



Short communication

Morphology and transport properties of the solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ prepared by the solid-state and citrate–nitrate methods

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ABSTRACT

Tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was synthesised by the solid-state and citrate–nitrate methods. The crystal structure of the samples was characterised by the X-ray diffraction method. The morphology of the particles was investigated using both optical microscopy and a particle size analysis method. The ceramic samples were studied by complex impedance spectroscopy in the frequency range from 12 to 10^5 Hz, in the temperature range of 20–400 °C. Synthesis by the citrate–nitrate method makes it possible to reduce both the temperature and time of the synthesis and also prepare the product with smaller particles. The conductivity of LLZ synthesised by the citrate–nitrate method ($5.2 \times 10^{-6} \text{ S cm}^{-1}$ at 20 °C) is higher than the conductivity of LLZ synthesised by the solid-state method ($1.3 \times 10^{-6} \text{ S cm}^{-1}$ at 20 °C).

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1. Introduction

The main requirements for solid electrolytes for batteries with a lithium anode are a high lithium-ion conductivity, stability against anode and cathode materials and a low value of the electronic component of conductivity. However, most known solid electrolytes with high lithium-ion conductivity, such as Li_3N and titanates with a perovskite-related structure, are unstable in direct contact with electroactive materials [1]. One promising solid electrolyte for application in lithium batteries is $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [2]. The cubic modification of this compound exhibits a total conductivity of approximately $10^{-4} \text{ S cm}^{-1}$ at room temperature [2,3] and chemical stability against lithium and humidity in the atmosphere [2]. In addition, LLZ has a tetragonal modification in which the ion conductivity is significantly lower ($1.63 \times 10^{-6} \text{ S cm}^{-1}$) at 27 °C [4]. Many of the reported works describing the synthesis of LLZ used the solid-state method [2–4]. However, using the sol–gel method reduces the temperature of the synthesis and leads to the formation of fine-dispersed grains and a homogeneous product [5]. In [6], LLZ was synthesised by the sol–gel method, but an individual compound was not obtained.

The objective of the present work was to synthesise the LLZ samples using the solid-state and citrate–nitrate methods and to

compare both the morphology of the LLZ particles and the conductivity of prepared ceramic samples.

2. Experimental

Li_2CO_3 , La_2O_3 and ZrO_2 were used as starting materials for the solid-state synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$. Zirconium and lanthanum oxides were pre-dried at 1000 °C to a constant weight. The starting materials were mixed in a stoichiometric ratio, except for Li_2CO_3 , which was added with 10 wt.% excess, as shown in [3]. After mixing, the starting mixture was heated in a platinum crucible in air. The synthesis was carried out by stepwise increasing the temperature from 900 °C to 1250 °C for 8 h and holding at the final calcination temperature for 2 h. After each stage of synthesis, the mixture of reagents was thoroughly ground in an agate mortar.

The crystalline structure of LLZ was determined by the X-ray diffraction method (XRD) after each stage of the synthesis. The mass of the product was compared with the calculated value.

Li_2CO_3 , La_2O_3 and an aqueous solution of $\text{ZrO}(\text{NO}_3)_2$ were used as starting components for the citrate–nitrate synthesis. These components were dissolved in a mixture of the dilute nitric and citric acids. The resulting solution was evaporated at 80 °C to a transparent gel. In the next step, the gel was dried and pyrolysed at ~200 °C. As a result, a black powder was obtained. Then, the powder was annealed at 900 °C for 3 h in a platinum crucible. The process of synthesis was controlled in the same way as the solid-state case.

The XRD analysis was carried out using a Rigaku D-MAX-2200 V diffractometer with a vertical goniometer and $\text{Cu K}\alpha$ -radiation,

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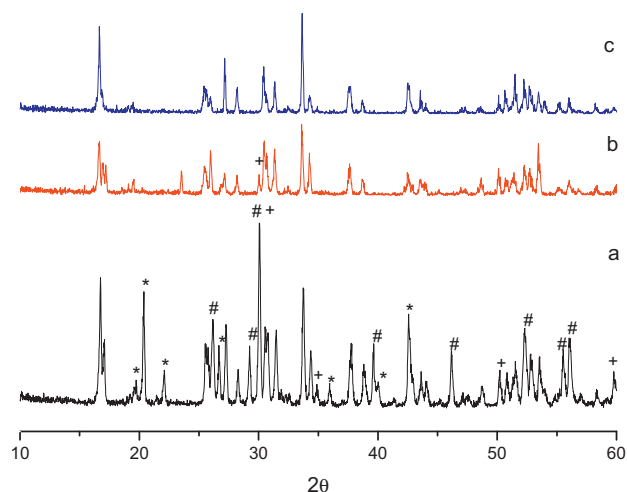


Fig. 1. XRD patterns of the intermediate and final products of the synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ prepared by the solid-state method: (a) 900 °C, 6 h; (b) 1200 °C, 2 h; and (c) the final product (* Li_2ZrO_3 , # La_2O_3 , + ZrO_2).

