Growth and characterization of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals by using floating zone method for use as fast Li-ion conductor

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Abstract. Large size high quality Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals were grown successfully by floating zone (FZ) technique. The grown crystals were characterized by X-ray diffraction, etch pits density measurement, Impedance analysis, Vibrating sample magnetometry (VSM) and UV-Visible spectrometry. The investigation of structural, electrical, optical properties and defect density of the Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals revealed that the crystals were high quality and free from defects. The chemical analysis showed that the grown crystals have uniform composition along cross-section and growth direction. The floating zone grown single crystals contain no low-angle grain boundaries, indicating that they can be used for high efficiency Li-ion batteries.

Keywords: Lithium lanthanum zirconium oxide, Laue method, Tilted floating zone technique, Defect densities, Optoelectronic materials

1. Introduction
Over the last decade rechargeable lithium-ion batteries have become a crucial component of a number of portable electronic devices such as laptop, mobile phones as well as large electrical power storage systems [1]. The core component of the rechargeable Li-ion batteries is electrolyte made of Li-ion conductors. Since the next generation of electric cars will also use Li-ion cells, fast Li-ion conductors are crucial in today’s industry and for social needs to design high efficiency Li-ion storage batteries [2]. Recently, most of the typical Li-ion batteries have liquid and polymer-type electrolytes, and there are a number of demerits such as dendrite formation, leakage and flammability. Thus, now it has a great current interest in finding and developing new solid-state fast Li-ion conductors that are thermally and chemically stable. Lithium-based layered transition metal oxides have been intensively studied because of their complex structural features and wide technological importance as positive electrode material and electrolytes in rechargeable Li-ion batteries. Li$_7$La$_3$Zr$_2$O$_{12}$ is one of the most important fast Li ion conductor used as potential electrolytes in solid-state batteries [3]. This material is a good electrolyte candidate for all solid-state rechargeable Li-ion batteries, especially for its good thermal performance and chemical stability.

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Although there have a number of studies on the powder form of this material, the nature of the bulk properties has not yet been fully clarified. To clarify the anisotropic nature of the physical properties of the ionic conductors, more experimental and theoretical investigations are highly desired. In this study, we succeeded in synthesizing Li$_7$La$_3$Zr$_2$O$_{12}$ bulk single crystals with a tetragonal symmetry for the first time by using infrared heating floating zone (IR-FZ) method. The grown crystals were characterized to investigate the effect of anisotropy on transport properties that might enhance the efficiency in device applications.

The polycrystalline Li$_7$La$_3$Zr$_2$O$_{12}$ are typically prepared by solid state reaction techniques. However, the solid state synthesis process has involved three steps that are time and energy consuming [4-6]. Floating zone (FZ) method is a powerful technique for growth of single crystals without contaminations because it is a crucible free zone melting method [7]. It was revealed that the quality of the FZ-grown single crystals is good [8] and the crystal quality increases with growth diameter [9]. In this study, we try to grow high quality Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal by FZ method for use in solid-state battery applications.

2. Experiment

An infrared heating image furnace (Crystal Systems Corporation: model FZ-T-4000-H )was used for our growth experiment. High-purity (> 99.99%) powders of Li$_2$CO$_3$, La$_2$O$_3$ and ZrO$_2$ were used as the starting material for feed preparation. 100g powder (7Li$_2$CO$_3$ + 3La$_2$O$_3$+ 4ZrO$_2$= 2Li$_7$La$_3$Zr$_2$O$_{12}$ +7CO$_2$) was ball milled and mixed powder was calcined at 900°C for 12 h in air. The powder was grinded and calcined again under the same condition. The powder was grinded again for preparation of rod. The grinded power was filled into a rubber tube using a long glass bar, and shaped into a rod. The rods were sealed and pressed up to 3×10$^8$ Pa using a cold isostatic pressing machine (Nikkiso Co., Ltd.: model CL3-22-60). The pressed rods were typically 18 — 20 mm in diameter and ~150 mm in length. After drilling a hole at one end of the rod it was tied with a Pt-Rh wire for hanging and then sintered at 1100°C for 12 h in air. After sintering we got the feed rod of 15 — 17 mm in diameter and ~130 mm in length.

