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Phase transition in lithium garnet oxide ionic conductors $Li_7La_3Zr_2O_{12}$: The role of Ta substitution and H_2O/CO_2 exposure

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HIGHLIGHTS

- Measures were taken to eliminate/minimize Al-contamination and air exposure.
- In-situ impedance measurement to probe phase transition temperature of LLZ.
- A minimum of 0.6 mol of Ta is needed to stabilize the cubic phase LLZ.
- H_2O interacts with LLZ through a proton exchange mechanism.
- CO_2 interaction with LLZ worsens the grain boundary conduction.

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ABSTRACT

High Li-content lithium garnet oxides are promising solid electrolyte materials for lithium batteries. Being the highest Li-content lithium garnet oxides, $Li_7La_3Zr_2O_{12}$ has been reported to crystallize in either the tetragonal or cubic phase with no consensus on the exact conditions under which these two phases are formed, which may be due to unintentional Al contamination and air exposure. In this work, the effects of Ta substitution and H_2O/CO_2 exposure have been studied under Al-contamination free conditions with minimal air exposure. We showed that 1) the Ta-substitution induced phase transition occurred through a two-phase mechanism and a minimum 0.6 mol of Ta substitution to Zr is needed to stabilize the cubic phase; 2) H_2O and CO_2 can individually induce the tetragonal-cubic phase transition in $Li_7La_3Zr_2O_{12}$ through proton exchange and Li extraction, respectively, which can have great influence on the transport properties of $Li_7La_3Zr_2O_{12}$.

1. Introduction

The lithium garnet oxide ionic conductors have become one of the most promising solid electrolyte candidates [1–3] for the potential application in all-solid-state, Li–S, and Li-air batteries due to their high ionic conductivity and good electrochemical stability [4–9]. The capability of Li transport in the garnet system was discovered by Weppner et al. in 2003 in $Li_5La_3Ta_2O_{12}$ [4]. Later, another garnet compound $Li_7La_3Zr_2O_{12}$ (LLZ) was found to possess very high ionic conductivity (5×10^{-4} S cm^{-1}) [6]. The LLZ was first identified to crystallize in the cubic symmetry ($Ia\bar{3}d$, No. 230). However, single crystal X-ray and neutron diffraction suggested that the LLZ crystallizes in the tetragonal symmetry ($I4_1/acd$, No. 142) [10]. The tetragonal $I4_1/acd$ space group is a subgroup of the cubic $Ia\bar{3}d$ space group. A complete ordering of Li-vacancies occurs in the tetragonal LLZ accompanying the symmetry reduction. As a result, the ionic conductivity of the tetragonal LLZ is about 2 orders of magnitude lower than the cubic counterpart.

Many studies were devoted to the synthesis and characterization of LLZ due to the high ionic conductivity of the cubic phase. The phase information from these studies is summarized in Table 1 [6,10–19]. Clearly, considerable inconsistencies exist. It has been found that cation substitution can stabilize the cubic phase by creating extra vacancies and lowering the Li content [16,20,21]. A large number of various garnet compounds have been synthesized by deliberate cation substitution and the best garnet-type Li ion conductors so far are derived from cation substitution of LLZ [7,9,20,22–24]. Therefore, the knowledge of the minimum substitution level for the stabilization of the cubic structure is crucial. The minimum substitution level of Al or Ga was experimentally

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Table 1
A summary of literature reports on $Li_7La_3Zr_2O_{12}$.

	Author	Synthesis temperature	Phase
1	Murugan et al.	1230 °C	Cubic
2	Shimonishi et al.	1180 °C	Cubic
3	Awaka et al.	1250 °C	Cubic
4	Janani et al.	700 °C	Cubic (Al free)
5	Xie et al.	750 °C	Cubic (Al free)
6	Awaka et al.	980 °C	Tetragonal
7	Wang et al.	1000 °C	Tetragonal
8	Geiger et al.	1100 °C	Cubic (Al_2O_3 vessel)
			Tetragonal (Pt vessel)
9	Kokal et al.	<705 °C	Cubic
		>774 °C	Tetragonal
10	Buschmann et al.	1130 °C	Tetragonal (Al free)
			Cubic (Al-doped)
11	Larraz et al.	980 °C	Tetragonal (fresh sample)
			Cubic (aged sample)

determined to be 0.2 mol per formula unit [20], which corresponds to 0.4 mol of extra vacancies as the trivalent Al^{3+}/Ga^{3+} enters the Li site creating twice as many vacancies. Ta or Nb substituted LLZ were reported to crystallize in the cubic phase with substitution level of less than 0.2 mol (each substitution creates one vacancy) [7,9]. A recent study by Thompson et al. concluded that the critical Ta substitution level is 0.5 mol for Al-free samples [25].

