Thermal Expansion in the Garnet-type Solid Electrolyte (Li_{7-x}Al_{x/3})La₃Zr₂O₁₂ as a Function of Al Content

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Abstract

The thermal expansion (TE) coefficients of the lithium-stable lithium-ion conducting garnet lithium lanthanum zirconium oxide (LLZ) and the effect of aluminum substitution were measured from room temperature up to 700°C by a synchrotron-based X-Ray diffraction. The typical TE value measured for the most reported composition (LLZ doped with 0.3 wt% or 0.093 mol% aluminum) was $15.498 \times 10^{-6} \text{ K}^{-1}$, which is approximately twice the value reported for other garnet-type structures. As the Al(III) concentration has been observed to strongly affect the structure observed and the ionic conductivity, we also assessed its role on thermal expansion and noted only a small variation with increasing dopant concentration. The materials implications for using LLZ in a solid state battery are discussed.

Keywords:

Garnet; Solid Electrolyte; Thermal Expansion; Battery

1. Introduction

There has been increasing interest in ceramic lithium ion conducting electrolytes due to their non-flammability, high ionic conductivity and electrochemical stability. These attributes make thin film ceramic electrolytes an important class of materials for many future energy storage needs [1-5]. Since the discovery of LiPON by Bates, et al., many possible uses of a lithium stable thin film electrolytes for lithium ion battery systems have been investigated as the advantages (increased safety, higher volumetric capacity) have the capability to enable their introduction into new cell designs [6]. Historically the most significant issues impeding the incorporation of these materials into an electrochemical cell has been their ionic conductivity when compared to conventional liquid electrolytes, low voltage stability, and impedance growth due to changes in cation diffusion across the interface with the active material electrode [7]. While select issues have been addressed in individual materials, few have been reported that show across the board progress [3, 5-7]. However, recent work on the garnet-based electrolytes has shown promise as they are stable to lithium potentials while offering room temperature ionic conductivities as high as 10^{-4} S/cm, two orders of magnitude better than the commonly studied LiPON family of solid electrolytes [7-8]. These lithium garnet materials have the general formula $\text{Li}_x(\text{Y})_3(\text{Z})_2\text{O}_{12}$ (Y = an alkaline earth or rare earth metal; Z = early transition metal; x = amount of lithium to charge balance) and have been identified containing a large variety of cations [3]. The choice of substituent cations controls the lithium content, site occupancies, low voltage stability and ionic conductivity. Of particular interest has been the phase $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) after it was reported to be stable to lithium metal and, in the cubic form, possess a good ionic conductivity [9]. Early work with this material focused on methods to stabilize the cubic form at lower temperatures while optimizing the ionic conductivity, most commonly by

advantageous aluminum substitution. In contrast to other solid electrolyte systems where aluminum cations substitute on the transition metal site, e.g. $\text{Li}_{1+x}(\text{Ti}_{2-x}\text{Al}_x)(\text{PO}_4)_3$, several spectroscopic and crystallographic studies found that in these garnets the aluminum substitutes onto the lithium sites, $(\text{Li},\text{Al})_7\text{La}_3\text{Zr}_2\text{O}_{12}$, leading to the conclusion the formation of the cubic phase at low temperature ($< 950^\circ\text{C}$) is driven by lithium site cation vacancies rather than any specific bonding changes [8]. Aluminum cation substitution levels > 0.09 mol %, appear to represent the minimum amount to stabilize the higher conductivity cubic form. Subsequent work has also shown that the cubic form of LLZ also can be stabilized below 750°C by initial synthesis in the presence of excess lithium salts or in a very dry environment to prevent proton/lithium exchange. Under these conditions it is not clear if longer term annealing will eventually result in formation of the tetragonal phase of LLZ by evaporation of lithia or advantageous protons [10,11]. With these properties, new uses for LLZ have been proposed that take advantage of its lithium metal stability and good conductivity, including lithium-air (O_2), lithium-sulfur, or lithium-metal cells based on charged cathodes [12-14]. For these beyond-lithium chemistries, the cells stability and performance are enhanced since the LLZ protects the lithium metal anode from deleterious side reactions with the electrolyte or dissolved cathode species [7, 13]. We report the thermal expansion behavior of the important solid electrolyte cubic LLZ at different levels of Al doping measured from room temperature up to 700°C using a high resolution X-Ray diffraction technique.

