

Structural Determination and Thin Film Preparation of LiYSiO₄ by Sol-Gel Method

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(Received January 30, 1995)

LiYSiO₄ was synthesized by sol-gel method and its crystal structure was determined by the Rietveld analysis. The structure was found to be an olivine-type structure with orthorhombic Pnma space group. The thin film deposited on a quartz substrate could be prepared by a dip-coating method using sol solutions consisting of lithium i-propoxides, silicon tetraethoxide and yttrium acetate.

High lithium ion conducting solids have potential use for electrolyte materials of high energy density batteries. Among lithium ion conductors reported up to date, materials containing oxo groups, such as PO₄, SiO₄, GeO₄, and ZrO₄, have superior high conductivities.¹ Since the increase in ion conductivity of these materials is usually taken place by doping various kinds of cations to introduce vacancies and interstitial ions into the matrix, the composition sometimes becomes so complicated. Therefore, it is not so easy to construct a thin film, which is quite effective for the applications to electrochemical devices.

Nakayama *et al.*² recently reported new classes of lithium ion conductors formulated as LiLnSiO₄ (Ln=rare earths). The compounds with Ln=La-Dy are hexagonal, while those with Ln=Ho-Lu and Y are orthorhombic. In the previous study,³ we reported the structure determination of LiLaSiO₄ and found an apatite structure as a possible structure of the bulk, the chemical formula of which can not be expressed as LiLaSiO₄ simply. We also suggested that the grain boundaries of this compound participated in the great deal of the lithium ion conduction. Although the structure of the latter compounds was still unknown, the indexing of the powder X-ray diffraction pattern strongly suggested an olivine-type structure with a simple stoichiometric composition. This fact seems to be quite suitable for the formation of a thin film by sol-gel process. We report here the structure refinement and the thin film formation of LiYSiO₄.

Starting materials for sol-gel method were lithium i-propoxide (LiOⁱPr), silicon tetraethoxide (Si(OEt)₄), and yttrium acetate

tetrahydrate (Y(OAc)₃•4H₂O). Methylalcohol was used as solvent for these materials. Figure 1 shows the flow charts for the preparation of the dip coating solutions used for thin films of LiYSiO₄. These two methods are substantially the same, and only the mixing sequence of the starting materials is different from each other. In the method I, a Si(OEt)₄ solution was added to the methylalcohol solution of LiOⁱPr, followed by adding the methylalcohol solution of Y(OAc)₃, while, in the method II, the addition of the Si(OEt)₄ and Y(OAc)₃ solutions was exchanged. The concentration of the methylalcohol solution of LiOⁱPr used in the starting solution was adjusted to be 0.04 molL⁻¹ for both two methods. The final stage of the preparation for the dip coating solution was obtained by adding the water with 50 times of moles for the LiYSiO₄ composition and then aging the solution at 80 °C for 2 h. A quartz substrate was dipped into the solution and withdrawn, and then heated at given temperatures for several hours. The thin film was obtained by repeating the above dipping-withdrawing and heating processes for several times. The bulk sample used for the structure determination was prepared by completely gelling the coating solution, followed by heating the gel at 1100 °C for 24 h. The powder X-ray diffraction patterns of the bulk sample were analyzed by the Rietveld method using a RIETAN94 profile refinement program.⁴

A powder sample of LiYSiO₄ was first prepared by the sol-gel method. The coating solution obtained from the method I was concentrated in an oven at 80 °C for 24 h to be gelled. The gels obtained were white and translucent. The gels were pulverized and heated at various temperatures for 3 h. Figure 2 shows the X-ray diffraction patterns of the samples together with that obtained by the solid state reaction among Li₂CO₃, Y₂O₃ and SiO₂ at 1100 °C for 3 h. A well crystalline phase of LiYSiO₄ was obtained by heating at relatively low temperatures over 700 °C, although small amounts of impurities such as Y₂O₃ and apatite-type "LiYSiO₄".³ Since the boundary from apatite