$2\theta = 10\text{--}60^\circ$. XRD patterns of compounds were compared with database PDF-2 and literature data [2–4].

Microphotographs were obtained using an optical microscope, the AmScope 3.0. The particle-size distribution was determined by a laser-diffraction particle size analyser, the Malvern Mastersizer 2000.

The surfaces of the LLZ samples were investigated with a scanning electron microscope JSM 5900LV in the secondary-electron mode.

The conductivity measurements were carried out for the pellets of LLZ powder, which were formed by pressing under 0.8 GPa and annealed at 1100 °C for 1 h. The density of the pellets was approximately 70% of the theoretical value. Both sides of the pellets were painted using gallium–silver electrode paste. The conductivity was measured by the AC impedance method using an LCR-meter 819 (Goodwill Instruments) in the frequency range from 0.012 to 100 kHz in air. The conductivity measurements were made over a temperature range between 20 and 400 °C during heating as well as during cooling in the two-probe leakproof cell with silver metal electrodes. The results were fitted using mathematical modelling. The bias in determining the conductivity does not exceed 10%.

Measurements of the electronic component of conductivity were carried out using a polarisation method with blocking nickel electrodes. The applied voltage was 0.1 V.

3. Results and discussion

Fig. 1 shows XRD patterns of the intermediate and final products of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ synthesised by the solid-state method. After the first stage of the synthesis (900 °C for 6 h), tetragonal LLZ, starting components (ZrO_2 and La_2O_3) and lithium metazirconate (Li_2ZrO_3) were observed. Then, after sintering at 1250 °C, the impurities disappeared and homogeneous tetragonal LLZ was determined to be the final product of the synthesis.

Fig. 2 shows XRD patterns of the intermediate and final products of the synthesis of LLZ by the citrate–nitrate method. After the initial stage of the synthesis, the formation of $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ was observed; however, the XRD patterns also show small peaks of unidentified compounds. It is possible that the excess lithium and lanthanum oxides above the stoichiometric ratio amorphised, and that their structure was invisible in the XRD pattern. Another reason is the formation of solid solutions based on $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$.

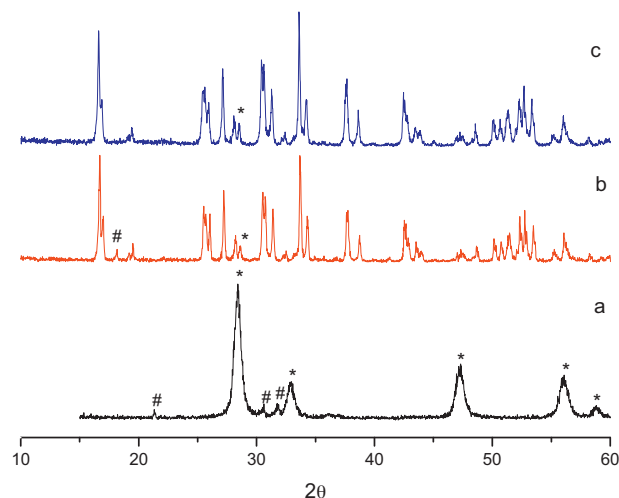


Fig. 2. XRD patterns of the intermediate and final products of the synthesis of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ prepared by the citrate–nitrate method: (a) 700 °C, 2 h; (b) 800 °C, 2 h; and (c) the final product. * $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$, #unidentified compounds.

X-ray peaks of the final product relate to peaks of the tetragonal modification of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ except the peak at $2\theta = 27$, which may be associated with $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$. Other peaks related to $\text{La}_{0.5}\text{Zr}_{0.5}\text{O}_{1.75}$ are not observed, so its presence in the final product can only be assumed with a certain degree of confidence.

