Preparation of High Lithium Ion Conducting $LiLnSiO_4$ (Ln=La, Sm) Thin Films by Sol-Gel Method

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A sol-gel method was applied to prepare thin films of $LiLnSiO_4$ (Ln=La,Sm). The coating solution was made from lithium isopropoxide, silicon tetraethoxide, and tris(acetylacetonato)rare-earth. Well crystalline films with 0.1~0.3 μm in thickness were obtained on alumina and quartz glass substrates by spin-coating, followed by firing over 400° C. The lithium ionic conductivity of the films was much greater than that of sintered samples prepared by a conventional solid state reaction at 1000° C.

High lithium ion conducting solids have potential use for electrolyte materials of high energy density batteries, gas sensing devices, and other electrochemical devices.[1] The establishment of thin film preparation methods for solid electrolytes seems to have an invaluable impact upon their application fields because of possibility of compactness and easiness in making micro-devices. The thin film ion conductor can also have an advantage in allowing us to utilize low ionic conducting materials.

Lithium ion conduction in crystalline materials has, in general, been achieved by tailoring the three dimensional rigid framework of PO_4, SiO_4, or GeO_4 oxo groups, which can make lithium ions mobile through their interstitial space. However, the high ion conducting materials reported so far are so complicated in composition because some of the components are replaced by making non-isovalent substitution in order to increase in the conductivity.[2] Therefore, these materials are not suitable for preparing thin films by using any film making techniques such as vacuum evaporation, CVD, and sputtering methods.

A new class of lithium ion conductors formulated by $LiLnSiO_4$ (Ln=rare-earth) was reported by Nakayama et al.[3,4] The compounds with Ln=La-Dy are hexagonal, while those with Ln=Ho-Lu and Y are orthorhombic. The former materials have much higher ion conductivity than the latter. In the previous study,[5,6] we have reported the structure examination of $LiLaSiO_4$ and found an apatite structure as a possible structure for the bulk, the chemical formula of which can not be expressed simply by $LiLaSiO_4$. We also suggested that the grain boundaries participate significantly the lithium ion conduction. We report here the thin film preparation methods for $LiLaSiO_4$ and $LiSmSiO_4$ ion conductors by using a sol-gel method.

Starting materials for the sol-gel method were lithium isopropoxide (LiO-i-Pr), silicon tetraethoxide ($Si(OEt)_4$), and tris(acetylacetonato)lanthanum (or samarium) ($Ln(acac)_3$). Methylalcohol was used as a solvent for these materials. Figure 1 shows a flow chart for the preparation of thin films of $LiLnSiO_4$(Ln=La,Sm). The concentration of the methylalcohol solution was 2.234×10^{-2} mol dm^{-3} for $La(acac)_3$ (15 cm^3). Methylalcohol solutions of $Si(OEt)_4$ and LiO-i-Pr were mixed with the $Ln(acac)_3$ solution with an equimolar ratio. The nitric acid solution with three times moles of the $LiLnSiO_4$ composition was added in the final stage to obtain a coating solution. The concentration of the coating solution thus obtained was 1.676×10^{-2} mol dm^{-3}. Before coating, the solution was aged for 24h at room temperature. All the operations were done in a glove box filled by nitrogen gas. A quartz glass or a silicon wafer was used as a substrate for the thin film. A spin coating was conducted with a rotation rate of 1000~1500 rpm. The film thickness was increased by repeating the coating and heating processes for several times. 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 100 μm. The thickness of the film was measured under observation with SEM.

The sol-gel method with using rare-earth acetate, as previously reported, made it possible to prepare a thin film of

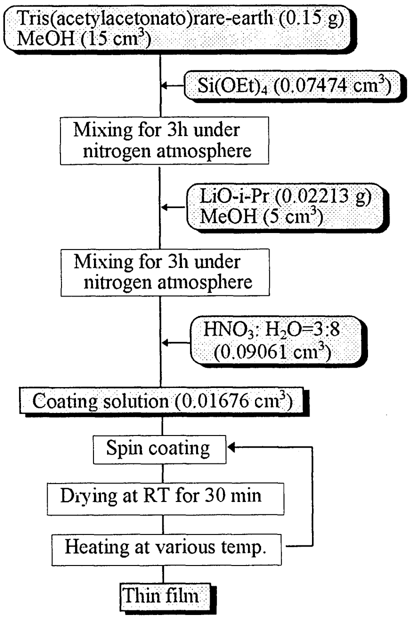

Figure 1. Synthesis procedure for $LiLnSiO_4$(Ln=La,Sm) thin film by sol-gel method.

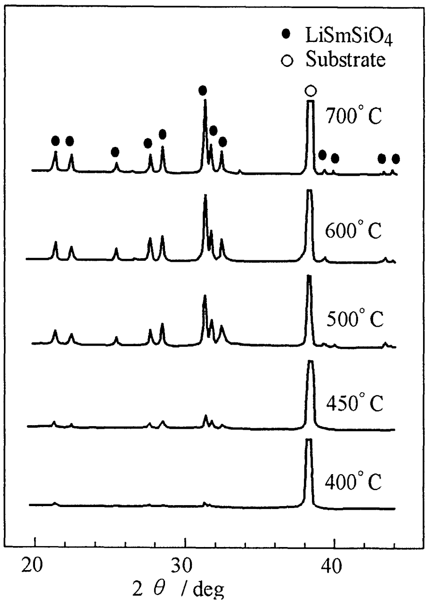

Figure 2. Powder X-ray diffraction patterns of $LiSmSiO_4$ thin films heat-treated at various temperatures.