2. Experimental

Powder samples of LLZ substituted with 0, 0.093, 0.16 and 0.31 mol % Al were prepared by a sol-gel technique at 700°C [15]. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ precursors were prepared by a sol-gel method

using metals nitrates, a citric acid complexing agent, and propan-2-ol as a polymerizing agent. All chemicals were purchased from Alfa Aesar and used as received. Stoichiometric amounts of lithium nitrate, lanthanum nitrate hexahydrate, aluminum nitrate nonahydrate, and zirconium oxynitrate hydrate were dissolved in deionized water to create the cation ratios of the desired final product. Ten wt. % excess lithium nitrate was added to compensate lithium loss during subsequent high temperature heat treatments. Citric acid and propan-2-ol were added to the solution such that the amount of citric acid was twice the total moles of cations and the molar ratio citric acid to propan-2-ol was 60:40. The mixture was stirred at 50 °C overnight, then heated at 250 °C for 1 hour (ramp rate: 1°C/min). The resulting expanded resin was ground and calcined at 500 °C for 2 hours (ramp rate: 5°C/min) to decompose remaining organics. The resulting powder was then reground, pressed into pellets and calcined at 700 °C for 12 hours (ramp rate: 10°C/min) in an alumina crucible. Al-free LLZ samples were synthesized under the same conditions (no added aluminum nitrate) except that the calcination steps were performed using large zirconia pellets (YSZ) as physical barriers to prevent contamination from the alumina crucibles.

Structural characterization of the samples was performed by X-Ray powder diffraction (XRD) with a Bruker D8 diffractometer using CuK α radiation in the 2Θ range from 10° to 80° with a step size of 0.02° and counting time per step of 1s. A quartz capillary ($\varnothing$ =4 mm) was filled with finely ground powder and mounted between ceramic rods. Heating elements were wrapped around the rods and a type-K thermocouple was inserted into the capillary to monitor temperature. The samples were heated to 700 °C at an approximate rate of 50°C per minute. All experiments were run in air. Images were collected on the sector 1-BM beamline at the Advanced Photon Source (Argonne, IL) using a wavelength of 0.615996 Å. The measured 2-

theta range was 5-30° (7.06 Å – 1.20 Å). Integration of 2D patterns was made by means of the FIT2D program [16]. The upper 2θ-limit was set to 30° and the 2θ-scale was split into 3000 bins for the integration and the resulting intensity patterns were subsequently transformed into a format suitable for input to data analysis software.

3. Results and Discussion

Recently significant attention has been given to garnet-type lithium lanthanum zirconium oxide (LLZ) due to its rare combination of stability against lithium metal and high ionic conductivity making it a promising candidate for lithium metal-based batteries including lithium-sulfur or lithium-oxygen [1,8]. Room temperature Li-ion conductivities of 10^{-6} S/cm for the tetragonal variant and 10^{-4} S/cm for the cubic variant of LLZ have been reported [8]. This two order of magnitude increase in conductivity is stabilized at lower temperatures by substituting a small amount (~0.093 at %) of aluminum onto the lithium sites. It is believed the increase in cation vacancies on the lithium site stabilizes the cubic phase. Even without aluminum (or other cation) substitution, several groups have reported that the cubic LLZ phase can be stabilized at lower temperatures by being formed in the presence of excess lithium salts or limiting exposure of the sample to water, as proton/lithium exchange is known to occur easily and may stabilize the tetragonal phase [10, 11]. In this study, we used approximately 10% excess lithium nitrate and noted obtained the cubic phase, in agreement with literature reports [11]. In either case, for LLZ to be used in a full electrochemical cell, knowledge of its physical properties is critical. Since many of the energy storage applications that use lithium-ion conducting solid electrolytes require it to be in the form of a tape cast monolith or thin film, knowledge of various thermal properties is especially important [2 - 4]. Specifically many devices that require high temperature

processing, experience heating/cooling cycles, or have complex interfacial tolerances must be synthesized with a knowledge of its thermal expansion properties as a poor match to another active material may cause cracking, delamination, or stress buildup. For example grid storage batteries built using a β - Al_2O_3 electrolyte, as in Na-S cells, can see significant stresses or displacements in response to moderate temperature changes that must be taken into account during operation [17, 18]. Since it is a ceramic, inclusion of LLZ into a battery is envisioned as either a thin film, stand-alone tape cast monolith, or as part of a polymer-ceramic hybrid electrolyte. However, since the cation transfer across the interface is typically a major cause of poor cycling performance or low electrode utilization, end-users seek to deposit the electrolyte onto one of the electrodes to make the best interface possible. For this cell design, the need to match as close as possible the thermal expansion of the electrolyte to the active material in a solid state battery while limiting the side reactions with the other phases present is critical.