The particles of LLZ prepared by the solid-state method (Fig. 3a) are transparent monocrystals with sizes in the range of 10–40 μm . The LLZ particles prepared by the citrate–nitrate method were smaller and disposed to agglomeration (Fig. 3b). Fig. 3c and d shows SEM pictures of the surface sintered LLZ samples prepared from the powders synthesised by the solid-state and citrate–nitrate methods.

The size distribution of particles is shown in Fig. 4. The average diameter of LLZ particles prepared by the solid-state method are approximately 3 times larger than the average diameter of LLZ agglomeration particles prepared by the citrate–nitrate method. The reduction in the size of the particles in the citrate–nitrate synthesis method can be explained by a lower final temperature and the total synthesis time.

The LLZ samples were changing their colour from white to dark grey during the solid-state synthesis and the following sintering. The colour change may be attributed to a variation in the oxidation degree of the metals. Such variation may lead to the appearance of an electronic conductivity. Therefore, measurements of the electronic conductivity were made at room temperature and at 500 °C. In both cases, the values of electronic conductivity do not exceed 0.001% from the total conductivity.

The typical impedance plots obtained at room and higher temperatures are shown in Fig. 5. The impedance spectrum at $\sim 20^\circ\text{C}$ may be separated into two semicircles. In [4] the semicircle near the origin can be attributed to the bulk resistance of LLZ, while the semicircle in the low-frequency range correlated with the grain-boundary resistance. Data for the bulk, grain-boundary and total conductivities that were found in the present work in comparison with literature data are shown in Table 1. The bulk conductivity of LLZ synthesised by the solid-state method was comparable with literature data, whereas the grain-boundary conductivity was an order of magnitude higher than literature values. As a result, the value of the total conductivity of our samples prepared by the solid-state method was an order of magnitude higher than values of the total conductivity of LLZ from literature. The cause of this difference may involve the various conditions involved

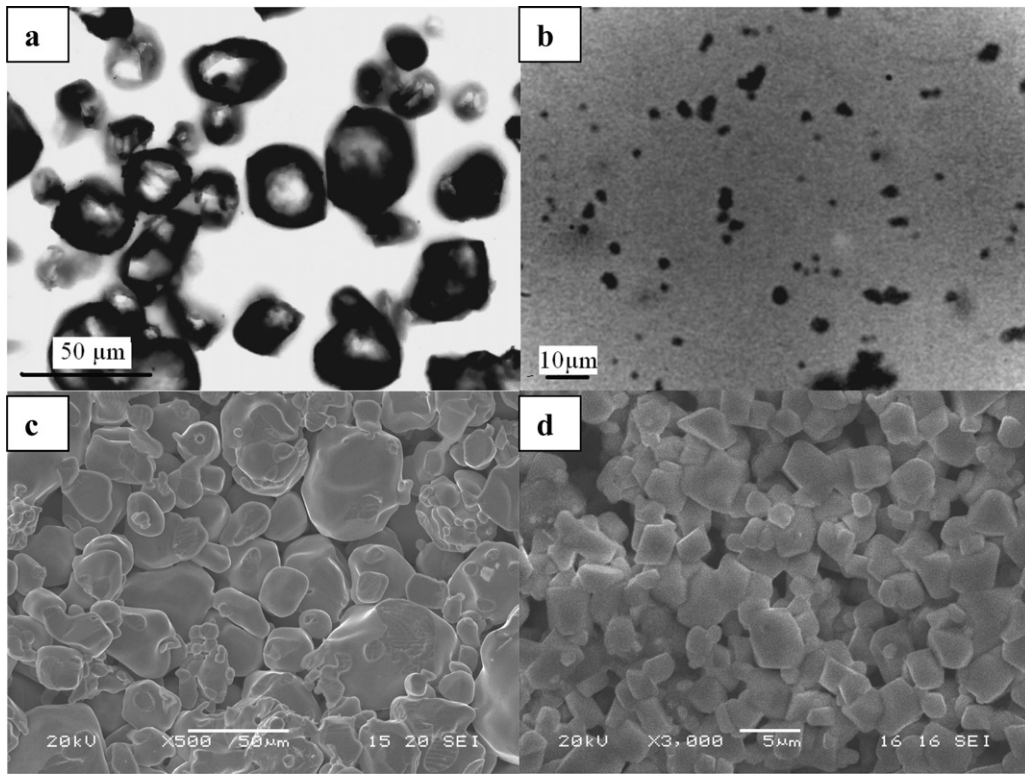


Fig. 3. Optical micrographs of the LLZ powder prepared by (a) the solid-state and (b) citrate–nitrate methods. SEM pictures of the surface sintered LLZ samples prepared from the powders synthesised by (c) the solid-state and (d) citrate–nitrate methods.

