

# **Processing and electrical conductivity property of lithium-doped high-entropy pyrochlore and perovskite ceramics**

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# Abstract

Lithium-doped  $Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})_2O_7$  (LLTNO),  $Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})_2O_7$ (LLTTO) high-entropy pyrochlore and  $Li_{0.5}Sr_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})O_3$  (LSTTO),  $Li_{0.5}Ba_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})O_3$  (LBTNO) high-entropy perovskite ceramics were synthesized by solid state reaction method and sintered. Crystal structure, microstructure and electrical properties of these high entropy ceramics were studied. The LLTNO and LLTTO pellets sintered at 1300 °C present a pyrochlore structure, while LSTTO and LBTNO pellets sintered at 1350 °C present a perovskite structure. The LBTNO ceramics has a total conductivity of  $1.25 \times 10^{-7} \, \text{S} \cdot \text{cm}^{-1}$  at room temperature while the LSTTO sample exhibits the highest conductivity of  $2.11 \times 10^{-7} \, \text{S} \cdot \text{cm}^{-1}$  among all samples. Both LSTTO and LBTNO ceramics present negligible electronic conductivity. Relative densities of the LLTNO, LLTTO, LSTTO and LBTNO ceramics were 82, 88, 86 and 87 %TD, respectively, which is the reason for low conductivity of these high entropy ceramics. The activation energies of the LSTTO and LBTNO samples were 0.39 and 0.38 eV, respectively, which is close to the traditional Li<sup>+</sup>-type conducting solid electrolytes.

Keywords: high-entropy ceramics, pyrochlore, perovskite, solid electrolyte, conductivity

## I. Introduction

High-entropy ceramics have gained more and more attention in recent years [1]. High-entropy ceramics are obtained by mixing five or more oxides, sulphides, nitrides or carbides and calcination/sintering of the obtained mixture at high temperature before quenching. The definition of high entropy ceramics implies mixing entropy higher than 1.5R [2]. The composition of high-entropy ceramics is disordered, but the long-range structure is ordered [3]. Many systems, such as perovskite [4–6], fluorite [7], spinel [8–10], pyrochlore [11], garnet [12,13] and rock-salt [14,15] have been developed for high-entropy ceramics. High-entropy ceramics have many remarkable properties that have the potential applications in thermal protection, energy storage and electro-catalysis [16].

Among them, development of solid state electrolytes based on high entropy ceramics is a promising research field. There are many similarities between ceramic and glass-type solid electrolytes and high entropy ceramics in design principles and preparation processes. The principle of ceramic-type solid electrolyte is to stabilize the high-temperature phase with high ionic conductivity at room temperature. The preparation process of some typical solid electrolytes such as  $Li_{0.34}La_{0.56}TiO_3$ requires quenching. The preparation of high entropy ceramics also requires quenching, and the purpose of this process is also to stabilize the high-temperature phase at low temperature. It is a feasible way to develop highperformance solid electrolytes based on high entropy ceramics.

Ceramic type solid electrolytes have been widely studied for the next generation energy storage devices such as all solid state Li/Na/Mg/Zn batteries [17–19] and fuel batteries [20]. All solid-state Li battery is a research hotspot nowadays. Ceramic type solid electrolytes have been widely investigated due to their high chemical stability in air and high mechanical strength [21]. Typical ceramic type solid electrolytes for all solid state Li batteries contain Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> garnet [22], Li<sub>3x</sub>La<sub>1/3-x</sub>NO<sub>3</sub> (N = Ti, Nb, Ta) perovskite [23] and

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 $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$  NASICON [11,12]. However, these solid electrolytes still have problems that hinder their practical application. The main challenge for all solid-state Li batteries is the development of novel solid state lithium electrolytes with high Li<sup>+</sup> conductivity at room temperature and high stability against lithium metal.

Bérardan et al. [26] reported the ionic conductivity of high entropy ceramics for the first time. They found that (MgCoNiCuZn)<sub>1-x-y</sub>Ga<sub>y</sub>A<sub>x</sub>O (A = Li, Na, K) were potential solid electrolytes for all solid state batteries. The room temperature conductivity of these Lidoped compounds was as high as  $10^{-3}$  S·cm<sup>-1</sup>, which can be seen as a superionic lithium-ion conductor. High lithium mobility in (MgCoNiCuZn)<sub>1-x</sub>Li<sub>x</sub>O (x =0 to 0.3) was attributed to charge compensation as well as the appropriate concentrations of oxygen vacancies/lithium [27]. However, Mozdzierz *et al.* [28] reported that (CoCuMgNiZn)<sub>1-x</sub>Li<sub>x</sub>O high entropy ceramics are mixed ionic-electronic conductors. Furthermore, (CoCuMgNiZn)<sub>1-x</sub>Li<sub>x</sub>O are chemically unstable against lithium metal.

