. Fig. 6 shows variation of lattice constants a(A) and c(A) for the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ discs at 1173K. The lattice constants a(A) and c(A) increased with the increase in Ga^{3+} up to $x = 0.4$ because the ionic radius of Ga^{3+} was slightly larger than that of Ti^{4+} . The single phase was formed up to $x=0.4$, while an impurity phase appeared for $x > 0.5$. The replaceable limit for a Ga^{3+} ion was around $x = 0.4$.

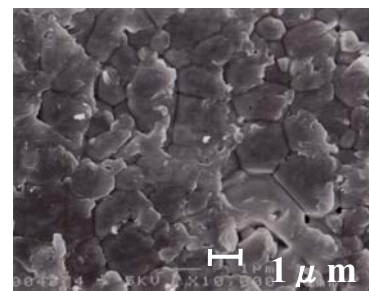


Fig. 4 SEM image of $\text{Li}_{1.3}\text{Ga}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ sintered at 1173K

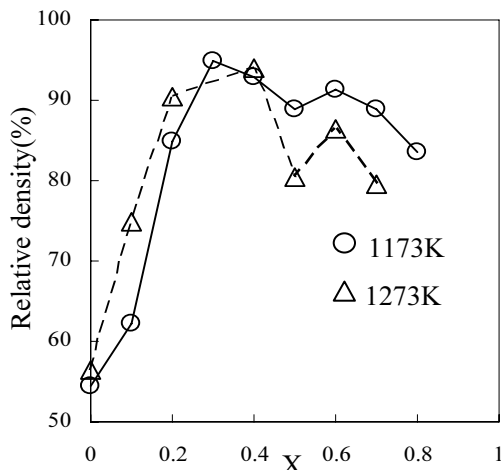


Fig.5 Variation of relative density for the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ discs at 1173,1273K.

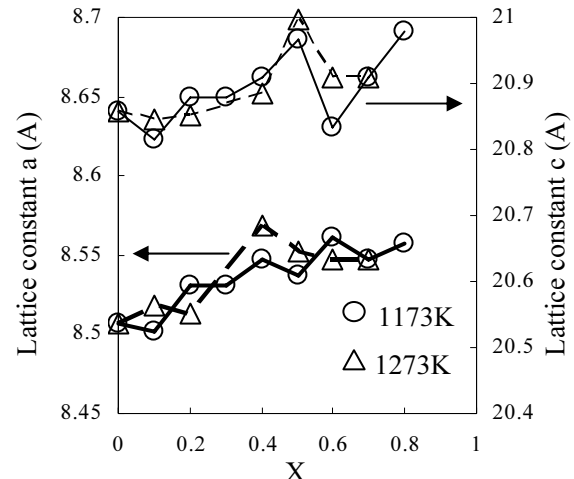


Fig. 6 Variation of lattice constant a and c for the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ at 1173 and 1273K.

3.4 Electrical conductivity and activation energy

Figure 7 shows the electrical conductivity results with x in the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ systems at 303K. The conductivity was greatly enhanced by Ga^{3+} substitution. The maximum conductivity of ca. 7.3×10^{-4} S/cm and activation energy of 0.30eV at 303K was obtained for the $\text{Li}_{1.25}\text{Ga}_{0.25}\text{Ti}_{1.75}(\text{PO}_4)_3$ discs prepared at 1223K. In order to clarify the effect of high densification on the conductivity increase, Li_3PO_4 or TiO_2 (rutile type) (2, 5, 10 wt%) was used as a binder [1]. They were added to $\text{Li}_{1.25}\text{Ga}_{0.25}\text{Ti}_{1.75}(\text{PO}_4)_3$ sintered 1223K, which had the maximum conductivity. The conductivity of all of these samples with binder was lower than the disk without binder in which the maximum conductivity was as high as 7.3×10^{-4} S/cm at 303K.

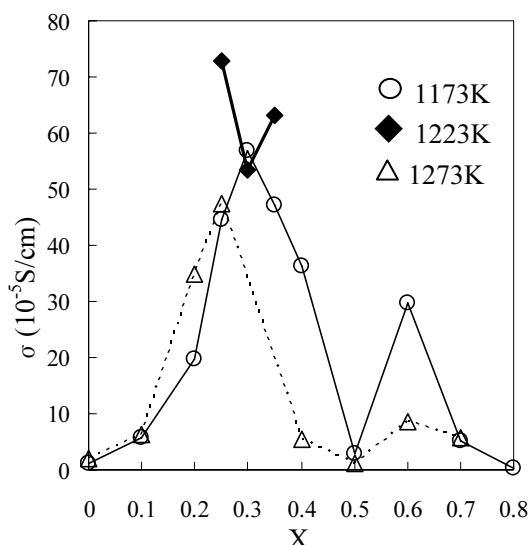


Fig. 7 Variation of the conductivity for the $\text{Li}_{1+x}\text{Ga}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ at 1173,1223,1273K.

4. Conclusion

$\text{LiTi}_2(\text{PO}_4)_3$ showed low ionic conductivity and density in the sintered discs. The partial substitution of Ti^{4+} site with Ga^{3+} in the $\text{LiTi}_2(\text{PO}_4)_3$ system was very effective for the enhancement of the conductivity. The maximum conductivity of ca. 7.3×10^{-4} S/cm and activation energy of 0.30eV at 303K was obtained for the $\text{Li}_{1.25}\text{Ga}_{0.25}\text{Ti}_{1.75}(\text{PO}_4)_3$ discs prepared at 1223K.

References

- [1] H. Aono, E Sugimoto, Y. Sadaoka, N. Imanaka and G Adachi, *J. Electrochem. Soc.*, **137**, 1023 (1990).
- [2] X. Xu, Z Wen, Z Gu and Z Lin, *Solid State Ionics*, **1671**, 207(2004).
- [3] K. Arbi, M. G. Lazarrage, D Ben Hassen Chehimi, M. Ayadi-Trabelsi, J. M. Rojo and J. Sanz, *Chem. Mater.*, **16**, 255 (2004).
- [4] M Catti, A Comotti, S Di Blas and R M. Ibberson, *J. Mater. Chem.*, **14**, 835 (2004).
- [5] H. Aono, M Asri bin Idris and Y. Sadaoka, *Solid State Ionics*, **166**, 52 (2004).
- [6] Y. Shimizu, S. Michishita and T. Murata, *Jpn. J. Appl. Phys.*, **34**, L833 (1995).
- [7] A. Roberton, J. G. Fletcher, J. M. S. Skakle and A. R. West, *J. Solid State Chem.*, **109**, 53 (1994).