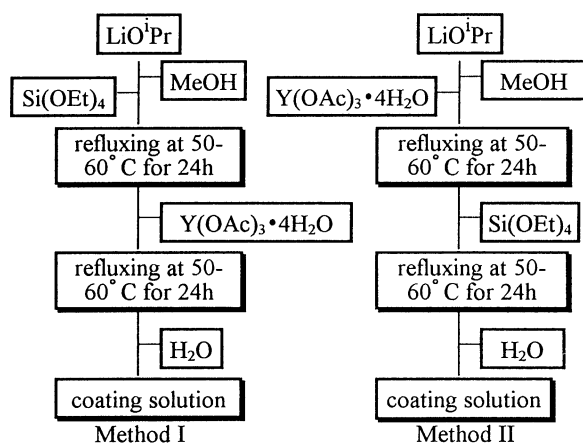


Figure 1. Flow Charts of preparation methods of coating solutions for thin film of LiYSiO₄.

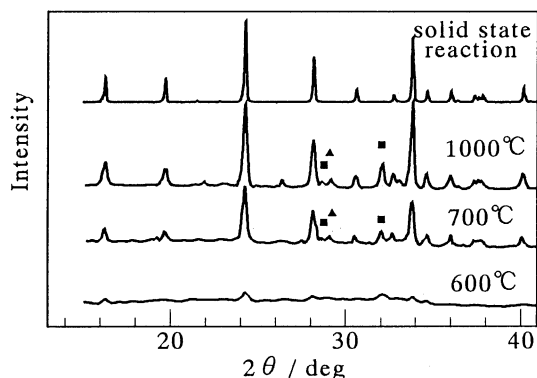


Figure 2. Powder X-ray diffraction patterns of LiYSiO₄ prepared by sol-gel method. The gel was heated for 3 h at given temperatures. The sample prepared by the solid state reaction was heated for 3 h at 1100 °C. ■, apatite phase, ▲, Y₂O₃.

Table 1. Positional parameters refined for LiYSiO₄. The cell constants are $a=10.831(1)$ Å, $b=6.3226(6)$ Å, $c=4.9266(5)$ Å, and $Z=4$ for Pnma. The reliable factors are $R_{wp}=7.70\%$ ($S=R_{wp}/R_e=1.61$), $R_p=5.87\%$, $R_f=2.29\%$, and $R_{\bar{r}}=1.41\%$

Atom site	g	x	y	z	B/Å ²	
Li	4a	1.0	0.0	0.0	1.1(6)	
Y	4c	1.0	0.2788(1)	0.25	-0.0329(3)	0.19(4)
Si	4c	1.0	0.0866(5)	0.25	0.402(1)	0.5(1)
O(1)	4c	1.0	0.0983(1)	0.25	0.736(2)	0.5(3)
O(2)	4c	1.0	0.446(1)	0.25	0.214(2)	0.1(1)
O(3)	8d	1.0	0.1617(9)	0.045(1)	0.265(1)	0.1(1)

structure to olivine structure lies near holmium element in a series of LiLnSiO₄ (Ln=rare earths), the olivine-type LiHoSiO₄ and LiYSiO₄ sometimes crystallize with a small amount of the apatite phase. These impurity phases disappeared when the heating temperature was raised over 1100°C. In further experiments, the thin film sample was prepared at 700°C for 3 h in order to avoid the reaction between the sample and the quartz substrate.

