Effects of alkaline earth metal elements and their synergistic roles with Ta for Li$_7$La$_3$Zr$_2$O$_{12}$

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1. Introduction

Energy plays an important role in many aspects of human lives [1]. To meet the increasing energy demand, renewable energy resources such as wind, solar, biomass, hydropower and hydrogen are always the research hotspot [2]. In recent years, to design suitable electrical energy storage devices has become a prerequisite to realize the potential of these renewable energies. A few famous energy storage devices like fuel cells [3–5], solar cells [6–9], supercapacitors [10, 11], rechargeable batteries [12–14], etc have been recognized as the most promising candidates for the purpose of alleviating energy crisis and reducing greenhouse gas emissions. Among alternative routes, although lithium ion batteries have world-widely emerged as energy storage devices for electronic products, electric vehicles, energy storage systems and special purpose devices, these conventional lithium ion batteries using organic liquid electrolytes are still suffering from several issues of safety risks and low energy density. Consequently, it is an extremely task to develop new-type lithium ion batteries of good safety and high energy density in the field of rechargeable batteries.

Unlike conventional lithium ion batteries using organic liquid electrolytes, solid electrolytes enable solid-state lithium batteries with higher energy densities and enhanced safety by their nonflammable nature, the high electrochemical stability as well as the compatibility with high capacity cathode/anode materials [12, 15–19]. Among the available solid electrolytes, garnet-type Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has received wide concerns since it was firstly reported by Murugan et al in 2007 [20]. LLZO has advantages of the high ionic conductivity ($10^{-4}$ ~ $10^{-3}$ S cm$^{-1}$), the wide electrochemical stability window, the good stability against lithium metal, showing great potential in the field of advanced solid-state lithium (ion) batteries [16, 21–25].

Two stable phases are found in typical LLZO. Tetragonal LLZO (space group $I4_1/acd$, no. 142) [26] with low ionic conductivity is stable at room temperature, whereas cubic LLZO (space group $Ia$ 3d, no. 230) [27] with high ionic conductivity cannot survive for long time below approximately 150 °C [28, 29]. So far, many works...
have been done to obtain cubic LLZO which can be stable at room temperature. Factors such as the synthesis method, the sintering process, the sintering container, as well as the element doping modification are deemed to have close relation to the properties of LLZO [13, 30–37]. It is confirmed that doping elements at Li-site, La-site and/or Zr-site is an effective strategy to assist generating and stabilizing LLZO with improved properties at room temperature [13, 31, 38–41]. As a general knowledge, lithium ion concentration and the mobility have great effects on lithium ionic conductivity, as the conductivity can be expressed as the product of the number of charge carriers, the charge of these carriers and mobility effects on lithium ionic conductivity, as the conductivity can be expressed as the product of the number of charge carriers, the charge of these carriers and mobility.

In this work, we try to synthesize Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) with the sole substitution of alkaline earth metal ions for Zr4+ and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) with the co-substitution of alkaline earth metal ions and Ta5+ for Zr4+ with the help of a wet chemical technique [1, 46, 57]. The influences of substituting alkaline earth metal elements on Zr site and their synergistic effect with Ta are comparatively discussed. Alkaline earth metal elements (Mg, Ca, Sr, Ba) and Ta co-doped LLZO can achieve cubic phase and the improved ionic conductivity, and ionic radii of these alkaline earth metal ions make a difference on the ionic conductivity. Too large ionic radius size of alkaline earth metal ions and Ta5+ to achieve the enhancement of LLZO systems. Especially, when the content of Ta is 0.6 per formula unit (pfu) in LLZO, the sample can normally achieve high ionic conductivity [31, 44–46]. Additionally, low-valence elements can also be introduced in LLZO to lead to the increased lithium ion concentration and the promoted lithium ion transport [40, 47–50]. The alkaline earth metal elements as typical low-valence elements, they have also taken attentions. For instance, some works have discussed the roles of alkaline earth ions in LLZO conductors [47, 48]. Lincoln J Miara et al [51] apply density functional theory (DFT) [52] to study the defect influence on ionic conductivity for Li6.5La3Zr1.35Ta0.6M0.05O12 and Li6.5La3Zr1.95M0.05O12, and co-doping the high-valence cation and the low-valence cation can balance the lithium ion concentration.

