

Formation of nano-sized particles of a solid electrolyte by laser ablation

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Abstract

Nano-sized particles of a lithium ion conductive solid electrolyte, $\text{LiTi}_2(\text{PO}_4)_3$, were prepared by laser ablation. The obtained particles were ca. 10 nm in diameter. X-ray powder diffraction and Raman spectroscopy showed that they were amorphous with local structure similar to the crystalline counterpart. They were crystallized by the heating at ca. 630 °C.

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1. Introduction

Solid electrolytes are attracting a great interest because they are fundamental solution to the safety issue of lithium batteries. In addition to the safety, ion selectivity of inorganic solid electrolytes effectively suppresses side reactions, which often take place in liquid systems, resulting in high reliability including long cycle life and long shelf life. However, solid-state lithium batteries with inorganic solid electrolytes have been generally lower in energy density and current drain than liquid systems. We have already succeeded in making their energy density comparable to those of liquid systems by adopting a unique battery construction where two different kinds of solid electrolytes were used [1]. A subject left is how to enlarge the current drain, or power density. Electrodes in bulk-type, i.e. not-thin-film, solid-state batteries are mixtures of electrode material and solid electrolyte powders in order to enlarge their contacting area. However, electrode areas in solid systems still tend to be smaller than those in liquid systems owing to the small contacting area at solid/solid interface between the particles of electrode materials and solid electrolytes; that is, it is difficult to completely cover the surfaces of particles of the electrode material by hard particles

of the solid electrolyte. Furthermore, there are many pores in such a composite electrode, which lower the energy density as well as the ionic conductivity in the electrode.

Very fine particles of solid electrolytes will be effective to solve the above problems. They will fill the pores and enlarge the contacting area. In the recent years, laser ablation has been available for the preparation of various kinds of nano-scaled ceramic powders [2]. Such very fine particles can be formed under low vacuum, e.g. near the ambient pressure, with well-controlled composition. The former feature is preferred for a large scale of preparation, while the latter is necessary for high ionic conduction, because ionic conduction is sensitive to the amounts of defects and interstitials, which are introduced by controlling the composition. In the present study, we prepared nano-sized particles of a solid electrolyte using laser ablation.

2. Experimental

2.1. Preparation of nano-scaled particles

A solid electrolyte with NASICON structure, $\text{LiTi}_2(\text{PO}_4)_3$ (LTP) [3], was used in the present study. Powder of LTP was synthesized from Li_2CO_3 , TiO_2 , and P_2O_5 as starting materials. They were mixed in an Ar-filled glove box. The

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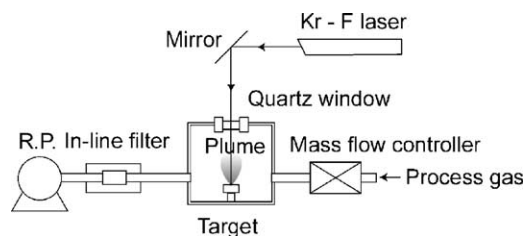


Fig. 1. A schematic drawing of the laser ablation system used in the present study.

mixture was heated at 1000 °C for 2 h in air. The synthesized powder was pressed into a pellet and sintered at 1000 °C for 2 h in air again to be used as a target, or an evaporation source, for the laser ablation.

Fig. 1 is a schematic drawing of the ablation system used in the present study. A Kr-F pulsed laser with a wavelength of 248 nm was used for the preparation. The laser pulse width, repetition rate, and power of the pulsed laser light were 30 ns, 10 Hz, and 120 mJ, respectively. The laser beam was focused onto the target through a quartz window. Oxygen gas was introduced into the chamber during the ablation, and it carried the formed nano-sized particles to an inline filter connected to a rotary pump, where they were collected. The pressure in the chamber was controlled to be ca. 20 Pa.

2.2. Characterization of the material

The morphology and the composition of the powder were observed by a transmission electron microscopy (TEM) and energy dispersive X-ray (EDX) spectroscopy, respectively, on a microscope (JEM-3000F, JEOL).

Differential thermal analysis (DTA) was carried out on a thermal analysis system (TG8120, Rigaku). The sample was heated and cooled between room temperature and 1000 °C at a rate of 5 °C min⁻¹ under oxygen gas flow.