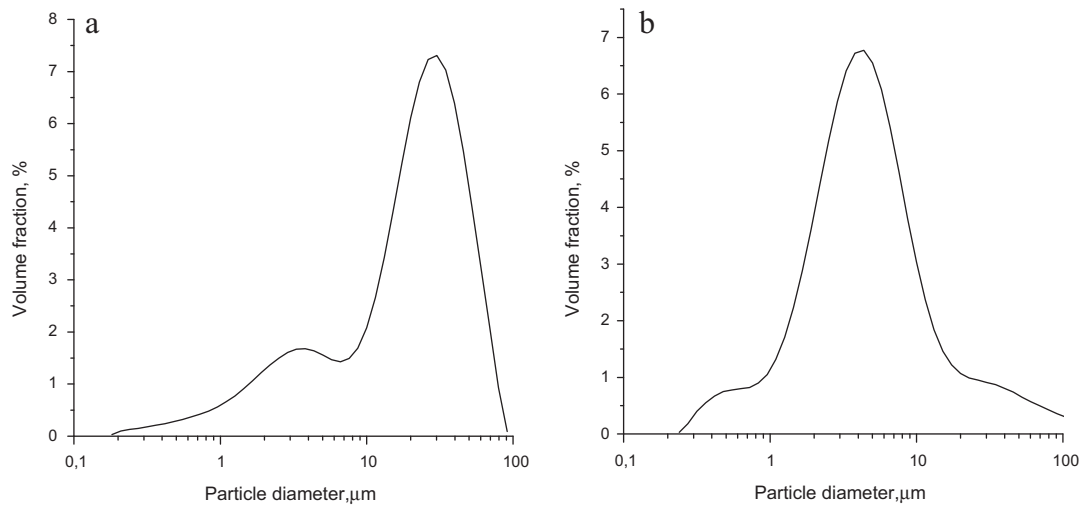


Fig. 4. The size distribution of the particles of LLZ powder prepared by (a) the solid-state and (b) citrate–nitrate methods.

Table 1

Data of the bulk, grain-boundary and total conductivities were found in present work and literature data.

| t (°C) | Bulk conductivity ($S \times cm^{-1}$) | Grain-boundary conductivity ($S \times cm^{-1}$) | Total conductivity ($S \times cm^{-1}$) | Density (%) from theoretical | Refs. |
|----------|--|--|---|------------------------------|---------------------------------------|
| 27 | 1.63×10^{-6} | 5.59×10^{-7} | 4.16×10^{-7} | 60 | [4] |
| 25 | 4.4×10^{-7} | 2.8×10^{-7} | 1.71×10^{-7} | | [6] |
| 25 | $\sim 10^{-6}$ | $\sim 10^{-7}$ | 3.12×10^{-7} | | [7] |
| 20 | 2.09×10^{-6} | 3.32×10^{-6} | 1.28×10^{-6} | 73 | Present work (solid-state method) |
| 20 | 8.91×10^{-6} | 1.24×10^{-5} | 5.19×10^{-6} | 66 | Present work (citrate–nitrate method) |