In this work, we try to synthesize Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) with the sole substitution of alkaline earth metal ions for Zr4+ and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) with the co-substitution of alkaline earth metal ions and Ta5+ for Zr4+ with the help of a wet chemical technique [1, 46, 57]. The influences of substituting alkaline earth metal elements on Zr site and their synergistic effect with Ta are comparatively discussed. Alkaline earth metal elements (Mg, Ca, Sr, Ba) and Ta co-doped LLZO can achieve cubic phase and the improved ionic conductivity, and ionic radii of these alkaline earth metal ions make a difference on the ionic conductivity. Too large ionic radius size of alkaline earth metal ions might have a negative impact on ionic conductivity for Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba). Among as-prepared samples, the modified LLZO with the joint substitution of Ta and Mg at Zr sites achieves a highest ionic conductivity.

2. Experimental

2.1. Materials and preparation

To obtain Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) with alkaline earth metal elements and Ta substituted at Zr sites, the preparation process is modified. The schematic diagram of the preparation process for the modified LLZO with alkaline earth metal elements (Mg, Ca, Sr, Ba) and Ta at Zr sites is shown in figure 1. All reagents are purchased from Sinopharm Chemical Reagent Co. Ltd Mg(OH)2/ CaCO3/ SrCO3/ BaCO3 for alkaline earth metal source and Zr(CH3COO)4 for Zr source and Ta2O5 as Ta source are weighed according to stoichiometric ratio and mixed in acetic acid to prepare precursors (I). Li2CO3 for Li source (30 wt% Li2CO3 excess is used to make up for the loss of Li during subsequent heat treatment) and La2O3 for La source are mixed to prepare precursors (II). The obtained precursors (I) as well as precursors (II) are transferred to an alumina crucible, and sequentially heated at 400 °C for 2 h and then at 750 °C for 8 h to obtain calcined powders (i) as well as calcined powders (ii), respectively. The powders (i) and powders (ii) are ground and mixed to obtain mixtures. Then, the mixtures are pressed under 30 MPa pressure into thin pellets with a diameter of about 14 mm and a thickness of about 1 mm. The pellets are sintered at 1125 °C for 6 h covered with the mixtures and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) can be obtained. Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) are prepared using the same operation except that Ta2O5 is not added.

2.2. Characterization

The crystal structure of materials is characterized by x-ray diffraction measurement (XRD, Bruker D8 Advance). All the pellets are ground to powders before XRD testing. Rietveld refinements of the synthesized samples are accomplished by GSAS software. Electrochemical Impedance Spectroscopy (EIS) measurement is applied with a Solartron Impedance Analyzer (1260 & 1287, Ametek) from 5 MHz to 100 Hz with a 10 mV amplitude to measure the ionic conductivity. Before EIS testing, both parallel surfaces of pellets are sputtered with gold as the lithium ion blocking electrode.
3. Results and discussion

In order to ensure the substitution of the alkaline earth metal elements at Zr sites, the mixtures of precursors are separated into (I) and (II), respectively. The relevant calcined powders are (i) and (ii), respectively (figure 1).

XRD patterns of calcined powders (i) for Li$_2$LaZr$_{1.95}$M$_{0.05}$O$_{3.95}$ (M = Mg, Ca, Sr, Ba) and Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) in which Ta and M synergistically substitute Zr are exhibited in figures 2(a) and (b), respectively. The XRD pattern of the control group (without elements doping) consists with that of ZrO$_2$ with monoclinic phase (PDF #65-1025). That is to say, monoclinic ZrO$_2$ will grow, as sole Zr(CH$_3$COO)$_4$ is heated at 400 °C for 2 h. However, when the mixture of Zr(CH$_3$COO)$_4$ with incorporation of M (M = Mg, Ca, Sr, Ba) element is calcined at 750 °C for 8 h, the patterns of main components exhibit the similar structure to ZrO$_2$ with tetragonal phase (PDF #50-1089). It is demonstrated that two main factors result in ZrO$_2$ structure changes from monoclinic phase to tetragonal phase. For one thing, Zr$_{1.95}$M$_{0.05}$O$_{3.95}$ (M = Mg, Ca, Sr, Ba) calcined powders (i) (at 750 °C) are obtained at higher temperature than that of pure ZrO$_2$ calcined powders (at 400 °C). With the increase of temperature, the monoclinic phase will change into tetragonal phase naturally [58]. For another, alkaline earth oxides are the common stabilizers for tetragonal ZrO$_2$, and a small amount of stabilizers can improve the stability performance of tetragonal ZrO$_2$ at low sintering temperature [59, 60]. As a result, in our work, the introduction of Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$ can stabilize tetragonal ZrO$_2$ and help to achieve the transformation from monoclinic to tetragonal at low sintering temperature.