The applied conditions for growth experiment were a growth rate of 3 mm/h, upper shaft rotation of 30 rpm, lower shaft rotation of 50 rpm, a growth direction of <001> using a seed crystal after first melting. The crystals were grown with oxygen pressure of 3 atm. The grown crystal was checked as single crystal by Laue technique using Rigaku X-ray diffractometer. The crystals were cut perpendicular to the growth direction. Then the crystals were cut parallel to the growth direction and the surface was polished like mirror. The polished surfaces were observed by optical microscope (Olympus U-MSSPG Japan) to investigate the phase purity and optical quality. The polished samples were soaked in a mixture NH$_4$(SO$_4$)$_2$ and H$_2$SO$_4$ solutions (1:1 in weight) for 3 h at 300°C to etch their surfaces for the purpose of observation of domain structure. The chemical composition was checked by Electron probe micro analyzer (EPMA) (JEOL: model JXA-8200). For qualitative analysis, a Li$_2$O, La$_2$O$_3$ and ZrO$_2$ single crystals were used as standard to characterize the quality and composition of the grown crystals. The frequency dependent ac conductance, impedance, dielectric constant and capacitance were measured using the Agilent Precision Impedance Analyzer (Agilent technologies, Model: 4294A Japan).The Quantum Design Dynacool physical properties measurement system (PPMS) was used for measuring the temperature dependent magnetic susceptibility of the sample.

3. Results and discussions

3.1. Structural properties and compositions

A bulk single crystal of Li$_7$La$_3$Zr$_2$O$_{12}$ shown in figure 1(a) was grown using sintered rod as seed by conventional FZ method in the oxygen pressure of 3 atm. The Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal shown in figure 1(b) was grown along the z-axis in the same conditions using seed at first. The grown crystals were free from any inclusions. The grown crystals were cut perpendicular to the growth direction and hence crystallinity and structure were checked by taking Laue X-ray diffraction pattern. Figure 2 shows the Laue x-ray diffraction pattern of floating zone grown Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals. This Laue diffraction
investigation reveals that the prepared samples were single crystalline and growth directions [001] were parallel to $c$-axis. This investigation also showed that crystals were tetragonal in structure.

The crystalline powders of sintered Li$_7$La$_3$Zr$_2$O$_{12}$ and grown crystals were characterized at room temperature by using a Rigaku Mutiflex diffractometer range from 2$\theta$ = 5$^\circ$ to 85$^\circ$ with Cu$K_{\alpha}$ radiation ($\lambda$ = 1.5418 Å), at 40 KV and 30 mA. Figure 3(a) shows the X-ray diffraction pattern of the sample after calcinated at 900$^\circ$C and figure 3(b) shows that of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals grown by using floating zone method. The x-ray diffraction data confirmed the single crystal of lithium lanthanum zirconium oxide without any intermediate phases. All diffraction peaks were indexed and assigned for single phase crystalline Li$_7$La$_3$Zr$_2$O$_{12}$. The unit cell refinement was accomplished using XRD data and CellCall software. The X-ray diffraction pattern of calcinated powder and single crystal of Li$_7$La$_3$Zr$_2$O$_{12}$ reveal that all of these samples have tetragonal crystal structure with $I4_{1}/acd$ (no. 142).

The prepared samples were identified as highly crystalline and homogeneous by indexing these XRD patterns using available literature [1]. Here the sharp peaks indicate the good crystallinity. In the
Figure 3. X-ray diffraction pattern of (a) Li$_7$La$_3$Zr$_2$O$_{12}$ crystalline powder after sintering (b) Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal grown by FZ method.

XRD pattern the impurity phase peaks of La$_2$O$_3$, ZrO$_2$, and Li$_2$CoO$_3$ are not present, so pure phase solid is obtained. The good crystallinity of Li$_7$La$_3$Zr$_2$O$_{12}$ crystals would improve the efficiency of the rechargeable storage batteries.