Crystal structures were investigated by X-ray powder diffraction (XRD) and Raman spectroscopy for the following three samples: the powder used to make the target, one obtained by the laser ablation, and one obtained by heating the ablated powder at 1000 °C. X-ray diffraction data of the samples were collected on a diffractometer (RINT2200/PC, Rigaku) with Cu K α radiation. Raman measurements were performed in a backward microconfiguration, using the 514.5 nm line from an Ar⁺ laser (\approx 0.1 mW) focused to a 2- μ m-diameter spot on individual grains of the samples. The scattered light was dispersed by a subtractive triple spectrometer (T64000, Jobin-Yvon/Atago Bussan) and collected with a liquid-nitrogen-cooled charge-coupled device (CCD) detector.

3. Results and discussion

The powder used for the target was characterized by XRD and Raman spectroscopy. The XRD pattern and Raman spec-

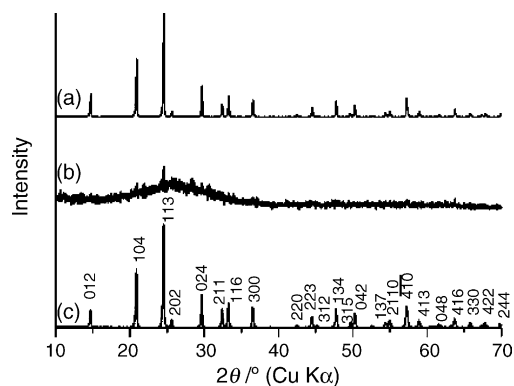


Fig. 2. XRD patterns for the target material (a), nano-sized particles prepared by the laser ablation (b), and the annealed nano-sized particles at 1000 °C (c). Miller indices based on a rhombohedral unit cell were labeled on the reflections for the annealed sample.

trum, shown in Figs. 2(a) and 3(a), were identical to those previously reported [4,5]. All the reflections were indexable on a rhombohedral unit cell (space group: *R*-3*c*) with $a = 8.5104(3)$ Å and $c = 20.840(3)$ Å for the hexagonal axes. The Raman spectrum had several peaks in the wavenumber range from 300 to 1400 cm⁻¹. According to the previous paper [5], the peaks observed for the target material were assigned as vibration modes of PO₄ groups: peaks at 353 cm⁻¹ to an external mode; ones at 435 and 449 cm⁻¹ to symmetric bending; one at 521 cm⁻¹ to asymmetric bending; ones at 975

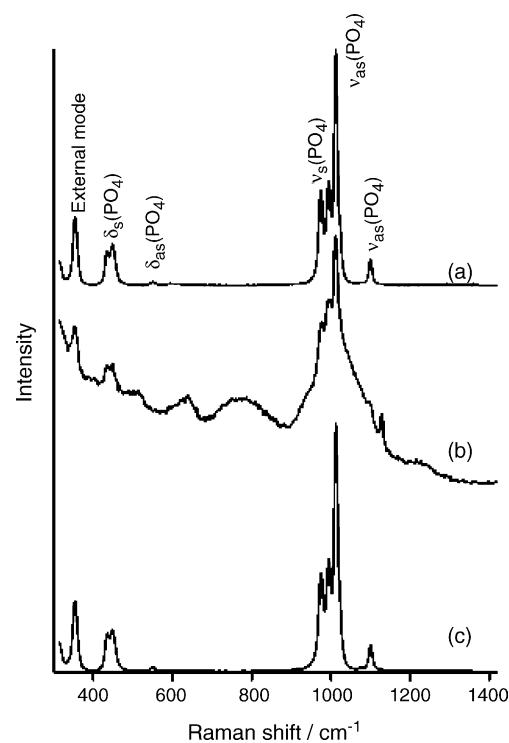


Fig. 3. Raman spectra for the target material (a), nano-sized particles prepared by the laser ablation (b), and the annealed nano-sized particles at 1000 °C (c).

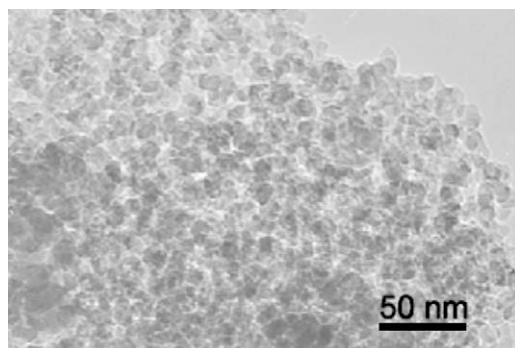


Fig. 4. A TEM image of the nano-sized particles.