Rietveld refinement results confirm that calcined powders with the incorporation of the alkaline earth metal element M (M = Mg, Ca, Sr, Ba) are mixture of solid solution based on tetragonal ZrO$_2$ and monoclinic ZrO$_2$. The refinement plots for crystal structure analysis and Rietveld refinement results are shown in figure 4 and table S1–S5 is available online at stacks.iop.org/MRX/7/125201/mmedia (supporting information), respectively. The results show that alkaline earth metal elements induce the formation of tetragonal ZrO$_2$ and they occupy the Zr site (8f) to form Zr$_{1.95}$M$_{0.05}$O$_{3.95}$ (M = Mg, Ca, Sr, Ba). Nevertheless, cell parameters of Zr$_{1.95}$M$_{0.05}$O$_{3.95}$ (M = Mg, Ca, Sr, Ba) distinctly differ.

When Ta synergistically substitutes Zr with alkaline earth metal element M (M = Mg, Ca, Sr, Ba) for calcined powders (i), XRD patterns seem more complicated. The patterns exhibit intensive peaks referring to tetragonal ZrO$_2$ structure (PDF #50-1089) and Ta$_2$O$_5$, while faint peaks referring to monoclinic ZrO$_2$ (PDF #65-1025) are also detected. The peaks referring to Ta$_2$O$_5$ are in well accord with XRD pattern of Ta$_2$O$_5$ raw material (figure 2(b)). It indicates that calcined powders (i) for Li$_{6.5}$La$_3$Zr$_{1.35}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) are the mixture of tetragonal ZrO$_2$, Ta$_2$O$_5$, and tiny amount of monoclinic ZrO$_2$. Furthermore, Ta$_2$O$_5$ may not participate in phase transition of calcined powders (i).

XRD patterns of the final sintered Li$_2$LaZr$_{1.95}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) and Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) are shown in figure 4. Patterns of Li$_{7.1}$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$
(M = Mg, Ca, Sr, Ba) demonstrate largely similar with the pattern of tetragonal Li7La3Zr2O12 from online database [61], whereas Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) mainly crystalize in parent cubic garnet-like Li5La3Ta2O12 [61] structure (PDF #45-0110), in spite of existent some impurities. The impurity in Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) detected at 2 Theta of around 24.7° is supposed to be La2Li0.5Al0.5O4 (PDF #40-1167), which should be attributed to the influence of the alumina crucible. In addition, smaller full width at half maximum (FWHM) [62] value calculated by analysis software proves the better crystallinity of Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba).

EIS curves of Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) and Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba) are displayed in figure 5. It should be noted that figure 5(a) contains curves of both the raw data and the simulation data, whereas figure 5(b) are plotted based on only the raw data owing to bad fitting accuracy. All curves of Li7.1La3Zr1.95M0.05O12 (M = Mg, Ca, Sr, Ba) consist of two flattened semi-circles and an inclined tail, whereas as with most previous articles [13, 31, 32, 45, 63] only a flattened semi-circle and an inclined tail line are observed for Li6.5La3Zr1.35Ta0.6M0.05O12 (M = Mg, Ca, Sr, Ba). The rest semi-circle is not observed because it is out of the frequency range of the analyzer. In an ideal (modified) Li7La3Zr2O12 without any impurities, the ionic conductivity only depends on the bulk and the grain boundary impedance [22, 40, 64]. Hence, the equivalent circuit of (RbCPEb)(RgbCPEgb)(CPEel) (figure 5(c)) associated with these two semi-circles and inclined tail line is app lie for understanding electrochemistry behaviors [54, 63–66]. Rb andRgb are referring to the bulk resistance and the grain boundary resistance, respectively, while CPEb and CPEgb are corresponding constant phase elements. The inclined tail line observed in low frequency is related to the blocking electrodes, which is represented by CPEel. The total resistance R is determined by the value of Rb + Rgb [31, 35]. Thus, as with most
articles [13, 67, 68], the intercept of the linear tail on the horizontal axis represents the total resistance arising from the bulk and grain boundary contributions.