To determine these values, samples of LLZ were synthesized with varying aluminum contents so as to judge the role of aluminum in the system as in practice Al-substituted LLZ will probably be the material used in full cells. The XRD pattern (shown in Figure 1) is for LLZ doped with 0.093 mol % Al. The XRD reflections (211), (420), and (631) were selected to be fitted to Gaussian curves using the data analysis software. The specific peaks were chosen as they did not overlap with nearby peaks, represented a mix of indices, and were spread across the spectra. Unit-cell parameters were calculated for the three reflections and thermal expansion coefficients were determined for each aluminum doping level. Figure 2 shows the evolution of the (211) peak of LLZ doped with 0.3 wt. % Al during the heating step. The complete results calculated for that sample are listed in Table 1 and the evolution of the lattice constant as a function of temperature is displayed in Figure 3. Table 2 summarizes the lattice constants, cell

volumes and thermal expansion coefficients for each aluminum concentration tested. It was noted that there is not a significant variation in TE coefficient with the increase in aluminum concentration suggesting that aluminum has little to no effect on the thermal properties of cubic LLZ. Since we did not observe any effect from the Al substitution, we may conclude that the TE expansion is dominated by the $[\text{LaO}_8]$ and $[\text{ZrO}_6]$ moieties within the LLZ structure [1]. Regardless of Al content, the range of observed thermal expansion coefficients determined in this study shows that LLZ has a thermal expansion coefficient that is approximately twice the value normally observed for garnets, even those that do not contain lithium, as indicated in Table 3 [19].

When compared to other possible cell components, the thermal expansion of LLZ garnet puts it in a range that makes devices with certain cathodes or anodes more likely to be successful, especially if it is used in the form of a thin film with tens of nanometer scale thickness. Specifically, the thermal expansion coefficient is within 3% of the common ‘zero-expansion’ anode $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which places it in a range that if in the correct format would be stable. The closest matches for common LIB cathodes are LiCoO_2 (~16%) and LiFePO_4 (~21%), which may or may not be close enough depending on the thicknesses and porosities of the electrodes. Electrodes based on elemental silicon (72% difference), $\text{Li}_{0.2}\text{La}_{0.6}\text{TiO}_3$ (72% difference), or LiMn_2O_4 (55% difference) are in a range that would probably yield unstable interfaces and poor performance in a solid state battery. The importance of interfacial stability in these systems was recently demonstrated by Ohta and co-workers in the LiCoO_2 – LLZ(Nb) system [30,31]. Using a full cell (with lithium metal anode) they reported a first cycle charge capacity of 98 mAh/g (78 mAh/g discharge) for a cell built using a co-sintering process in a voltage window between 4.2-3.0V indicative of a good interfacial structure between the active components and the electrolyte.

4. Conclusions

The thermal expansion properties of the promising lithium stable solid electrolyte ($\text{Li}_{7-x}\text{Al}_{x/3}\text{La}_3\text{Zr}_2\text{O}_{12}$) has been studied. The expansion was found to fall above the normal range typically seen for garnet type structures, as reported in the literature. The role of Al substitutions into the structure, an important variable in controlling the ionic conductivity, was also evaluated but found to have only a small effect. Since previous neutron diffraction, ^{27}Al , and ^7Li NMR had shown that Al substitution occurs mainly on the crystallographic Li – sites, the La/O and Zr/O structural components must dominate the rigid three dimensional structure, as there is only a small relationship between Al content and bulk thermal expansion properties. The thermal expansion restrictions identify LiCoO_2 , LiFePO_4 , and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as the most compatible electrode materials for a thin film solid state battery.

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Figure Captions:

Figure 1. The indexed XRD powder pattern of LLZ sample (0.093 mol% Al), $\lambda = 0.615996 \text{ \AA}$. Asterisks mark the peaks used for the TE calculation.

