



Stabilization of cubic $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ by Al-doping

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HIGHLIGHTS

- Cubic $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ can be stabilized by Al^{3+} doping.
- Polycrystalline Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ was prepared by a modified solid state method.
- Powder consists of μ -size grains encapsulated by a glassy phase.
- Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ crystallizes in garnet-related structure with cubic unit cell.
- Total conductivity is close to values obtained for cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ garnets.

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ABSTRACT

In this paper we report on the stabilization of cubic $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ by Al^{3+} doping and present a detailed crystal structure study and lithium ion conductivity measurements of the obtained compound. Polycrystalline Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ was prepared by a modified solid state method. The compound consists of micrometer size grains encapsulated by a glassy phase, which helps preventing the volatilization of lithium during annealing. Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ crystallizes in the garnet-related structure with a cubic unit cell (sp. gr. $Ia\bar{3}d$ (230)). A structural refinement using X-ray and neutron powder diffraction data showed that the Al^{3+} ions occupy only tetrahedral Li^+ sites in the structure. The presence of overextended leading edges of the peaks on the XRD and NPD data is described by the introduction of an additional phase with rhombohedral distortion that occurs through a stretching of the cubic phase along the body diagonal. The activation energy as well as the total conductivity at room temperature are close to values obtained for un-doped cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ garnets, which make Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ a potential candidate for the application as solid electrolyte in solid-state rechargeable lithium-ion batteries.

1. Introduction

In recent years, Li-containing garnets $\text{Li}_x\text{A}_3\text{M}_2\text{O}_{12}$ ($A = \text{La}, \text{Y}; M = \text{Zr}, \text{Nb}, \text{Sn}, \text{Sb}, \text{Te}, \text{Hf}, \text{Ta}; x = 3-7$) have attracted a lot of interest mainly as potential electrolytes in solid-state lithium ion batteries [1,2]. The ionic conductivity in these compounds depends on several factors: overall Li content, polymorph structure, Li occupancy on the different sites (octahedral and tetrahedral coordination) within these structures and the Li/vacancy ratio. For example: the ionic conductivity of the $\text{Li}_x\text{A}_3\text{M}_2\text{O}_{12}$ ($x = 3-7$) cubic garnets generally increases with increasing Li ion content [1,3,4]; $\text{Li}_3\text{A}_3\text{Te}_2\text{O}_{12}$ garnets exhibit a low conductivity of $10^{-5} \text{ S cm}^{-1}$ at 600 °C, which is explained by the presence of only

tetrahedral coordinated Li ions in the structure [1,2]; $\text{Li}_x\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Zr}, \text{Nb}, \text{Sn}, \text{Sb}, \text{Hf}, \text{Ta}; x = 5-7$) [1,2,4] garnets have Li ions in the octahedral site displaying high Li ion conduction.

One of the most extensively studied compounds of this family is lithium zirconate $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. Two stable phases of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ with cubic (high temperature polymorph) and tetragonal (low temperature polymorph) unit cells have been reported [5–7]. Long-term high-temperature heat treatment at above 1200 °C is required for the synthesis of the cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ polymorph whereas the tetragonal phase forms at 980 °C. Cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ exhibits high bulk conductivity around $10^{-4} \text{ S cm}^{-1}$ at room temperature, and has good thermal and chemical stability against molten lithium [5]. The tetragonal phase is

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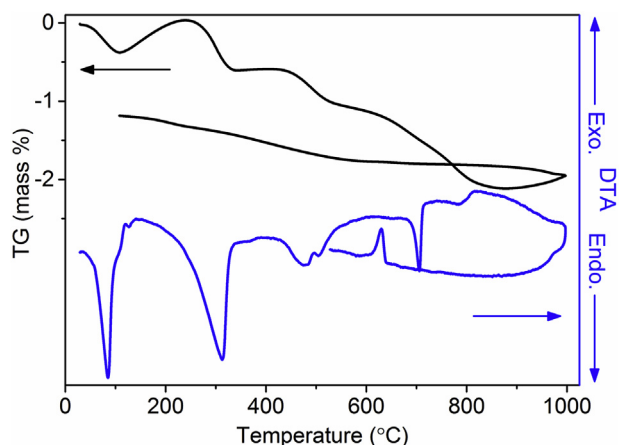


Fig. 1. The TG (black lines) and DTA (blue lines) results for tetragonal Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ powder. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

thermodynamically stable relative to lithium metal, but exhibits an ionic conductivity two–three orders of magnitude lower than the cubic phase [7,8]. Both polymorphs show a similar structural motif, but in the tetragonal structure Li atoms and vacancies are ordered in the tetrahedral and octahedral sites, whereas these sites in the cubic structure have mixed occupancies [6,7].