Fu and Ferguson [29] synthesized the pure high-entropy type lithium ion solid electrolyte,  $Li_7La_3Zr_{0.5}Nb_{0.5}Ta_{0.5}Hf_{0.5}O_{12}$  (LLZNTH), with a single cubic garnet structure. The relative density of LLZNTH was as high as 94 %TD. LLZNTH presents a high room temperature Li+ conductivity of 4.67 × 10<sup>-4</sup> S·cm<sup>-1</sup> with a low activation energy of 0.25 eV. The electronic conductivity of LLZNTH is lower than  $10^{-8}$  S·cm<sup>-1</sup>. The electronic transportation in LLZNTH is negligible. LLZNTH is a pure lithium conductor in nature.

High entropy strategy can be developed into a universal collaborative modification technology, simultaneously realizing the sintering-aids method, doping

method and other modification technologies. The advantage of high entropy ceramics is that the components and their contents can be adjusted on a large scale. This is an important difference between high entropy modification strategy and other modification technologies such as doping. For example, through the high entropy transformation of Li<sub>0.5</sub>La<sub>0.5</sub>TiO<sub>3</sub> (LLTO), it is possible to: i) replace part of Ti<sup>4+</sup> with Zr<sup>4+</sup>, Ta<sup>5+</sup>, Hf<sup>4+</sup>, Nb<sup>5+</sup>, Sn<sup>4+</sup>,  $Te^{6+}$ , etc. reduce the content of Ti to improve the stability when contacting with lithium; ii) reduce the sintering temperature and improve the grain boundary ion transport by introducing low melting point compounds such as  $V_2O_5$  and  $TeO_2$ ; iii) expand the bottleneck size and promote ion conduction by introducing large radius cations such as  $Zr^{4+}$  (0.72 Å),  $Ta^{5+}$  (0.64 Å),  $Hf^{4+}$ (0.72 Å), Nb<sup>5+</sup> (0.64 Å) larger than Ti<sup>4+</sup> (0.605 Å).

Perovskite and pyrochlore are typical functional ceramics with many interesting properties, such as electrochemical catalysis, thermal protection, permanent magnetic properties and electrical insulation [30]. In this work, four Li<sup>+</sup> solid electrolytes based on high-entropy perovskite and pyrochlore: Li<sub>0.5</sub>Sr<sub>0.5</sub>(Ti<sub>0.2</sub>Zr<sub>0.2</sub>Hf<sub>0.2</sub>Sn<sub>0.2</sub>Ta<sub>0.2</sub>)O<sub>3</sub> (LSTTO),  $\begin{array}{c} Li_{0.5}Ba_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})O_3\\ Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})Q_3\\ \end{array}$ (LBTNO), (LLTNO) and Li<sub>0.66</sub>La<sub>1.12</sub>(Ti<sub>0.2</sub>Zr<sub>0.2</sub>Hf<sub>0.2</sub>Sn<sub>0.2</sub>Ta<sub>0.2</sub>)<sub>2</sub>O<sub>7</sub> (LLTTO), were synthesized by a traditional solid state reaction route. The first two high-entropy ceramics were designed based on ABO3-perovskite Li05La05TiO3, whereas the second two high-entropy ceramics were designed based on A2B2O7-pyrochlore La2Zr2O7. Lithium was introduced into ceramic matrix to provide mobile ions. The structure and electrical conductivity of these high entropy ceramics were studied.

