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Synthesis and Lithium Ionic Conductivity of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ ($0 \leqq x \leqq 0{\cdot}20$)

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Abstract

Lithium ion conductors, $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ ($0 \leqq x \leqq 0{\cdot}20$)*, were synthesized by a solid state reaction. A superionic conductive phase of* $Li_3In_2(PO_4)_3$ *was stabilized down to room temperature, assisted by the substitution of* Zr^{4+} *for* In^{3+} *sites of* $Li_3In_2(PO_4)_3$*. TG-DTA analysis indicated no phase transition in the samples with* x *superior to 0·05. The substituted samples showed much higher ionic conductivity by a couple of magnitude than that of* $Li_3In_2(PO_4)_3$*. In particular, the highest conductivity at room temperature was* $1{\cdot}42\times10^{-5}$ *Scm*$^{-1}$ *for* $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$*. Thin films with the composition of* $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ *was prepared by a sol–gel method. A coating solution was made from lithium isopropoxide, indium isopropoxide, zirconium isopropoxide and diphosphorus pentaoxide. Well crystallized films were obtained on silicon dioxide and quartz glass substrates by dropping the coating solution, followed by firing over 873 K. In the temperatures above 473 K the lithium ionic conductivity of the film was slightly higher than that of sintered samples prepared by the solid state reaction at 1373 K. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: stabilization, films, sol–gel processes, ionic conductivity.

1 Introduction

Lithium-ion batteries have been extensively studied because of their high cell voltage and high energy density, which can fulfill an advanced battery system demanded in future energy resources. Nonaqueous solutions and polymers are at present used as the electrolyte for the practical batteries. However, these electrolytes cannot meet the requirements of size-compactness, integration, stability at high temperatures and safety problems owing to the burnable electrolytes. Therefore, lithium superionic conductors exhibiting an enough high ionic conductivity at ambient temperature are desired in order to develop a new lithium-ion battery system. Although some nitrides and non-oxide glasses show a high conductivity, $\sim10^{-3}$ Scm^{-1}, at room temperature, they are not necessarily stable in an air.[1–3] Oxide lithium ion conductors have some advantages in practical applications to solid state electrolytes for batteries, such as easy synthesis, easy handling and high decomposition voltage.

Recently, $Li_3In_2(PO_4)_3$ was reported as a new lithium ionic conductor.[4] $Li_3In_2(PO_4)_3$ exists at room temperature in either modification of rhombohedral NASICON type or monoclinic β-$Fe_2(SO_4)_3$ type depending on the synthetic conditions. The former is synthesized at low temperatures (LT-$Li_3In_2(PO_4)_3$), while the latter is synthesized at high temperatures (HT-$Li_3In_2(PO_4)_3$) and has a higher ionic conductivity. HT-$Li_3In_2(PO_4)_3$ has the same structure features of $Li_3Sc_2(PO_4)_3$ with three polymorphous phases: a monoclinic α-phase below 360 K, a monoclinic β-phase between 360 and 368 K, and an orthorhombic γ-phase above 368 K. The phase transitions are all reversible.[5] The γ-phase exhibits what is called a superionic conductivity.

In this study, the partial substitution of Zr^{4+} ions for In^{3+} was investigated with a view to stabilizing the γ-phase of $Li_3In_2(PO_4)_3$ and to improving the ionic conductivity. Further, the preparation of a $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ thin film stabilized in the γ-phase was tried by a sol–gel method, bearing in mind a practical application to a solid electrolyte for lithium ion batteries.

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2 Experimental

The sintered samples of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ with $0\leqq x\leqq 0{\cdot}20$ were prepared by a conventional solid state reaction. The starting materials were high purity Li_2CO_3, In_2O_3, $ZrO(NO_3)_2{\cdot}2H_2O$ and $NH_4H_2PO_4$. The stoichiometric mixtures of them were ground in an agate mortar, and then preheated at 573 K for 2 h in air. The preheated powder was pressed into a pellet under 300 MPa and heated in an alumina crucible at 1373 K for 10 h in air. The completion of the reaction and the phase purity of the product were confirmed by a powder X-ray diffractometer (Rigaku Geigerflex, SG-7). Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were conducted between 298 and 573 K with a heating rate of 5 $K\,min^{-1}$ using a Seiko Electronic Industry thermal analyzer system EXSTAR6000.