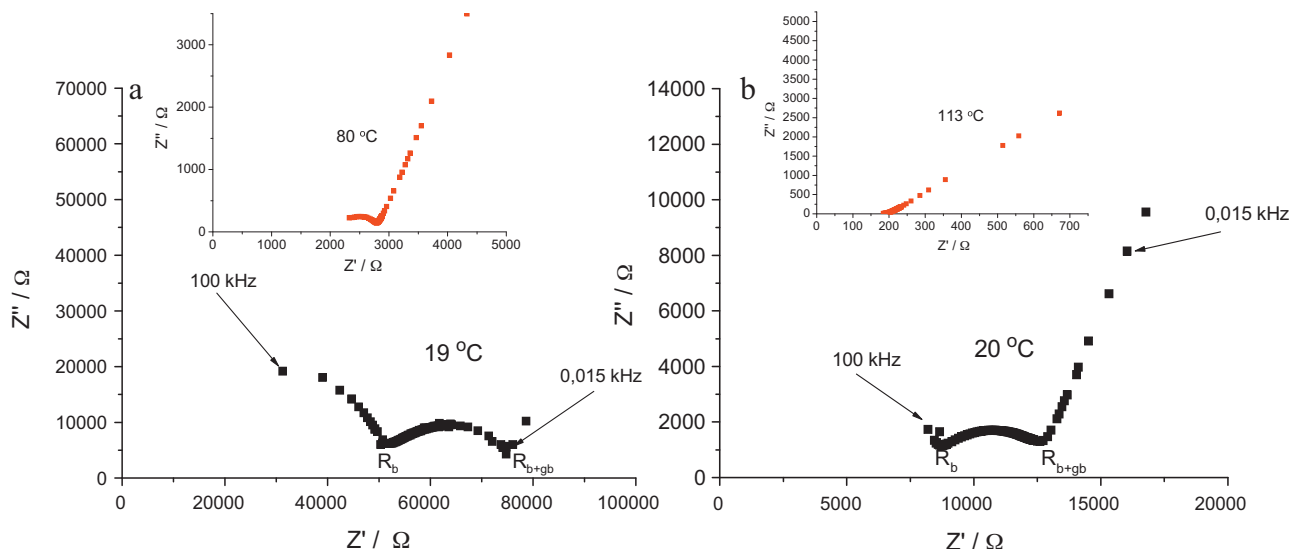


Fig. 5. Impedance plots of LLZ synthesised by (a) the solid-state and (b) citrate–nitrate methods.

in making samples for the conductivity measurements, which resulted in the different density of the prepared samples. For example, in [4], the density of the samples was 60% of the theoretical value.

The values of the bulk, grain-boundary and total conductivities of samples prepared by the citrate–nitrate method were several times higher than values for LLZ prepared by the solid-state synthesis method. We assume that the reason for this may involve nonstoichiometry in the lithium cations during the solid-state synthesis, which cannot be detected by traditional analytic methods. On the one hand, 10 wt.% excess of lithium carbonate was added during the synthesis of LLZ described in the literature [4,5] and in the solid-state synthesis used in the present work. On the other hand, the lithium component may be lost by volatilisation at temperatures higher than 1000 °C [4]. Therefore, the final stoichiometry of the lithium cation will depend on a number of different factors. This may explain the different values of the conductivity given in different literature sources. In the case of the citrate–nitrate method, an excess of lithium carbonate was not introduced because the temperature and synthesis time were significantly smaller than in the case of the solid-state synthesis. Therefore, we suggest that in the case of the citrate–nitrate synthesis, the product is most similar to the formula $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$.

At temperatures higher than 100 °C, it is difficult to separate the bulk and grain-boundary contributions of a resistance. Fig. 6 displays the temperature dependences of the total conductivity in Arrhenius coordinates. In the temperature range of 20–400 °C, the plots are linear, and bends associated with phase transitions and subsequent cooling processes, hysteresis was not observed. That means that there is no influence of adsorbed water on the conductivity, which was observed in article [8]. The energies of activation of the ionic conductivity of LLZ synthesised by the solid-state and citrate–nitrate methods are similar, 44.5 ± 0.6 and 46.7 ± 0.7 kJ mol^{-1} , respectively.

Because the densities of samples synthesised by the two methods differ from one another, we recalculated the conductivity values to 100% density for the entire measured temperature range using equation [9]:

$$\sigma^* = \sigma_1 \frac{-(2\sigma_1 + \sigma_2/\sigma_2 - \sigma_1) + 2m_2 - (1.65/\pi)(\sigma_2 - \sigma_1/4\sigma_1 + 3\sigma_2) \times m_2^{10/3}}{(2\sigma_1 + \sigma_2/\sigma_2 - \sigma_1) - m_2 - (1.65/\pi)(3(\sigma_2 - \sigma_1)/4\sigma_1 + 3\sigma_2) \times m_2^{10/3}}, \quad (1)$$

where σ^* is the ionic conductivity of the sample, σ_1 is the conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, σ_2 is the conductivity of air and m_2 is the volumetric concentration of air.