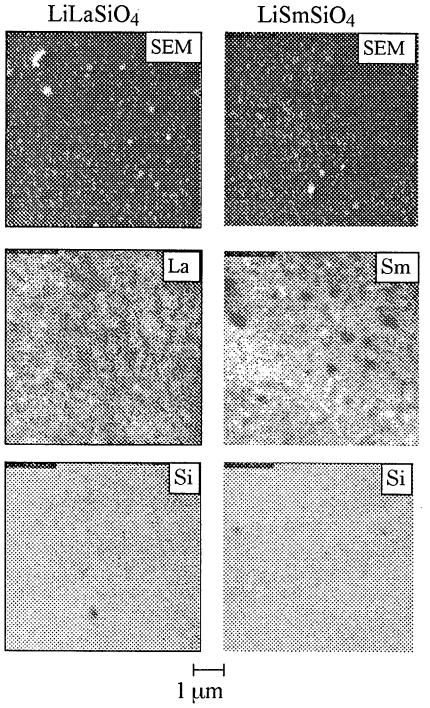

Figure 3. Surface morphology and surface analysis of $LiLnSiO_4$(Ln=La,Sm) thin film by EPMA. SEM, La, Sm, and Si, represent SEM, La-Kα, Sm-Kα, and Si-Kα images, respectively.

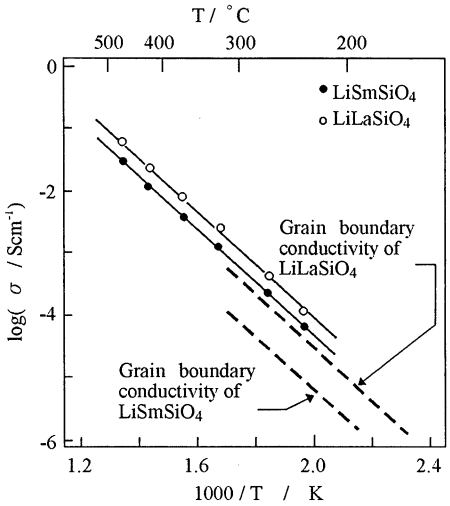

Figure 4. Temperature dependence of conductivity of $LiLnSiO_4$(Ln=La,Sm). The dashed lines represent the conductivity for the amorphous silicon-rich grain boundary phase of $LiLnSiO_4$(Ln=La,Sm) sintered samples in Ref.6.

$LiYSiO_4$ with an olivine structure at 700° C.[7] The powder X-ray diffraction patterns of the thin films made in this study by using tris(acetylacetonato)rare-earth used were shown in Figure 2. The apatite phase in the thin film crystallized at a much lower temperature, 400° C, and its crystallinity became much better, comparing with the previous one made by using rare-earth acetate.[7] From the TG-DTA data, it was shown that the thermal decomposition of the gel prepared by this method was completed at 400° C. This temperature is also quite lower than that in the previous method. Metal alkoxides chemically modified with acetylacetone are well known to be very effective for control of reactivities and condensation process in binary or ternary metal alkoxide systems, such as in case of $PbZrO_3$-$PbTiO_3$ thin films prepared by sol-gel method.[8] In such cases metal-oxygen-metal bridges assisted by alkoxide-acetylacetonato complexes may be formed,[9] giving a similar hydrolysis rate to each metal component. Our case could be the case, leading to the low crystallization temperature of the bulk apatite phase.

Figure 3 shows the surface morphology examined by EPMA for the thin film of $LiSmSiO_4$ prepared by doubly repeated coating and heating. The thickness of the film is about 0.1~0.3 μm. The thin film prepared shows a fairly smooth surface and almost homogeneous metal distribution. This is quite in contrast to the case of the sintered materials obtained by a solid state reaction, where the EPMA clearly showed the existence of a rare-earth rich bulk phase and a silicon rich grain boundary phase.[6]

The ionic conductivity was determined by Cole-Cole diagrams obtained from the complex impedance measurements. The diagrams clearly showed one somewhat depressed semicircle followed by an almost straight line with a slope of about 45° due to the Warburg impedance, implying only one predominant conduction path. The ionic conductivity of the thin film was estimated from the intercept of the real impedance axis in the diagram. Figure 4 shows the temperature dependence of conductivity. The conductivity of the thin films at any temperatures becomes significantly greater than that for the grain boundary phase in the sintered materials with the same nominal composition, especially greater by almost an order of magnitude for $LiSmSiO_4$. The activation energy seems to be invariant whichever the material is a sintered pellet or a thin film. These facts indicate that the increase in the conductivity observed in the thin films comes from the increase in the high ion conductive paths of the amorphous silicon-rich grain boundary. Because the metal components are well distributed in the film prepared by the spin-coating method, the high conductive grain boundary becomes well extended in the film. Therefore, the conductivity attributed to the grain boundary seems to overcome the contribution from the bulk.

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