Specimens were prepared for conductivity measurement by pressing the powder sample into a compact disk at a pressure of 490 MPa in a 9 mm diameter steel die. The disk was sintered at 1473 K for 5 h. The sintered disk was of typical thickness of about 1·0 mm. The two opposite sides of the disk were coated with a platinum paste, and then heated at 1073 K for 2 h. The conductivity was determined by a complex impedance analyzer (Hewlett Packard, HP4192A) in the temperature range 298–573 K under a nitrogen atmosphere.

The thin film of $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ was prepared by a sol–gel method. Starting materials for the sol–gel method were lithium isopropoxide (LiO-i-Pr), indium isopropoxide ($In(O\text{-}i\text{-}Pr)_3$), zirconium isopropoxide ($Zr(O\text{-}i\text{-}Pr)_4$) and diphosphorus pentaoxide. Ethylalcohol and isopropylalcohol were used as a solvent for these materials. Figure 1 shows a preparation sequence of the thin film with the composition of $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$. The concentration of the coating solution thus obtained was about 0·025 mol dm^{-3}. All the operations were done in a glove box filled by nitrogen gas. A quartz glass and a silicon wafer were used as a substrate for the thin film. The conductivity measurement was performed for the thin film prepared on the quartz substrate, on which two lines of platinum electrode were previously sputtered with a distance of 50 μm. The surface state of the thin film was observed with a scanning electron microscope (SEM; Shimadzu, EPMA8705).

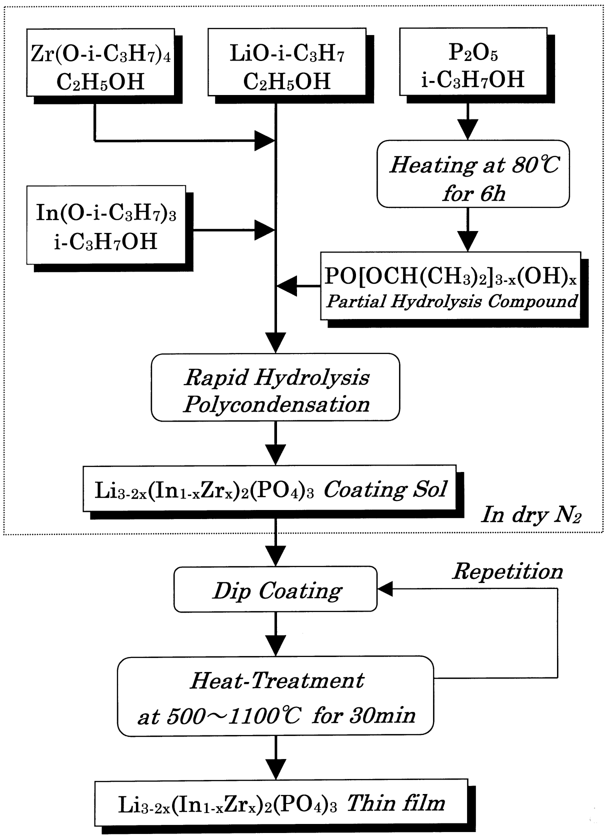

Fig. 1. Thin film preparation process.