All the reflections in the powder X-ray diffraction pattern of the bulk sample were completely indexed on an orthorhombic crystal system, giving Pnma and Pn2₁a space groups. The cell parameters roughly estimated from the program CELL⁵ were $a=10.827$ Å, $b=6.306$ Å and $c=4.925$ Å. Considering the deduced space groups and the dimensions of cell parameters, the structure of LiYSiO₄ can be easily derived from the olivine-type structure. The site assignment for the Rietveld analysis was done by reference to that of isostructural mineral chrysoberyl, Al₂BeO₄, with Pnma space group.⁶ From the Fourier maps obtained from the refinement stages, the site for lithium was deduced. The finally refined results are listed in Table 1. The reliable factor for R_{wp} is 7.70%, quite smaller than that obtained for the sample prepared by the solid-state reaction, $R_{wp}=10.32\%$. In Figure 3 the structure of LiYSiO₄ is shown. Although the

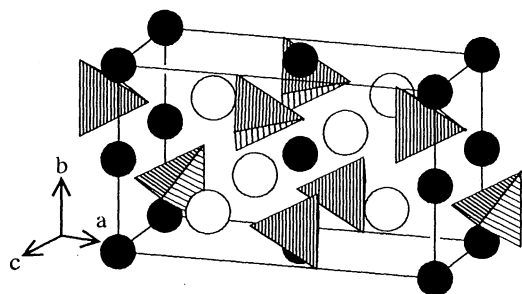


Figure 3. Crystal structure of olivine-type LiYSiO₄. The tetrahedra are SiO₄ units. The filled and open circles are lithium ions and yttrium ions, respectively.

position of the lithium atoms cannot be, in general, assigned by X-ray structural analysis, the proposed crystal structure is very reasonable in a viewpoint of the Li-O bond distance, *i.e.*, the average observed distance is 2.23 Å, comparable with the distance calculated from Shannon's ionic radius,⁷ 2.11 Å. The structure consists of isolated SiO₄ tetrahedral units. Both lithium and yttrium atoms are in octahedra composed of oxygen atoms, which are almost in hexagonal-close-packing.

The thin film of LiYSiO₄ was prepared by using the coating

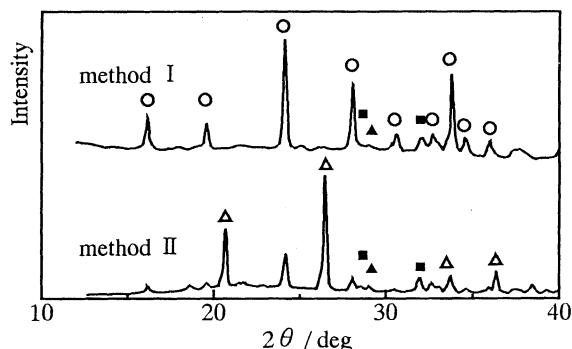


Figure 4. Powder X-ray diffraction patterns of LiYSiO₄ prepared at 700°C for 3 h by using coating solutions obtained from two methods. ○:LiYSiO₄, ■, apatite phase, ▲, α-quartz, △; Y₂O₃.

solutions obtained from the methods I and II. Because the prepared thin films are less than 0.1 μm in thickness, the phase analysis by X-ray diffraction was done for the powder samples collected from the thin film on the substrate (Figure 4). The sample from the method I has an almost single phase, while α-quartz is the main product in the sample from the method II. Generally each alkoxide hydrolysis in the mixture with more than binary metal alkoxides is different from metals to metals, and its rate is dependent on both the kinds of metals and alkoxy groups. So, the formation of bimetallic alkoxides in the coating solution is desirable for the crystallization of binary metal oxides in a low temperature preparation. It is well known that bimetallic alkoxides are easily formed by simple reactions between their monometallic alkoxides, *e.g.*, the system between alkali metal alkoxides and aluminum alkoxides.⁸ A bimetallic alkoxide of lithium and silicon in the method I is probably formed, whereas that in the method II may not be formed sufficiently because the hydrolysis of LiOⁱPr is taken place gradually by the water from Y(OAc)₃·4H₂O in the first refluxing (Figure 1) before addition of Si(OEt)₄. Therefore, the formation of lithium-silicon bimetallic alkoxide is crucial factor for the low temperature crystallization of LiYSiO₄ thin film.

The present work was supported by a Grant-in-Aid for Scientific Research on Priority Areas "New Development of Rare Earth Complexes" No.06241229 from The Ministry of Education, Science and Culture.

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