Total ionic conductivities of Li\textsubscript{7.1}La\textsubscript{3}Zr\textsubscript{1.95}M\textsubscript{0.05}O\textsubscript{12} (M = Mg, Ca, Sr, Ba) and Li\textsubscript{6.5}La\textsubscript{3}Zr\textsubscript{1.35}Ta\textsubscript{0.6}M\textsubscript{0.05}O\textsubscript{12} (M = Mg, Ca, Sr, Ba) at room temperature are summarized in Table 1. Ionic conductivities of all the samples with alkaline earth metals (Mg, Ca, Sr, Ba) solely doped in LLZO are at a low level of $\sim 10^{-6}$ S cm$^{-1}$, which implies that alkaline earth metal elements solely substitution for Zr have little effects on improving ionic conductivity. Low ionic conductivities are in accord with the corresponding XRD tests. Moreover, we further determine the bulk conductivity ($\sigma_b$) and the grain boundary conductivity ($\sigma_{gb}$) of Li\textsubscript{7.1}La\textsubscript{3}Zr\textsubscript{1.95}M\textsubscript{0.05}O\textsubscript{12} (M = Mg, Ca, Sr, Ba) (Table 2). Interestingly, the order of total ionic conductivity ($\sigma_{total}$) influenced by four alkali metal ions substituted for Zr$^{4+}$ is Ca$^{2+}$ > Mg$^{2+}$ > Sr$^{2+}$ > Ba$^{2+}$, whereas the order of both $\sigma_b$ and $\sigma_{gb}$ differ. Obviously, Mg-doped Li\textsubscript{7.1}La\textsubscript{3}Zr\textsubscript{1.95}M\textsubscript{0.05}O\textsubscript{12} delivers the minimum $\sigma_b$ of $8.34 \times 10^{-6}$ S cm$^{-1}$, but Ba-doped Li\textsubscript{7.1}La\textsubscript{3}Zr\textsubscript{1.95}Ba\textsubscript{0.05}O\textsubscript{12} has the lowest value of $\sigma_{gb}$. The Li\textsubscript{7.1}La\textsubscript{3}Zr\textsubscript{1.95}Mg\textsubscript{0.05}O\textsubscript{12} sample shows uniqueness in ionic conductivity, which agrees with other reports [31, 51]. Nevertheless, when Ta element synergistically

Figure 3. Refinement plots for (a) ZrO\textsubscript{2} and (b)–(e) Zr\textsubscript{1.95}M\textsubscript{0.05}O\textsubscript{3.95} (M = Mg, Ca, Sr, Ba).
substitutes Zr with alkaline earth metal elements (Mg, Ca, Sr, Ba) in LLZO, all the samples, namely Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba), achieve a great enhancement of the ionic conductivity. Further, the order of total ionic conductivity influenced by four alkaline earth metal ions (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and Ta$^{5+}$ co-substitution for Zr$^{4+}$ is Mg$^{2+}$ > Ca$^{2+}$ > Sr$^{2+}$ > Ba$^{2+}$. Clearly, sorting by total ionic conductivity demonstrates strong correlation with ionic radii of these alkaline earth metal ions. More definitely, the sequences of ionic radii of metal ions [44, 53, 69] is (1) Mg$^{2+}$ < Ca$^{2+}$ < Sr$^{2+}$ < Ba$^{2+}$ and (2) Ta$^{5+}$ < Zr$^{4+}$. In addition to substitution of Ta$^{5+}$ for Zr$^{4+}$, alkaline earth metal ions with the smaller ionic radii are likely to bring the better gain effect on ionic conductivity. This finding agrees with the discussion from Yuki Kihira et al [53] in spite of the substitution of alkaline earth metal ions for La$^{3+}$ in their work. The samples of Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ and Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$Ca$_{0.05}$O$_{12}$ deliver the higher ionic conductivities than that of Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$Ca$_{0.05}$O$_{12}$ (1.95 $\times$ 10$^{-4}$ S cm$^{-1}$) in the previous reported work [46]. Synergetic effects should be deemed to be responsible for the improvement and the two factors are proposed. First, Ta substitution for Zr can induce the formation of cubic phase which exhibits short Li-Li distance in the migration pathway and isotropic three-dimensional Li-diffusion network that allow for easy and fast Li diffusion [27, 28]. Second, low valence alkaline earth ions substitution for Zr$^{4+}$ can balance the Li content, as high temperature sintering and Al element from crucible can decline Li concentration of LLZO system. However, Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$Sr$_{0.05}$O$_{12}$ and Li$_6.5$La$_3$Zr$_{1.35}$Ba$_{0.6}$Ca$_{0.05}$O$_{12}$ show poorer ionic conductivities in comparison with solely Ta-doped LLZO, which should be attributed to the probable matter that too large ionic radius sizes of Ba$^{2+}$ as well as Sr$^{2+}$ relative to that of Zr$^{4+}$ can hinder Li diffusion.

Notably, the modified LLZO with the joint substitution of 0.6 pfu Ta and 0.05 pfu Mg at Zr sites (Li$_6.5$La$_3$Zr$_{1.35}$Ta$_{0.6}$Mg$_{0.05}$O$_{12}$) achieves a highest ionic conductivity of 3.45 $\times$ 10$^{-4}$ S cm$^{-1}$. For one thing, Mg$^{2+}$

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Figure 4. XRD patterns of (a) the Li$_7.1$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) pellets and (b) the Li$_6.5$La$_3$Ta$_{0.6}$Zr$_{1.35}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) pellets.
is supposed to be stable on Zr sites, while the substitution changes of Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$ in LLZO prefer to occur at La sites [51, 54]. For another, the ionic radii of both Mg$^{2+}$ and Ta$^{5+}$ are small, which might stand a good chance to structure a better lithium ion conductive framework, thereby enhancing lithium ion migrations. The

![EIS curves](image)

**Figure 5.** EIS curves of (a) Li$_{7.1}$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba), (b) Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ (M = Mg, Ca, Sr, Ba) and (c) the equivalent circuit.