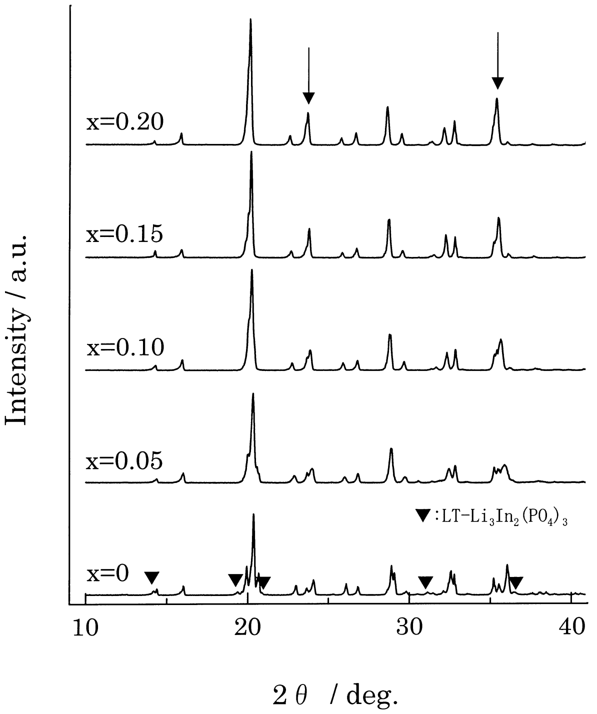

Fig. 2. Powder X-ray diffraction patterns of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$.

3 Results and Discussion

Figure 2 shows the powder X-ray diffraction patterns of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ ($0\leqq x\leqq 0{\cdot}20$) prepared by the solid state solution. The indexing and the Rietveld analysis showed that all the samples had a single phase with an orthorhombic symmetry except for the samples with $x=0$ and $x=0{\cdot}05$, which was found to be a mixture of LT-$Li_3In_2(PO_4)_3$ and HT-$Li_3In_2(PO_4)_3$ similar to the previous work on $Li_3In_2(PO_4)_3$.[4] The two neighboring reflection peaks indicated by arrows in Fig. 2 become closer to each other on increasing the substitution ratio of Zr^{4+} for In^{3+}, and seemingly become a single peak over

$x = 0{\cdot}10$, where the trigonal LT-$Li_3In_2(PO_4)_3$ also disappeared completely. This indicates a transition to a higher crystal symmetry, i.e. the phase transition from monoclinic to orthorhombic. The results of the DTA analysis for $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ ($0 \leqq x \leqq 0{\cdot}20$) were shown in Fig. 3. The sample with $x = 0$ has two reversible phase transitions at about 378 and 403 K. Referred to the previous work for $Li_3In_2(PO_4)_3$,[4] the low temperature peak corresponds to the transition from β to γ for HT-$Li_3In_2(PO_4)_3$, and the high temperature peak corresponds to that for LT-$Li_3In_2(PO_4)_3$. In the samples with x higher than 0·05 such a phase transition was not detectable any more. Although the presence of the $\alpha \rightarrow \beta$ transition of HT- and LT-$Li_3In_2(PO_4)_3$ was confirmed by single crystal analyses and conductivity measurements, DTA could not detect the $\alpha \rightarrow \beta$ transition because of its considerably small free energy change due to the phase transition based only on the rearrangement of the lithium position without any drastic framework structural change.

The Wagner's polarization technique using Pt blocking electrodes clearly showed no electronic conduction for $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ samples. The complex impedance diagrams for all the samples consist of part of a semicircle terminated with a sloping line. The conductivity was determined from a low frequency intercept of the semicircle by means of a nonlinear least-squares method. The variations of the ionic conductivity with temperature are shown in Fig. 4. The behavior of the unsubstituted sample of $Li_3In_2(PO_4)_3$ is quite similar to that reported previously.[4] All the samples with $x \geqq 0{\cdot}05$ shows a liner conductivity behavior in the whole temperature range measured. The slopes of the lines corresponding to an activation energy for lithium ion conduction seem to be nearly equal to that of the γ-phase of the unsubstituted sample. These results clearly indicate that the γ-phase was stabilized at the whole temperature range in all the substituted samples. The sample with $x = 0{\cdot}10$ shows the highest conductivity in almost the whole temperature range. The room temperature conductivity of the sample is $1{\cdot}42 \times 10^{-5}$ Scm^{-1}. The structures of α- and β-phase for $Li_3In_2(PO_4)_3$ are somewhat different from those for $Li_3Sc_2(PO_4)_3$, respectively, in a view point of the local occupation in available sites for lithium, although basic structural features of these phases for both compounds are quite similar.[6,7] The stabilization of the γ-phase in $Li_3In_2(PO_4)_3$ seems to be taken place by the same manner as those for $Li_3Sc_2(PO_4)_3$,[8] i.e. the substitution of aliovalent ions for In sites can introduce some vacancies to the lithium site due to the charge compensation, bringing about a disorder into the available lithium sites. The stabilized γ-phase of $Li_3In_2(PO_4)_3$ has a little higher conductivity that of $Li_3Sc_2(PO_4)_3$. This seems to come from a larger size of bottle necks for the ion conduction path than that in the case of $Li_3Sc_2(PO_4)_3$.