We have used the FTIR spectroscopy to get chemical bonding and phase formation information. FTIR spectroscopic technique is powerful for investigating the local structure and cation environment in oxides [10,11]. Figure 4 shows the Fourier transform infrared (FTIR) spectrum of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals. The spectrum of Li$_7$La$_3$Zr$_2$O$_{12}$ contains the following main absorption bands at 240, 1198, 1469, 1719 and 3521 cm$^{-1}$. These results were confirmation of the X-ray diffraction investigations showing that the vibration bands for precursors vanished and the vibration bands for the oxide network developed. We observed the single well-resolved band at 240 cm$^{-1}$ which is in the far infrared region. The sharp band in Li$_7$La$_3$Zr$_2$O$_{12}$ is assigned for an asymmetric stretching motion of the LiO$_6$ octahedra [12]. It is the unique finger print of the Li site occupancy in the tetragonal structure. The sharp medium absorption peak around 1198 cm$^{-1}$ represents the vibrations of the LLZ crystal lattice. The FTIR spectroscopic results were good agreement with XRD data. Therefore, we conclude that the single phase LLZ single crystals of 10 mm in diameter are obtained at optimum conditions.

3.2. Phase purity and defect analysis
The compositional profile of floating zone grown Li$_7$La$_3$Zr$_2$O$_{12}$ crystals along growth direction is shown in the figure 5. It shows that the compositions of lithium, lanthanum and zirconium are uniform along growth direction. There are no significant variations in weight percent of constituent elements through growth length. These observations reveal that Li$_7$La$_3$Zr$_2$O$_{12}$ crystals were homogeneous in composition. The chemical analysis by electron probe micro analyzer showed that there were no secondary phases produced in the crystal during growth. Hence single phase Li$_7$La$_3$Zr$_2$O$_{12}$ crystals was obtained by floating zone method.
Figure 4. FT-IR spectrum of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal grown by FZ method.

Figure 5. Weight percentage of lithium, lanthanum and zirconium in Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals along growth direction.

The crystals grown by floating zone method were characterized by measurement of etch pit density (EPD) because Hirthe et al. showed that etch pits are known to be a good measure of the dislocation density [13]. Kinoshita et al. showed that etch pits arise in the presence of low-angle grain boundaries [14]. As the presence of defects like dislocations, grain boundaries etc. degrades the quality of the grown crystals, we measure the etch pits to clarify crystal quality.

Figure 6 shows optical microphotographs of the samples on the (100) surface after chemical etching. The observed etch pits are clearly few. On the other hand seed grown crystal was almost free of etch pits. These results reveal that Li$_7$La$_3$Zr$_2$O$_{12}$ crystals grown by FZ method were defect free high quality single crystal.

3.3. Electronic and magnetic properties

Figure 7 shows the temperature dependence electrical resistivity of FZ grown Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals along cross-section and growth direction. The results revealed that the grown crystal is anisotropic in resistivity along growth direction and perpendicular to the growth direction. This anisotropic property of resistivity of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals may play an important role when it is used as electrolyte in Li ion solid-state batteries. The anisotropic resistivity of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals might enhance the efficiency of devices as it is used.
Figure 6. Optical microphotographs of etch pits on (100) of (a) non-seed grown (b) seed grown Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals.

Figure 7. Temperature dependence electrical resistivity of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal along (a) cross-section and (b) growth direction.

Electrical conductance of the samples was measured by impedance analyzer, where the signal frequency was varied from 100 Hz to 1 MHz with applied oscillating voltage of 300 mV. All measurement has been carried out at room temperature. The frequency dependent electrical conductance Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals grown by floating zone method is shown in the figure 8(a). The electrical conductance increases slowly with frequency at the lower frequency range. The electrical conduction in the crystal requires the hopping of charges between the allowed sites. Figure 8(a) shows that low frequency region (up to 300 kHz) the conductance increases linearly with frequency and that increases exponentially in the high frequency region. Low frequency response indicates the long range transport of activated charges (dc conductivity) with regard to the applied electric field. The dispersive region at high frequencies can be explained within diffusion controlled relaxation model.

Impedance spectroscopy is established as a relatively new and powerful method of characterizing many of the electrical properties of electrolyte materials and their interfaces with electronically conducting electrodes. The frequency dependent impedance of the Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals is shown in the figure 8(b). The electrical impedance has been measured by impedance analyzer at room temperature in the same conditions as conductance measurement. During the measurement a sinusoidal potential is applied while the impedance and phase shift of the current are measured. At higher frequencies range (above 600 KHz) impedance ($Z$) is almost independent of frequency, which is attributed to the resistance effect. In the low frequency range, impedance appreciably decreases as the frequency increases.