Sample	Molar content [mol]										
	Li	Sr	Ba	La	Ti	Zr	Hf	Sn	Та	Nb	
LSTNO	0.5		0.5	0.2	0.2	0.2	0.2	0.2		0.2	
LSTTO	0.5	0.5		0.2	0.2	0.2	0.2	0.2	0.2		
LLTNO	0.66			1.12	0.4	0.4	0.4	0.4		0.4	
LLTTO	0.66			1.12	0.4	0.4	0.4	0.4	0.4		

Table 1. Theoretical compositions of the target ceramic samples

Table 2. Details of reagents							
Reagent	Specification	Manufacturer					
Li <sub>2</sub> CO <sub>3</sub>	AR, ≥99%	Aladdin Biochemical Technology Co. Ltd.					
BaCO <sub>3</sub>	SP, ≥99%	Sinopharm Chemical Reagent Co. Ltd.					
SrCO <sub>3</sub>	AR, ≥99%	Tianjin Guangfu Technology Development Co. Ltd.					
La <sub>2</sub> O <sub>3</sub>	4N	Sinopharm Chemical Reagent Co. Ltd					
$ZrO_2$	AR, ≥99%	Tianjin Guangfu Technology Development Co. Ltd.					
$Nb_2O_5$	99.50%	Sinopharm Chemical Reagent Co. Ltd.					
Ta <sub>2</sub> O <sub>5</sub>	99.5% metals basis	Aladdin Biochemical Technology Co. Ltd.					
$HfO_2$	98%, Zr <1.5%	Aladdin Biochemical Technology Co. Ltd.					
$SnO_2$	AR, ≥98%	Tianjin Guangfu Technology Development Co. Ltd.					
TiO <sub>2</sub>	AR, ≥99.5%	Tianjin Guangfu Technology Development Co. Ltd.					
$C_2H_5OH$	AR, ≥99.7%	Tianjin Guangfu Technology Development Co. Ltd.					

#### **II. Experimental**

High entropy ceramics (Table 1) were prepared by simple solid state reaction method.  $Li_2CO_3$ ,  $BaCO_3$ ,  $SrCO_3$ ,  $La_2O_3$ ,  $ZrO_2$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $HfO_2$ ,  $SnO_2$  and  $TiO_2$  were used as starting materials. The specification and manufacturers of reagents were listed in Table 2.

Reagents were weighted according to the stoichiometric amounts (Table 1), whereas 20 wt.% excess  $\text{Li}_2\text{CO}_3$  were added into starting materials to equate high-temperature evaporation loss. All reagents were mixed by ball-milling for 24 h with absolute ethanol (AR, 99.7%) as the liquid ball-milling media. Polyurethane tank and zirconia balls were used for the ball milling process. The obtained mixture was dried at 80 °C, put into an alumina crucible and calcined at 900 °C for 12 h in air. The calcined powder was re-ground, pressed into pellets and sintered at high temperatures (1300 °C/12 h for LLTNO and LLTTO, 1350 °C/6 h for LBTNO and LSTTO). Finally, both surfaces of the obtained pellets were polished before characterization.

The phase composition of the sintered pellets was detected by X-ray diffraction (XRD, Bruker D8 Discovery equipment, Cu K $\alpha$  radiation,  $\lambda = 1.54178$  Å). XRD data were recorded in the  $2\theta$  range of 5–80°. The microstructure of the ceramic pellets was characterized by a scanning electron microscope (SEM, Hitachi S3000N).

The silver paste was applied on both surfaces of the ceramic pellets and dried at 300 °C for 15 min to get the Ag electrode. Ag is a typical Li<sup>+</sup> blocking electrode. Electrodes were led out with silver wire. The pellets were placed in an incubator to obtain a stable temperature during the test. The conductivity of each ceramic sample was characterized by AC impedance spectroscopy (Chenhua CHI660E) in a frequency range of 1 Hz to 1 MHz with 50 mV amplitude. The electronic conductivity of each ceramic sample was determined by DC polarization method with a polarization voltage of 2 V for 10000 s.

#### III. Results and discussion

Figure 1a shows the XRD patterns of the LLTNO and LLTTO ceramic pellets sintered at 1300 °C. The main diffraction peaks correspond to pyrochlore type La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> PDF# 13-0082. Weak peaks of impurity were found in the XRD patterns of the LLTNO sample, but the LLTTO presents a pure pyrochlore structure. The main peaks shifted to higher angles compared to La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> for both LLTNO and LLTTO. Figure 1b shows the XRD patterns of the LBTNO and LSTTO ceramic pellets sintered at 1350 °C. The main diffraction peaks correspond to perovskite type SrZrO<sub>2</sub> PDF# 23-0561. Diffraction peaks of impurities were found in the XRD patterns of both LBTNO and LSTTO. The main peaks for both LBTNO and LSTTO shifted to higher angles compared to SrZrO<sub>3</sub>. Both pyrochlore or perovskite as the main phase were obtained successfully for high entropy ceramics after sintering at corresponding high temperatures.