Figure 5 shows the powder X-ray diffraction patterns of the $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ thin films prepared at various temperatures. A precursor of $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ crystallized already at a much lower temperature of 873 K. From the TG-DTA results, it was shown that the thermal decomposition of the gel prepared by the sol-gel method was completed at 873 K. This temperature is also quite lower than the crystallization temperature in

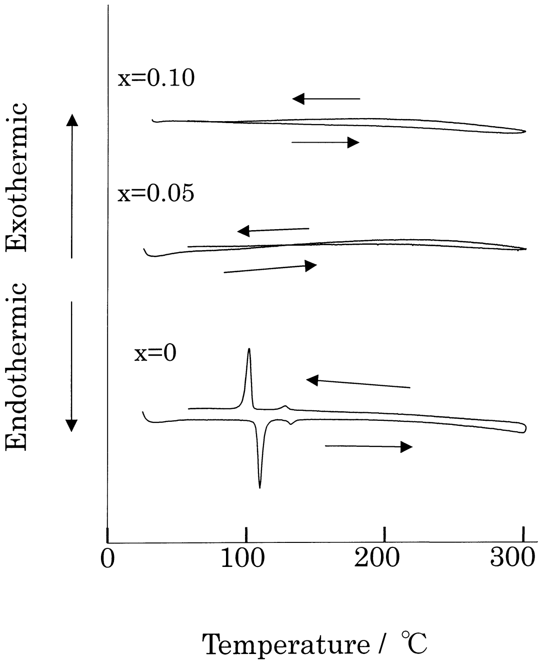

Fig. 3. DTA curves of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$.

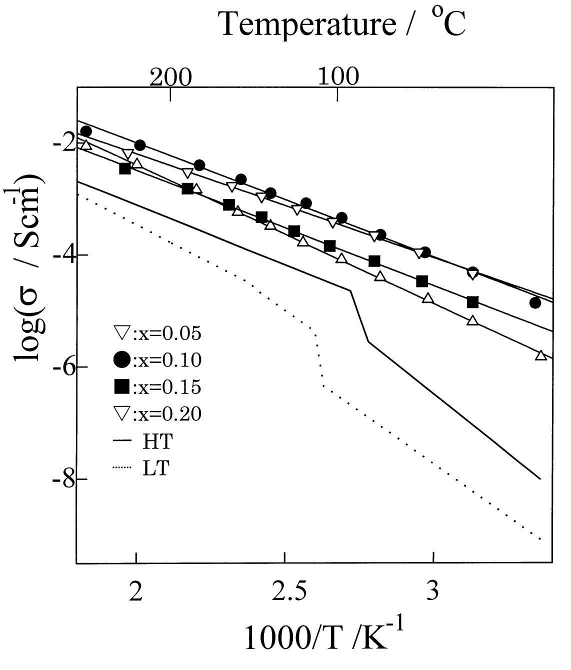

Fig. 4. Ionic conductivity of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$. The data for HT-$Li_3In_2(PO_4)_3$ and LT-$Li_3In_2(PO_4)_3$ are referred to Ref. [4].