**Table 1.** Total ionic conductivities of Li$_{7.1}$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$ and Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ at room temperature.

| Alkaline earth metal element (M) | Li$_{7.1}$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$ | Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ |
|---------------------------------|---------------------------------|---------------------------------|
| Mg                              | $4.25 \times 10^{-6}$           | $3.45 \times 10^{-4}$           |
| Ca                              | $7.85 \times 10^{-6}$           | $2.25 \times 10^{-4}$           |
| Sr                              | $3.32 \times 10^{-6}$           | $1.67 \times 10^{-4}$           |
| Ba                              | $1.41 \times 10^{-6}$           | $8.16 \times 10^{-5}$           |
differences of stable substitution sites as well as ionic radius sizes between Mg$^{2+}$ and other alkaline earth metal ions (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) result in a vital impact on the ionic conductivity.

4. Conclusion

Li$_{7.1}$La$_3$Zr$_{1.95}$M$_{0.05}$O$_{12}$ (alkaline earth metal elements M = Mg, Ca, Sr, Ba solely substituted at Zr sites) and Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$M$_{0.05}$O$_{12}$ (alkaline earth metal elements M = Mg, Ca, Sr, Ba and Ta both substituted at Zr sites) have been prepared through the modified wet chemistry strategy. The sole substitution of the alkaline earth metal cations for Zr have little effects on improving ionic conductivity, whereas the co-substitution of the alkaline earth metal element and Ta$^{5+}$ for Zr$^{4+}$ greatly enhances the quality of samples. The order of total ionic conductivity influenced by the co-substitution of four alkaline earth metal ions (Mg$^{2+}$, Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) and Ta$^{5+}$ is Mg$^{2+}$ > Ca$^{2+}$ > Sr$^{2+}$ > Ba$^{2+}$. In the co-doped LLZO, alkaline earth metal ions with the smaller ionic radii are likely to make the more positive gain effect on improving the total ionic conductivity. Notably, Li$_{6.5}$La$_3$Zr$_{1.35}$Ta$_{0.6}$Mg$_{0.05}$O$_{12}$ sample can achieve the highest ionic conductivity.

Additional information

There are no conflicts to declare.

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References

[1] Ramakumar S, Deviannapoorani C, Dhiyva L, Shankar I S and Murugan R 2017 Lithium garnets: synthesis, structure, Li$^+$ conductivity, Li$^+$ dynamics and applications Prog. Mater. Sci. 88 325–411
[2] Kumar G, Kim S H, Lay C H and Ponnusamy V K 2020 Recent developments on alternative fuels, energy and environment for sustainability Biosour. Technol. 317 124010
[3] Tsalapati E, Johnson C W D, Jackson T W, Jackson L, Low D, Davies B, Mao L and West A 2021 Enhancing polymer electrolyte membrane fuel cell system diagnostics through semantic modelling Expert Syst. Appl. 163 113550
[4] Wu C W, Zhang W, Han X, Zhang Y X and Ma G J 2020 A systematic review for structure optimization and clamping load design of large proton exchange membrane fuel cell stack J. Power Sources 476 228724
[5] Obara S Y and Miyazaki W 2021 Numerical modeling to determine the limits on photovoltaic capacity when operating in a microgrid with solid-oxide fuel cell triple combined-cycle plants Int. J. Electr. Power Energy Syst. 124 106325
[6] Zhou J, Zhang X, Chen H, Tang Z, Meng D, Chi K, Cai Y, Song G, Cao Y and Hu Z 2020 Dual-function of CdCl$_2$ treated SnO$_2$ in Sb$_2$Se$_3$ solar cells Appl. Surf. Sci. 534 147632
[7] Zitouni H, Tahiri N, El Bouanaghi O and Ez-Zahraouy H 2020 Electronic, transport and optical properties in perovskite compound LaGaO$_3$ Mater. Res. Express 7 035501
[8] Cao Y, Zhu X, Jang J, Liu C, Zhou J, Ni J, Zhang J and Pang J 2020 Rotational design of charge carrier transport layers for optimal antimony trisulfide solar cells and its integration in tandem devices Sol. Energy Mater. Sol. Cells 206 110279
[9] Cao Y, Zhu X, Chen H, Zhang X, Zhou J, Hu Z and Pang J 2019 Towards high efficiency inverted Sb$_2$Se$_3$ thin film solar cells Sol. Energy Mater. Sol. Cells 200 109945
[10] Samuel E, Aldababi A, El-Newehy M, El-Hamshary H and Yoon S S 2021 Nickel ferrite beehee-like nanosheets for binder-free and high-energy-storage supercapacitor electrodes J. Alloy. Compd. 852 156929
[11] Kumar S, Saeed G, Zhu L, Hui K N, Kim N H and Lee J H 2021 0D to 3D carbon-based networks combined with pseudocapacitive electrode material for high energy density supercapacitor: A review Chem. Eng. J. 403 126352
[12] Gao Z, Sun H, Fu L, Ye F, Zhang Y, Luo W and Huang Y 2018 Promises, challenges, and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries Adv. Mater. 30 e1705702