Figure 2 shows the cross-sectional SEM images of sintered ceramic pellets. All ceramic pellets present a polyhedral microstructure. There is a loose connection between grains. The density of ceramics was determined by the Archimedes method. The relative density of the samples is the ratio of the volume density to the theoretical density. MDI Jade 6.5 software was used to calculate the lattice constant and theoretical density of the samples. We do not consider the influence of impurities but regard the whole ceramic pellet as pure phase during calculation. As a result, the relative densitis of the LLTNO, LLTTO, LSTTO and LBTNO were 82, 88, 86 and 87 %TD, respectively.

Pores between grains were observed in all samples as shown in Fig. 3. Pores and the low density were attributed to the element's volatilization during hightemperature sintering. The density of these samples is very low compared to traditional ceramic oxide solid electrolytes. The low density is detrimental for achieving high conductivity for ceramic type solid electrolytes.



Figure 1. XRD patterns of LLTNO and LLTTO ceramic pellets sintered at 1300 °C (a) and LBTNO and LSTTO ceramic pellets sintered at 1350 °C (b)



Figure 2. SEM images of: a) LLTNO, b) LLTTO, c) LSTTO and d) LBTNO ceramics



Figure 3. Low magnification SEM images of: a) LLTNO, b) LLTTO, c) LSTTO and d) LBTNO ceramics

Figure 4 shows the AC impedance spectra of ceramic pellets. The AC impedance spectra of all ceramic samples consist of a sloping straight line in the low-frequency region and a semicircle in the highfrequency range. AC impedance data were fitted by using the equivalent circuit of Q(((QR)(QR))W). The sloping straight line represents the so-called Warburg resistance, i.e. the resistance caused by Li-ion diffusion in the Li<sup>+</sup>-blocking Ag electrode. The intercept of the semicircle on the real (*x*) axis represents the total resistance  $(R_{total})$  of ceramics. The conductivity of each sample was calculated by using the following formula:

$$\sigma = \frac{d}{R \cdot S} \tag{1}$$

where  $\sigma$  is the conductivity of sample, *d* is the thickness of ceramic pellet and *S* is the single-surface area of Ag electrode on pellet. The calculated results were listed in Table 3. The conductivity of the LLTNO ceramics is  $5.61 \times 10^{-8}$  S·cm<sup>-1</sup> at room temperature, which is too low for application in solid state batteries. Similarly, the LLTTO sample has a low conductivity of  $8.03 \times 10^{-8}$  S·cm<sup>-1</sup> at room temperature. The LSTTO and LBTNO ceramics have a conductivity of  $2.11 \times 10^{-7}$  and  $1.25 \times 10^{-7}$  S·cm<sup>-1</sup> at room temperature, respectively.

The conductivity of the perovskite ceramics is significantly higher than pyrochlore. The low conductivity of these high entropy ceramics was related to the low density of pellets. Although the conductivities of the LSTTO and LBTNO samples were low, there is still much room for improvement of conductivity, such as reducing impurity contents and improving the density of high entropy ceramics. Adopting new synthesis methods, sintering techniques and optimizing sintering processes to reduce sintering temperature and increase density will be beneficial for improving the performance of these high entropy ceramics.

Figure 5 shows the Arrhenius plots of the conductivity for ceramic pellets. The activation energy was calculated using the formula described in the literature [31]. The activation energies of the LLTNO and LLTTO ceramics were 0.46 eV and 0.43 eV, respectively. These



Figure 4. Nyquist plots for: a) LLTNO, b) LLTTO, c) LSTTO and d) LBTNO measured at room temperature

Table 3. Conductivity and activation energy for ceramic pellets

Sample	$\sigma_{total}  [\text{S} \cdot \text{cm}^{-1}]$	$\sigma_{ele}  [\mathrm{S} \cdot \mathrm{cm}^{-1}]$	$E_a$ [eV]
$Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})_2O_7$	$5.61 \times 10^{-8}$	$4.71 \times 10^{-9}$	0.46
$Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})_2O_7$	$8.03 \times 10^{-8}$	$1.08 \times 10^{-9}$	0.43
$Li_{0.5}Sr_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})O_3$	$2.11\times10^{-7}$	$2.23\times10^{-9}$	0.39
Li <sub>0.5</sub> Ba <sub>0.5</sub> (Ti <sub>0.2</sub> Zr <sub>0.2</sub> Hf <sub>0.2</sub> Sn <sub>0.2</sub> Nb <sub>0.2</sub> )O <sub>3</sub>	$1.25 \times 10^{-7}$	$2.57\times10^{-9}$	0.38