Since cubic garnets show a higher conductivity compared to tetragonal ones a large number of studies has been devoted to the stabilization of high temperature cubic phases $\text{Li}_7\text{La}_3\text{M}_2\text{O}_{12}$ ($M = \text{Zr}, \text{Sn}$) [9–14]. $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ was synthesized in the absence of any dopant by H. Xie et al. [15], N. Janani et al. [16] and Kokal et al. [17] by modified sol-gel methods at low temperatures as well as by J. Awaka et al. who prepared a $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ single crystal by a self-flux method using LiNO_3 at 1150°C [18]. The conductivity of these samples was significantly lower than that of compounds obtained by the solid-state method at high temperatures. The subsequent increase in annealing temperature to $800\text{--}900^\circ\text{C}$ leads to the formation of a tetragonal modification [17]. Recently, it was found that in the case of highly conducting cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, Al contamination from the alumina crucibles at high temperatures leads to the incorporation of small

amounts of aluminium ($\sim 0.58\text{--}0.61$ wt%) in the garnet structure and the stabilization of the cubic phase [10,11]. Rangasamy et al. studied the effect of cubic phase $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ stabilization by Al^{3+} and concluded that at least 0.204 mol of Al is required to stabilize the cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ phase [19]. As the Al concentration is increased above to 0.389 mol, the impurity phase LaAlO_3 forms. It has been shown in many publications using different experimental techniques, in particular neutron powder diffraction and nuclear magnetic resonance that Al^{3+} substitutes for Li^+ in the garnet related structures [10–14,19]. This substitution creates charge compensating Li vacancies and it is these Li vacancies which determine phase stability of cubic phase [19]. A significant improvement of conductivity has been recently achieved through substitution of Li^+ and Zr^{4+} in $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ for Al^{3+} , Ga^{3+} [19–21], and for Nb^{5+} and Ta^{5+} [21–25], respectively. It is worth to mention that substitution on the M^{4+} sites does not block the lithium ion pathways and thus leads to higher conductivity than that observed for the Al^{3+} and Ga^{3+} substitutions [21].

Recently, $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ with tetragonal and cubic structure has been synthesized using the same temperature treatment as for $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [26,27]. The crystal structure of the tetragonal polymorph was refined using neutron powder diffraction data. Its Li-ion conductivity was found to be slightly lower than that of tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. The highest Li^+ -ion conductivity, $3.45 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature with an activation energy of 0.43 eV, has been reported for a tantalum doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ [28]. However, to the best of our knowledge, neither a detailed crystal structure study of cubic $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ nor an investigation of the Li^+ substitution for other cations has been reported. In this paper we report a detailed structural study and lithium ion conductivity measurements of cubic $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ stabilized by Al^{3+} doping.

2. Experimental

A polycrystalline sample of Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ (Al amount is ~ 0.61 wt%, which corresponds to the formula $\text{Li}_{6.04}\text{Al}_{0.32}\text{La}_3\text{Hf}_2\text{O}_{12}$) was prepared by a modified solid-state method. La_2O_3 (99.99%), which was calcined beforehand at 900°C for 5 h, HfO_2 (99.99%), Li_2CO_3 (99.99%) and $\alpha\text{-Al}_2\text{O}_3$ (99.9%) were used as initial compounds. A 20% molar excess of Li_2CO_3 was added to a stoichiometric mixture in order to compensate lithium loss during subsequent high-temperature heat treatments. The main part of the obtained mixture of powder was

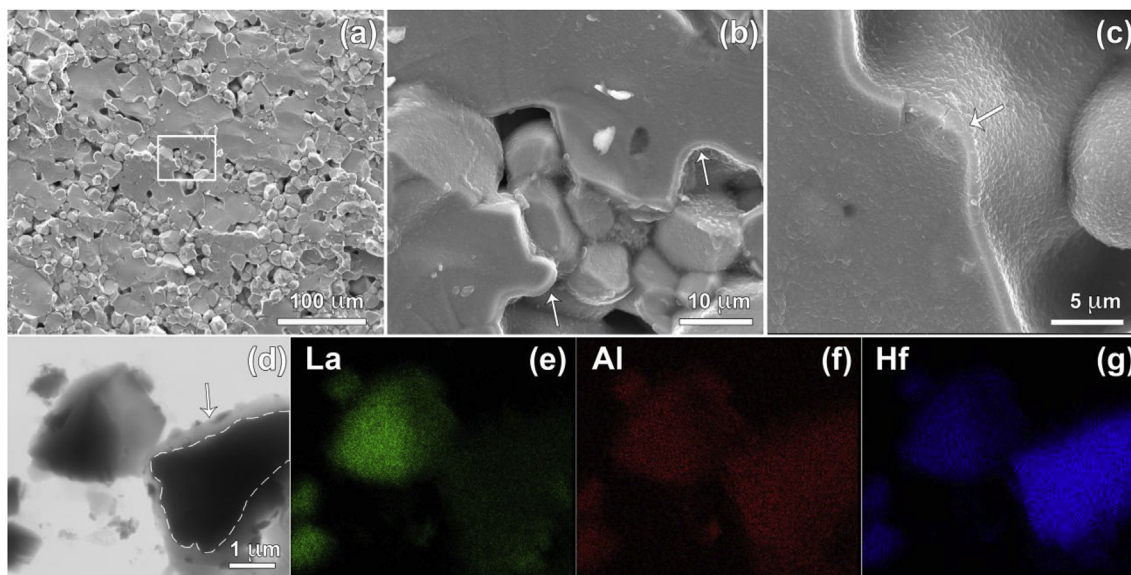


Fig. 2. (a–c) Scanning electron microscopy images of the fractured surface of Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$, (d) bright-field scanning transmission electron microscopy image of the crushed Al-doped $\text{Li}_7\text{La}_3\text{Hf}_2\text{O}_{12}$ and corresponding EDX maps: (e) for La L_α -line, (f) for Al K_α -line, (g) for Hf L_α -line. Arrows indicate a glassy-like phase with high aluminum content, covering grains.

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