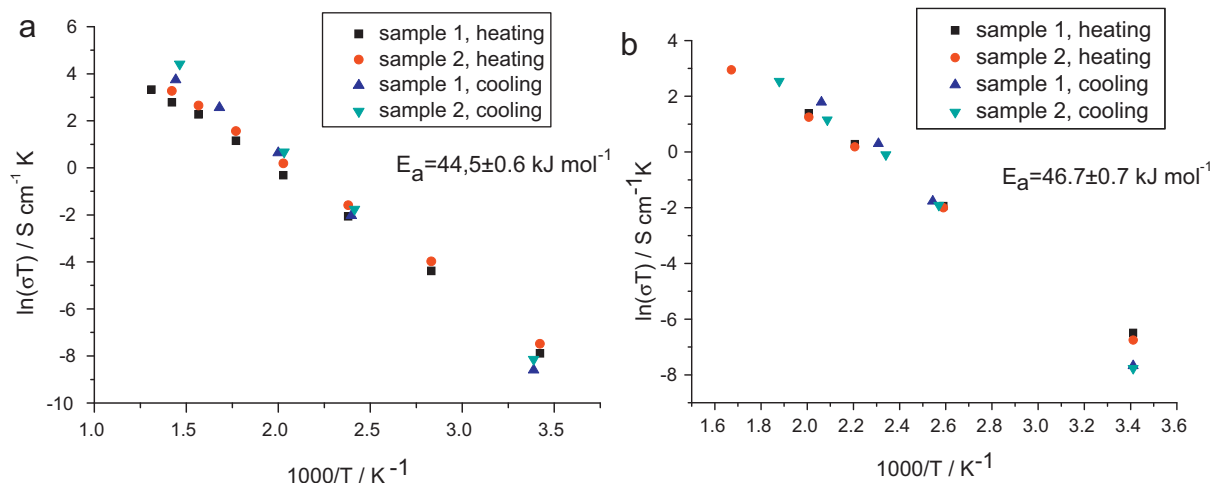


Fig. 6. Arrhenius plots for the total conductivity of the LLZ samples prepared by (a) the solid-state and (b) citrate–nitrate methods.

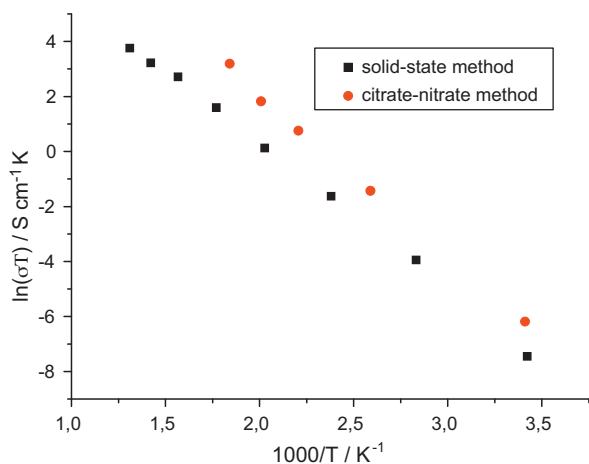


Fig. 7. A comparison of the total conductivity of the LLZ samples recalculated to 100% density.

Because the conductivity of air can be treated as zero, Eq. (1) may be presented as:

$$\sigma^* = \sigma_1 \frac{-2 + 2m_2 + (1.65/4\pi) \times m_2^{10/3}}{-2 - m_2 + (1.65 \times 3/4\pi) \times m_2^{10/3}}, \quad (2)$$

The recalculated total conductivity of LLZ synthesised by the citrate–nitrate method is higher than the conductivity of LLZ synthesised by the solid-state method for the entire measured temperature range (see Fig. 7).

The conductivity of LLZ synthesised by the citrate–nitrate method was $1.2 \times 10^{-2} \text{ S cm}^{-1}$ at 300 °C. Such values of the conductivity in combination with stability against lithium metal make

the tetragonal modification of LLZ a prospective material for use in high-temperature lithium batteries.

4. Conclusion

The samples of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ were synthesised by the solid-state and citrate–nitrate methods. It was shown that the citrate–nitrate method makes it possible to reduce the temperature and time required for the synthesis and yields a product with smaller particles. The total Li-ion conductivity of tetragonal LLZ synthesised by the citrate–nitrate method was $5.2 \times 10^{-6} \text{ S cm}^{-1}$ at 20 °C, which exceeds the conductivity of LLZ synthesised by the solid-state method ($1.3 \times 10^{-6} \text{ S cm}^{-1}$ at 20 °C). At 300 °C, the total Li-ion conductivity of LLZ samples fabricated by the citrate–nitrate method was $1.2 \times 10^{-2} \text{ S cm}^{-1}$.

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