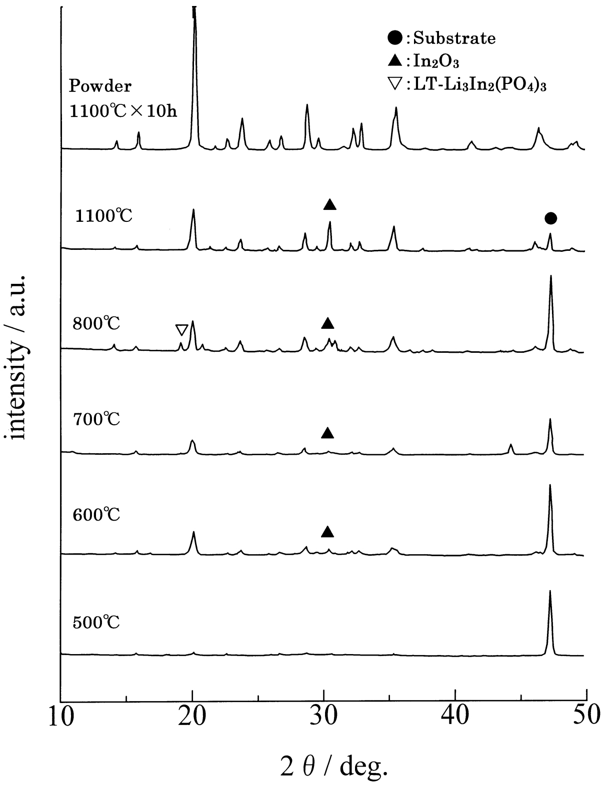

Fig. 5. Powder X-ray diffraction patterns of $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ ($x = 0{\cdot}10$) thin films heated at various temperature.

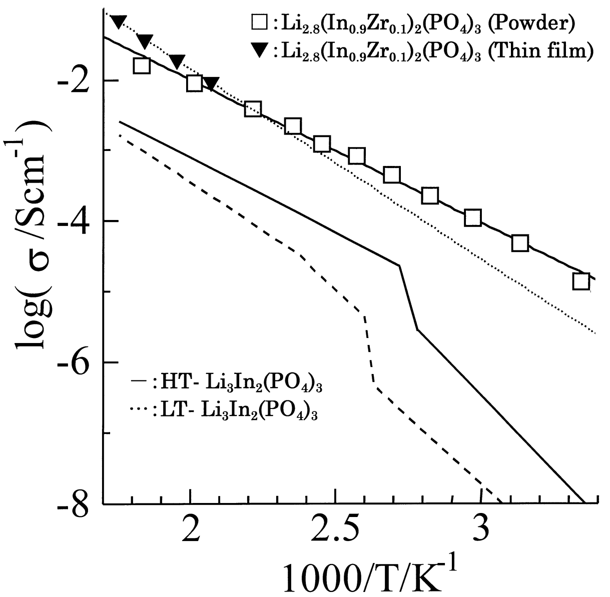

Fig. 6. Ionic conductivity of thin film and powder (sintered) for $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$. The data for HT-$Li_3In_2(PO_4)_3$ and LT-$Li_3In_2(PO_4)_3$ are referred to Ref. 4.

the solid state reaction. A small amount of In_2O_3 impurity was observed in the films prepared at 873–1373 K. This is probably due to a faster hydrosis reaction and/or less solubibly of indium isopropoxide in the organic solution, compared with other alkoxides.

Figure 6 shows the temperature dependence of conductivity. Above 473 K the lithium ionic conductivity of the film was slightly higher than that of the sintered sample prepared by the solid state reaction at 1373 K. But the lithium ionic conductivity could not be estimated from the impedance measurement below this temperature. The diagrams of the Cole–Cole plots obtained in this temperature range consisted of a slightly curved line starting from the origin of the real and imaginary axes of the impedance diagram. In order to estimate a reliable conductivity value, lower frequencies than 5 Hz should be necessary.

4 Conclusion

The high temperature phase (γ-phase) of HT-$Li_3In_2(PO_4)_3$ was successfully stabilized at room temperature in $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ for $x \geqq 0{\cdot}05$. The room temperature ionic conductivity was increased by three orders of magnitude, providing $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ for a promising solid electrolyte in a practical application to lithium-ion batteries. The highest ionic conductivity at 298 K ($\sigma \simeq 10^{-4}$ Scm^{-1}) was observed in $Li_{3-2x}(In_{1-x}Zr_x)_2(PO_4)_3$ with $x = 0{\cdot}10$.

The thin film of $Li_{2{\cdot}8}(In_{0{\cdot}9}Zr_{0{\cdot}1})_2(PO_4)_3$ could be synthesized by the sol–gel method at lower temperatures than that in the case of the sintered powder sample. Above 473 K the lithium ionic conductivity of the film was slightly higher than that of the sintered samples prepared by the solid state reaction at 1373 K.

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