[13] He M, Cui Z, Chen C, Li Z and Guo X 2018 Formation of self-limited, stable and conductive interfaces between garnet electrolytes and lithium anodes for reversible lithium cycling in solid-state batteries J. Mater. Chem. A 6 11463–70

[14] Qi Y, Gao W, Wang H, Liu D, Deng J, Guo B, Bao S and Xu M 2020 Na0.6TiOP3.2 F microspheres as a long-life anode for Na-ion batteries Chem. Eng. J. 402 126118

[15] Zhang Z et al 2018 New horizons for inorganic solid state ion conductors Energy Environ. Sci. 11 1945–76

[16] Samson A J, Hofstetter K, Bug S and Thangadurai V 2019 A bird’s eye view of Li-stuffed garnet-type Li3La2Zr2O12 ceramic electrolytes for advanced all-solid-state Li batteries Energy Environ. Sci. 12 9257–75

[17] Schnell J, Günther T, Knoch T, Vieider C, Kohler L, Just A, Keller M, Passerini S and Reinhart G 2018 All-solid-state lithium-ion and lithium metal batteries—paving the way to large-scale production J. Power Sources 382 160–75

[18] Deiner I J, Bezerra C A G, Howell T G and Powell AS 2019 Digital Printing of Solid-State Lithium-Ion Batteries Adv. Eng. Mater. 21 18

[19] Kalhoff J, Esheu G G, Bresser D and Passerini S 2015 Safer electrolytes for lithium-ion batteries: state of the art and perspectives Chem. Sus. Chem. 8 2194–75

[20] Murugan R, Thangadurai V and Weppner W 2007 Fast lithium ion conduction in garnet-type Li3La2Zr2O12 Angew. Chem. Int. Edit. 46 7778–81

[21] Liu Q, Geng Z, Han C, Fu Y, Li S, He Y–R, Kang F and Li B 2018 Challenges and perspectives of garnet solid electrolytes for all-solid-state lithium batteries J. Power Sources 389 120–34

[22] Thangadurai V, Narayanan S and Pinzar D 2014 Garnet-type solid-state fast Li ion conductors for Li batteries: critical review Chem. Soc. Rev. 43 4714–27

[23] Thompson T, Yu S, Williams L, Schmidt R D, Garcia–Mendez R, Wolfenstine J, Allen J L, Kioupakis E, Siegel D J and Sakamoto J 2017 Electrochemical window of the Li-ion solid electrolyte Li2Sn2O5F2 ACS Energy Lett. 2 462–8

[24] Han F, Zhu Y, He X, Mo Y and Wang C 2016 Electrochemical stability of Li4GeP2S12 and Li3La2Zr2O12 solid electrolytes Adv. Energy Mater. 6 1501590

[25] Ma C, Cheng Y, Yin K, Luo J, Sharafi A, Sakamoto I, Li L, More K L, Dudney N I and Chi M 2016 Interfacial stability of Li-metal solid electrolyte elucidated via in situ electron microscopy Nano Lett. 16 7030–6

[26] Awaka J, Kijima N, Hayakawa H and Akimoto J 2019 Synthesis and structure analysis of tetragonal Li6.4La3Zr1.4M0.6O12 using Couette reactor for all-solid lithium batteries J. Mater. Chem. A 7 9050–5

[27] Xu W, Xu B, Duan H, Guo Y, Kang H, Li H and Liu H 2016 Ionic conductivity and air stability of Al3-doped Li7La3Zr2O12 ceramics for lithium-ion batteries J. Korean Ceram. Soc. 54 278–84

[28] Huang X, Xiu T, Bading M E and Wen Z 2018 Two-step sintering strategy to prepare dense Li–Garnet electrolyte ceramics with high Li+ conductivity Ceram. Int. 44 5644–50