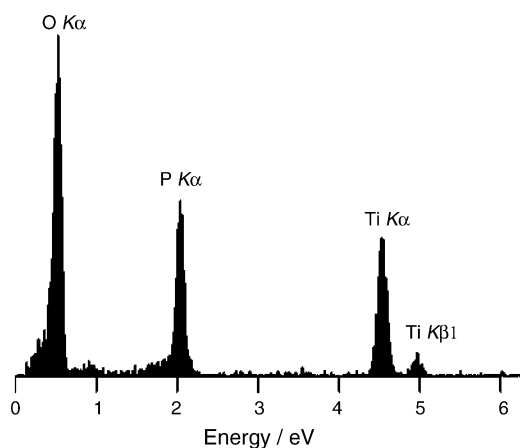


Fig. 5. An EDX spectrum for the nano-sized particle.

and 995 cm^{-1} to symmetric stretching; 1013 and 1100 cm^{-1} to asymmetric stretching.

A TEM image of the particles obtained by the laser ablation is displayed in Fig. 4. It revealed that the obtained particles were of the order of 10 nm in diameter. Its EDX spectrum and its composition determined from the spectrum are indicated in Fig. 5 and Table 1, respectively. The composition determined by the EDX was almost the same as the theoretical one, indicating that the composition of the nano-sized particles was well-controlled in the ablation.

Table 1

Comparison between the compositions of the nano-sized particles determined by EDX and theoretical one

Particle no.	Atomic percent		
	Ti	P	O
1	9.2	14.2	76.6
2	11.8	15.7	72.5
3	11.3	15.7	73.1
4	10.2	16.0	73.9
Theoretical	11.8	17.6	70.6

The compositions of four individual particles were investigated. Sum of the atomic percents of Ti, P, and O is 100%, because Li is not detectable by EDX.

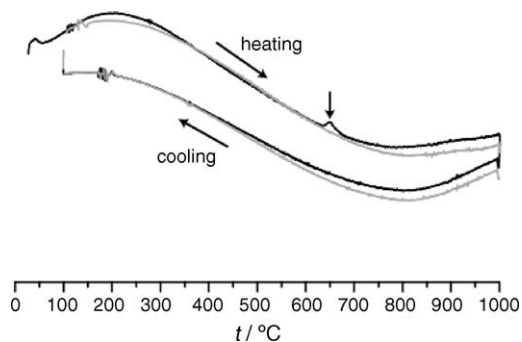


Fig. 6. DTA curves for the nano-sized LTP. Black and gray lines were obtained for the first and the second heating and cooling cycles, respectively. An exothermic peak corresponding to the crystallization is indicated by an arrow.

The XRD pattern of the nano-sized LTP did not give distinguished reflections but a halo centered at $2\theta = 25^\circ$ as shown in Fig. 2(b), indicating the amorphous nature of the nano-sized particles. On the other hand, the local structure of the nano-sized particles is considered to be similar to the crystalline LTP. Fig. 3(b) shows a Raman spectrum for the nano-sized particles of LTP. They gave broadened peaks; however, their positions were kept unchanged, which suggested the similarities in the local structure. The broadening is considered to be caused by the increasing degree of the disordered structure of the nano-sized particles, which also brought about the appearance of additional bands in the wavenumber range of $600\text{--}900\text{ cm}^{-1}$.

When the powder was heated, an exothermic peak appeared with an onset of 630°C in the DTA curves displayed in Fig. 6. The exothermic peak was observed only in the first heating process, suggesting that the exothermic reaction is the crystallization of the amorphous LTP. Indeed, the sharp reflections in the XRD pattern and the peaks in the Raman spectrum observed for the original material used for the target were recovered in the sample after the heating up to 1000°C as shown in Figs. 2(c) and 3(c). All of the reflections were indexable based on a hexagonal cell with $a = 8.5133(4)\text{ \AA}$ and $c = 20.877(4)\text{ \AA}$, of course, which were consistent with those of LTP. This crystallization temperature was in coincidence with those observed in the syntheses of LTP by sol–gel methods [6,7].

Taking into account that the ionic conductivity of amorphous $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ was much lower than that of the crystalline form [8], the conductivity of the amorphous nano-sized particles is expected to be low. NMR spectroscopy will be powerful to investigate the lithium ionic conduction in the nano-sized particles and carried out near future. It should be mentioned that we can obtain crystalline nano-sized particles from the amorphous ones by heat treatment. A heat treatment at 700°C to crystallize the nano-sized particles did not bring about significant particle growth; they still remained of the order of 10 nm in size after the heating.

4. Conclusion

Nano-sized particles of $\text{LiTi}_2(\text{PO}_4)_3$ were prepared by laser ablation. The formed particles were of the order of 10 nm in diameter with identical composition to the target material. They were amorphous and crystallized by the heating at 630 °C.

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