It is suspected that these inconsistencies stem from contamination during the garnet sample preparation. A typical procedure involves high-temperature firing in Al_2O_3 vessels in air. The unintentional introduction of Al from the vessel was claimed to be responsible for the observed cubic phase in some reports [11,16]. Nevertheless, Al-free cubic LLZ has also been reported [13,14]. It was recently found that the tetragonal LLZ can be transformed into cubic phase through aging in air [19]. Similar tetragonal-cubic phase transformation was also observed in naturally aged $Li_7La_3Sn_2O_{12}$ samples [26]. Therefore, it is crucial to control both the Al contamination and air exposure during the synthesis in order to truly understand the phase transition of LLZ. However, no such attempts have been made so far. In addition, it is unclear how the exposure to H_2O/CO_2 affects the transport properties of Li conducting garnets. This knowledge is of great technological significant for the application of garnet-type solid electrolytes in lithium batteries. It should be noted that aforementioned reports on the role of H_2O and CO_2 employed a post-mortem approach, i.e., the analysis was done on naturally aged sample, so the H_2O/CO_2 effect were neither separated nor studied in real-time.

In this study, we take measures to eliminate the Al contamination and air exposure during the garnet sample preparation. These samples were confirmed to be contamination-free by thermal gravimetric analysis (TGA) and Energy-dispersive X-ray spectroscopy (EDS). The minimum substitution level of Ta to stabilize the cubic structure is determined by powder X-ray diffraction (PXRD). The effects of H_2O and CO_2 separately on the phase transition and transport properties of porous LLZ samples are investigated through in-situ impedance spectroscopy.

2. Experimental

The garnet powder $Li_{7\text{-}x}La_3Zr_{2\text{-}x}Ta_xO_{12}$ (LLZTx, $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6) was prepared by the solid–state reaction method. $LiOH \cdot H_2O$ (Alfa–Aesar) was dried at 200 °C before use. A stoichiometric amount of LiOH, La_2O_3 (Sigma–Aldrich), ZrO_2 (Alfa–Aesar) and Ta_2O_5 (Alfa–Aesar) were wet-milled on a roller mixer for 24 h in polyethylene jars filled with isopropyl alcohol. 10% excessive lithium precursor was added to compensate for lithium loss during the synthesis. 5 mm yttria-stabilized zirconia balls were used as grinding media. The mixture was then dried and transferred to MgO crucibles for calcination at 900 °C for 10 h with a heating rate of 3 °C min^{-1} and cooling rate of 2 °C min^{-1}. To eliminate the air effect, all powders were heat-treated in a tube furnace at 750 °C for 2 h under constant Ar flow. A MgO tray was used to hold the garnet samples. The samples were transferred to an Ar-filled glovebox with moisture level <0.1 ppm for storage immediately after the heat-treatment.

To prepare porous LLZ pellets, the dried starting mixture was pressed into pellet form with stainless steel dies and a hydraulic press. The pellets were sintered at 1050 °C for 24 h in MgO crucibles. The density and open porosity were measured with the Archimedes method. All samples have about 30% of porosity. Gold paste was applied to both sides of the pellet as blocking electrodes. A 700 °C heating step was employed to improve adhesion between the garnet pellet and gold electrodes.

The phase of the garnet powders and pellets were characterized by XRD using Cu$K\alpha$ radiation operated at a voltage of 40 kV and current of 40 mA (Bruker D8 ADVANCE). The measurement range was 10°–70° with a step interval of 0.02° and a scan rate of 0.04 s^{-1}. Rietveld refinement implemented by the GSAS [27,28] was employed to extract the lattice parameters and relative phase fractions. TGA (TA instrument, TGA 500) with a temperature range of room temperature to 800 °C under N_2 flow was performed on the garnet samples. The elemental information was characterized by EDS (Carl Zeiss, EVO LS25).

A setup combining a tube furnace and a potentiostat (Bio-Logic SP-200) as shown in Fig. 1 was used for the in-situ impedance measurement of LLZ pellets under various gas flows. Prior to the measurement, the pellets were heat-treated in Ar at 750 °C for 2 h. This step ensures that the whole system is free of H_2O/CO_2. The tube was then cooled to measurement temperatures. The system was allowed to equilibrate before turning on the H_2O or CO_2 gas flow. Ar gas was passed through a bubbler to generate the moisture gas flow. A tank of compressed Ar with 5% CO_2 was used to supply the CO_2 flow. A sinusoidal voltage signal with amplitude of 20 mV was applied for the frequency range of 5 MHz to 1 Hz.

3. Results and discussion

3.1. Sample purity

The purity of garnet samples can be severely compromised if the Al-contamination and air exposure are allowed during the synthesis. We highlight two measures taken to eliminate these effects: the use of MgO crucible and heat-treatment in Ar. In our prior experience, discoloration of the garnet samples is commonly observed especially when heated to high temperatures (>1000 °C) if Al_2O_3 crucible were used. Using MgO crucibles, no discoloration was observed for the sintered LLZ pellet at 1050 °C indicating very little or no interaction between the samples and crucibles. This is confirmed by EDS analysis (Fig. 2) which showed no observable

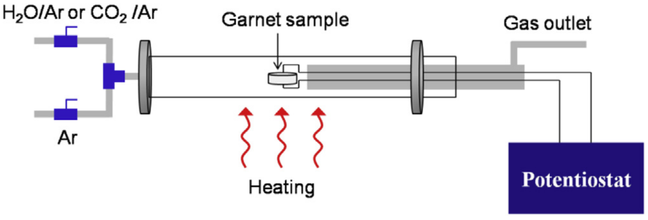

Fig. 1. Illustration of In-situ impedance measurement setup.