[29] Wachtler–Welzl A et al 2018 The origin of conductivity variations in Al-stabilized Li3La2Zr2O12 ceramics Solid State Ion. 319 203–8

[30] Zhang Y, Deng Y, Hu D, Chen F, Shen Q, Zhang L and Dong S 2019 Synergistic regulation of garnet-type Ta-doped Li3La2Zr2O12 solid electrolyte by Li+ concentration and Li+ transport channel size Electrochem. Acta 296 823–9

[31] Zhi Y et al 2019 Dopant-dependent stability of garnet solid electrolyte interfaces with lithium metal Adv. Energy Mater. 9 1803440

[32] Zhao P, Cao G, Jin Z, Ming H, Wen Y, Xu Y, Zhu X, Xiang Y and Zhang S 2018 Self-consolidation mechanism and its application in the preparation of Al-doped cubic Li3La2Zr2O12 Mater. Des. 139 65–71

[33] Luo Y, Li X, Zhang Y, Ge L, Chen H and Guo I 2019 Electrochemical properties and structural stability of Ga- and Y- co-doping in Li2Sn2O5F2 ceramic electrolytes for lithium-ion batteries Electrochim. Acta 294 217–25

[34] Xia W, Xu B, Duan H, Guo Y, Kang H, Li H and Hu D 2016 Ionic conductivity and air stability of doped Li3La2Zr2O12 sintered in alumina and Pt crucibles ACS Appl. Mater. Interfaces 8 3335–42

[35] Pan X, Wang J X, Zhang X H, Li Y D and Guan W B 2018 A novel solid-liquid route for synthesizing cubic garnet Al-substituted Li3La2Zr2O12 Solid State Ion. 317 1–6

[36] Yang S H, Kim M Y, Kim D H, Jung H Y, Ryu H M, Han J H, Lee M S and Kim H S 2017 Ionic conductivity of Ga-doped LLZO prepared using Cotuette–Taylor reactor for all-solid lithium batteries J. Ind. Eng. Chem. 56 622–7

[37] Wang X, Liu J, Yin R, Xu Y, Cui Y, Zhao L and Yu X 2018 High lithium ion conductivity of garnet-type oxide Li2+xLa2+xZr2O12 (x = 0–0.1) ceramics Mater. Lett. 231 43–6

[38] Huang M, Shoji M, Shen Y, Nan C W, Munakata H and Kanamura K 2014 Preparation and electrochemical properties of Zr-site substituted Li3La2Zr2O12 (M = Ta, Nb) solid electrolytes J. Power Sources 261 206–11

[39] Gai J, Zhao E, Fu E, Sun D, Ma X, Jin Y, Wu Q and Cui Y 2018 Improving the Li+ ion conductivity and air stability of cubic Li2La2O5F2 by the co-doping of Nb, Y on the Zr-site J. Eur. Ceram. Soc. 38 1673–8

[40] Thompson T, Sharafi A, Johannes M D, Huq A, Allen J L, Wolfenstine J and Sakamoto J 2015 A tale of two sites: on defining the carrier concentration in garnet-based ionic conductors for advanced Li batteries Adv. Energy Mater. 5 1500096

[41] Xiong C, Chen F, Yang W, Yang J, Ma X, Chen D, Su K, Shen Q and Zhang L 2019 Dual regulation of Li+ migration of Li6-xLa2Zr2O12 (M = Nb, Ta, Nb) by bottleneck size and bond length of M–O J. Am. Ceram. Soc. 103 2483–90

[42] Huang X, Lu Y, Guo H, Song Z, Xiu T, Bading M E and Wen Z 2018 None–mother–powder method to prepare dense Li–garnet solid electrolytes with high critical current density ACS Appl. Energy Mater. 1 265–6

[43] Chen X, Cao T, Xue M, Lv H, Li B and Zhang C 2018 Improved room temperature ionic conductivity of Ta-doped Li3La2Zr2O12 via a modified solution method Solid State Ion. 314 92–7

[44] Song S, Kotsobuki M, Zheng F, Xu C, Wang Y, Li W D Z, Hu N and Lu L 2017 Roles of alkaline earth ions in garnet-type superionic conductors Chem. Electro. Chem. 4 266–71

[45] Song S, Sheptyakov D, Korsunsky A M, Duong H M and Lu L 2016 High Li ion conductivity in a garnet-type solid electrolyte via unusual solid state occupation of the doping Ca ions Mater. Des. 93 232–7