The frequency dependent capacitances of the Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals were also measured by impedance analyzer in the same conditions. The frequency dependent capacitance of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals is shown in figure 8(c). At the low frequency region capacitance decreases sharply
Figure 8. Frequency dependence of (a) Electrical conductivity (b) Impedance and (c) Capacitance of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals.

and then decreases slowly with frequency. The capacitance of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal is high at low frequency region for contribution of all kinds of polarizations at low frequency region. Hence the capacitance decreases with increase of frequency and finally becomes to an almost constant value above 850 kHz. This result is due to the change of space charge, ionic and orientation polarization at higher frequency regions [15].

The thin pallet samples of Li$_7$La$_3$Zr$_2$O$_{12}$ were prepared and ionic conductivity by ac impedance was calculated using the Nyquist impedance plot of the imaginary part ($Z''$) versus the real part ($Z'$) of the complex impedance as shown in the figure 9. The complex impedance plots show two well-defined regions: the linear region, which is in the low-frequency range is attributed the effect of the blocking electrodes and the semicircle observed in the high frequency region, which is due to the bulk effect of the electrodes [16]. The step rise of the impedance plot in the low frequency region after linearity is typically expected for the blocking of mobile Li-ions at the electrode interface, which is a evidence that tetragonal Li$_7$La$_3$Zr$_2$O$_{12}$ crystal is a Li-ion conductor [1].

The point where the semicircle intersects the real axis ($Z'$) gives the value of bulk resistance ($R_b$). By knowing the value of bulk resistance ($R_b$) along with the dimensions of the sample, the conductivity of the sample has been calculated by using the relation $\sigma = d/R_bA$, where $d$ is the thickness of the thin sample and $A$ is the surface area of the sample. The ionic conductivity of the bulk Li$_7$La$_3$Zr$_2$O$_{12}$ crystal
Figure 9. The impedance plot of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals grown by FZ method.

Figure 10. Temperature dependence magnetic susceptibility of Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal grown by FZ method.

was calculated as $9.7 \times 10^{-4}$ S cm$^{-1}$ (at 298 K) that is highest among reported values. The high ionic conductivity in an electrolyte is attributed to increased ionic mobility and increased ionic charge carrier concentration [17].

The magnetic susceptibility of the bulk Li$_7$La$_3$Zr$_2$O$_{12}$ single crystal was measured using a Quantum Design PPMS Magnetometer in a 1000 Oe applied field at temperature range 2–310 K. The figure 10 shows temperature dependent magnetic susceptibility of FZ grown Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals in the field cooling (FC) condition.

The absence of impurity peaks in the plot reveals that the sample was free from magnetic defects. The magnetic susceptibility FC data exhibit a decrease in the magnetization with the temperature due to magnetic anisotropy-induced loss of long-range magnetic ordering of the material. The magnetic behavior in the single crystals of Li$_7$La$_3$Zr$_2$O$_{12}$ under applied magnetic field is rather complex, similar to that of LiCoO$_2$ compounds [18].
3.4. Optical properties
The variation of absorption of LLZ crystals in the wavelength from 200 nm to 800 nm is shown in the figure 11. In the visible region the absorption increases with increase of wavelength. There are two broad and a sharp absorption peaks in the ultraviolet region. The sharp absorption peak at 205 nm is very strong one. The absorption peak at 227 nm is very weak and peak at 285 nm is broad and medium. The absorption criteria of LLZ crystals in the ultraviolet region was revealed by these peaks. No significant peaks were found in the visible region. This observation shows that Li$_7$La$_3$Zr$_2$O$_{12}$ is not a strong absorber of visible light. The absorptive power decreases slightly at the end of visible region and then increases again.

4. Conclusions
Li$_7$La$_3$Zr$_2$O$_{12}$ is one of the most widely studied functional materials because of its diverse applications. The large size Li$_7$La$_3$Zr$_2$O$_{12}$ single crystals were grown successfully by using floating zone (FZ) method for the first time which was defect free. The powder X-ray diffraction and Laue results show that the grown crystals were single phase with tetragonal crystal structure. The ionic conductivity of the Li$_7$La$_3$Zr$_2$O$_{12}$ bulk single crystal is comparatively higher than that of the sintered polycrystalline sample. Hence, it may be used as a potential electrolyte in the all solid-state Li-ion rechargeable batteries by industrial manufacturing. The characterization results of structural, electronic and optical properties established that the crystals are suitable for use in high efficiency device applications. The characterization of magnetic properties showed that the samples were free of magnetic impurities.

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