Figure 5. Arrhenius plots of conductivity for ceramic pellets

values are larger than the activation energy values of traditional ceramic solid electrolytes, indicating that lithium ions conduction is challenging in high entropy pyrochlore. The activation energies of the LSTTO and LBTNO ceramics were 0.39 and 0.38 eV, respectively. These values are still slightly higher but close to the traditional values.

DC polarization plots for the electronic conductivity of the ceramics were shown in Fig. 6. With the increase

of polarization time, the current decreases continuously. Finally, the current reaches a steady state. The steady current is attributed to the electronic transport in ceramics since Li<sup>+</sup>-blocking Ag were used as electrodes [32]. Electronic conductivity can be calculated by the following equation:

$$\sigma_{ele} = \frac{d \cdot I}{S \cdot U} \tag{2}$$

where  $\sigma_{ele}$  is electronic conductivity, d is the thickness of ceramic pellet, I is the final steady state current shown in Fig. 6 and U is the polarization voltage (2 V in this experiment) applied for the test. The electronic conductivity of the LLTNO sample was  $4.71 \times$  $10^{-9}$  S·cm<sup>-1</sup> at room temperature, which is close to its ionic conductivity. The ratio of electronic conductivity to total conductivity is 8.4%. A suitable solid electrolyte should have a low electronic conductivity to prevent short circuits when the device is working [33]. So, the high entropy LLTNO ceramics is not suitable for a solid electrolyte. The electronic conductivities of the LLTTO, LSTTO and LBTNO samples were 1.08, 2.23 and  $2.57 \times 10^{-9} \,\mathrm{S} \cdot \mathrm{cm}^{-1}$  at room temperature, respectively. As it can be seen, the electronic conductivities of the LSTTO and LBTNO ceramics were nearly two orders of magnitudes lower than their ionic conductivity at room temperature. Thus, lithium-ion transporta-



Figure 6. DC polarization current-time curves of: a) LLTNO, b) LLTTO, c) LSTTO and d) LBTNO

tion dominates the conducting property in the LSTTO and LBTNO high entropy perovskite ceramics.

## **IV.** Conclusions

In this paper, a series of high entropy ceramics have been designed and synthesized via the solid-state reaction route.  $Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})_2O_7$ (LLTNO) and  $Li_{0.66}La_{1.12}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})_2O_7$ (LLTTO) sintered at 1300 °C present pyrochlore strucwhereas  $Li_{0.5}Sr_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Ta_{0.2})O_3$ ture, (LSTTO) and  $Li_{0.5}Ba_{0.5}(Ti_{0.2}Zr_{0.2}Hf_{0.2}Sn_{0.2}Nb_{0.2})O_3$ (LBTNO) ceramics sintered at 1350 °C have perovskite structure. The LLTTO ceramics has a pure pyrochlore structure, while the LLTNO, LSTTO and LBTNO samples in addition to the main pyroclore or perovskite XRD peaks contain a small amount of impurity phases. The conductivity of the LLTNO sample was  $5.61 \times 10^{-8} \,\mathrm{S \cdot cm^{-1}}$  (a little bit lower than that for LLTTO), while its electronic conductivity was  $4.71 \times 10^{-9} \,\mathrm{S} \cdot \mathrm{cm}^{-1}$  at room temperature. LSTTO and LBTNO have the conductivities of  $2.11 \times 10^{-7}$  and  $1.25\times10^{-7}\,{\rm S}{\cdot}{\rm cm}^{-1}$  at room temperature, respectively. The electronic conductivity of the LSTTO and LBTNO samples is nearly two orders of magnitudes lower than their ionic conductivity. The activation energies of the LSTTO and LBTNO samples were 0.39 and 0.38 eV, which is close to the traditional ceramic type solid electrolytes. The LLTTO and LLTNO ceramics are not suitable for solid electrolytes, but the LSTTO and LBTNO regarded as ceramic solid electrolytes. However, the room temperature conductivity of these high entropy ceramics needs to be further improved for application.

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