Figure 2. Evolution of the (211) peak of LLZ (0.093 mol % Al) during heating step

Figure 3. Evolution of the lattice constant of LLZ (0.093 mol % Al) during the heating step

Tables:

Table 1. Evolution of the lattice constant of LLZ (0.093 mol % Al) during the heating step

Table 2. Lattice constants, volumes and thermal expansion coefficients for different Al contents

Table 3. Lattice constants, volumes and thermal expansion

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Scan#	T (K)	$2\Theta_{211}$	d_{211}	a_{211}	$[\Delta a/a]/\Delta T$
1	308.15	6.6579	5.3040	12.9922	16.933×10^{-6}
2	315.15	6.6571	5.3047	12.9937	30.010×10^{-6}
3	316.15	6.6569	5.3048	12.9941	12.004×10^{-6}
4	318.15	6.6568	5.3049	12.9944	12.005×10^{-6}
5	333.15	6.6556	5.3059	12.9968	16.486×10^{-6}
6	384.15	6.6500	5.3104	13.0077	17.514×10^{-6}
7	439.15	6.6436	5.3155	13.0202	17.922×10^{-6}
8	497.15	6.6367	5.3210	13.0338	18.046×10^{-6}
9	558.15	6.6293	5.3269	13.0481	1.727×10^{-6}
10	606.15	6.6288	5.3273	13.0492	5.888×10^{-6}
11	654.15	6.6270	5.3287	13.0527	9.171×10^{-6}
12	702.15	6.6241	5.3311	13.0585	8.525×10^{-6}
13	748.15	6.6215	5.3332	13.0636	15.091×10^{-6}
14	793.15	6.6170	5.3368	13.0725	12.932×10^{-6}
15	848.15	6.6123	5.3406	13.0818	13.540×10^{-6}
16	898.15	6.6078	5.3442	13.0906	15.197×10^{-6}
17	938.15	6.6038	5.3475	13.0986	23.158×10^{-6}
18	951.15	6.6018	5.3491	13.1025	13.052×10^{-6}
19	967.15	6.6004	5.3502	13.1053	18.160×10^{-6}
20	970.15	6.6008	5.3499	13.1045	12.485×10^{-6}
21	974.15	6.6004	5.3502	13.1052	na

Table 1. Evolution of the lattice constant of LLZ (0.3 wt. % Al) during the heating step

x wt. % Al	a (Å)	V (Å ³)	α (K ⁻¹)
0	13.0871	2241	13.016 x10 ⁻⁶
0.3	13.0584	2227	15.498 x10 ⁻⁶
0.5	13.0791	2237	16.172 x10 ⁻⁶
1	13.0464	2221	14.526 x10 ⁻⁶

Table 2. Lattice constants, volumes and thermal expansion coefficients for different Al contents

COMPOUND	α (K ⁻¹)	REFERENCE
Y ₃ FeGa ₄ O ₁₂ (garnet)	9.21x10 ⁻⁶ (817K) 9.84 x10 ⁻⁶ (1373K)	[19]
Ca ₂ LaZr ₂ Ga ₃ O ₁₂ (garnet)	7.34 x10 ⁻⁶ (473K) 7.63 x10 ⁻⁶ (873K) 8.27 x10 ⁻⁶ (973K) 8.44 x10 ⁻⁶ (1173K)	[19]
Ca ₃ Sn ₃ Ga ₂ O ₁₂ (garnet)	8.70 x10 ⁻⁶ (836K) 9.22 x10 ⁻⁶ (1381K)	[19]
La _{0.6} Li _{0.2} TiO ₃ (perovskite)	2.66 x10 ⁻⁵ (300-1200K)	[20]
Li ₃ Na ₃ In ₂ F ₁₂ (garnet)	27.0 x10 ⁻⁶ (298K)	[21]
Li ₂ O.Na ₂ O.2P ₂ O ₅ (glass)	20 x10 ⁻⁶ (300-473K)	[22]
Li ₂ O (fluorite)	34 x10 ⁻⁶ (298-1273 K)	[23]
LiTi ₂ (PO ₄) ₃	12.2 x10 ⁻⁶ (1273 K)	[24]
Li ₄ Ti ₅ O ₁₂	15 x10 ⁻⁶ (298- 1273 K)	[25]
Silicon	4.3 x 10 ⁻⁶ (1273 K)	[26]
Li(LiMn) ₂ O ₄	7 x10 ⁻⁶ (298-1073 K)	[27]
LiCoO ₂	13 x10 ⁻⁶ (1073 K)	[28]
LiFePO ₄	12.2 x 10 ⁻⁶ (1073 K)	[29]
Alumina	7.5 x10 ⁻⁶ (1273 K)	[26]

Table 3. Reported linear thermal expansion coefficients of related phases.

Figure

Figure

Figure