[46] Song S, Chen B, Ruan Y, Sun J, Yu L, Wang Y and Thokchom J 2018 Ga-doped Li3La2Zr2O12: garnet-type solid electrolytes for all-solid-state Li-Ion batteries Electrochim. Acta 270 501–8
[50] Song S, Yan B, Zheng F, Duong H M and Lu L 2014 Crystal structure, migration mechanism and electrochemical performance of Cr-stabilized garnet Solid State Ion. 268 135–9
[51] Miara L J, Richards W D, Wang Y E and Ceder G 2015 First-principles studies on cation dopants and electrolyte/cathode interphases for lithium garnets Chem. Mater. 27 4040–7
[52] Yaseen M et al 2020 Investigation of LaAlO3 perovskite compound for optoelectronic and thermoelectric devices under pressure Mater. Res. Express 7 015907
[53] Kihira Y, Ohta S, Imagawa H and Asaoka T 2013 Effect of simultaneous substitution of alkali earth metals and Nb in Li7La3Zr2O12 on lithium-ion conductivity ECS Electrochem. Lett. 2 A55–6
[54] Jiang Y, Zhu X, Qin S, Ling M E and Zhu J 2017 Investigation of Mg2+, Sc3+ and Zn2+ doping effects on densification and ionic conductivity of low-temperature sintered Li4La7Zr2O12 garnets Solid State Ion. 300 73–7
[55] Yang X, Kong D, Chen Z, Sun Y and Liu Y 2017 Low-temperature fabrication for transparency Mg doping Li1+xLa2-xZr2O12 solid state electrolyte J. Mater. Sci.-Mater. Electron. 29 1523–9
[56] El-Shinawi H, Cussen E J and Corr S A 2017 Enhancement of the lithium ion conductivity of Ta-doped Li7La3Zr2O12 by incorporation of calcium Dalton Trans. 46 9415–9
[57] Sanad M M S 2019 Organic acid precursors effects on synthesis, microstructure and electrochemical performance of LiCoPO4 olivine compound Mater. Res. Express 6 105508
[58] Kiisi E H and Howard C J 1998 Crystal structures of zirconia phases and their inter-relation Key Eng. Mater. 153–154 1–36
[59] Dickerson R M, Swain M V and Heuer A H 1987 Microstructural evolution in Ca2-PSZ and the room-temperature instability of tetragonal ZrO2 J. Am. Ceram. Soc. 70 214–20
[60] Mustafa E, Wilhelm M and Wruss W 2003 Phase stability and microstructural characteristics of 12 mol% (Mg, Ca)-PSZ prepared via polymeric route Ceram. Int. 29 189–94
[61] Cussen E J 2006 The structure of lithium garnets: cation disorder and clustering in a new family of fast Li+ conductors Chem. Commun. 412–3
[62] Liu W, He J-J, Li Z-G, Jiang W-L, Yang J-B, Zhang Y and Sun Y 2012 Effect of Na on lower open circuit voltage of flexible CIGS thin-film solar cells prepared by the low-temperature process Phys. Scr. 85 055806
[63] Rao R P, Gu W, Sharma N, Peterson V K, Avdeev M and Adams S 2015 In situ neutron diffraction monitoring of Li1+xLa2-xZr2O12 garnet formation: toward a rational synthesis of garnet solid electrolytes Chem. Mat. 27 2903–10
[64] Xue W, Yang Y, Yang Q, Liu Y, Wang L, Chen C and Cheng R 2018 The effect of sintering process on lithium ionic conductivity of Li5+xLa3−xZr2O12 garnet produced by solid-state synthesis RSC Adv. 8 13083–8
[65] Tang Y, Luo Z, Liu T, Liu P, Li Z and Lu A 2017 Effects of B2O3 on microstructure and ionic conductivity of Li5+xLa3−xZr2−xNb2xO12 solid electrolyte Ceram. Int. 43 11879–84
[66] Hettemawerden D et al 2016 Structural and electrochemical consequences of Al and Ga cosubstitution in Li5+xLa3−xZr2O12 solid electrolytes Chem. Mat. 28 2384–92
[67] Li Y, Han J-T, Wang C-A, Xie H and Goodenough J B 2012 Optimizing Li+ conductivity in a garnet framework J. Mater. Chem. 22 15357
[68] Huang X, Song Z, Xiu T, Badding M E and Wen Z 2019 Sintering, micro-structure and Li+ conductivity of Li5−xLa2−xZr2−xNb2xO12/MgO (x = 0.2–0.7) Li-Garnet composite ceramics Ceram. Int. 45 56–63
[69] Begum Z A, Rahman I M M, Takase T and Hasegawa H 2019 Formation and stability of the mixed-chelator complexes of Sr2+, Mg2+, Ca2+, Ba2+, and Y3+ in solution with bio-relevant chelators J. Inorg. Biochem. 195 141–8