

A new promising high temperature lithium battery solid electrolyte

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Abstract

Lithium lanthanoid silicates find importance as a solid electrolyte in high temperature lithium batteries in view of its high ionic conductivity at high temperatures. An first ever attempt is made to synthesis a new high temperature solid electrolyte viz., lithium samarium holmium silicate by sol–gel process and it has been characterized by thermal analysis (TGA–DTA), X-ray diffraction (XRD), infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). Lithium ion conductivity of $0.8087 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 25 °C was obtained and it increases with increasing temperature. For the first time a highest conductivity of $0.1095 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ was obtained at 850 °C which is high compared to other high temperature lithium battery solid electrolytes.

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1. Introduction

Development of solid-state lithium batteries with high-energy density and high reliability is strongly desired to replace the commercially available lithium ion secondary batteries using a conventional liquid electrolyte. Solid electrolytes have many advantages over liquid electrolytes in terms of design flexibility and miniaturization of electronic devices. The ionic conductivity of many available solid electrolytes is too low to be useful for high-energy power sources. Commercial development of a solid-state lithium battery relies on the successful development of a solid electrolyte with high ionic conductivity [1]. In the same manner research on high temperature lithium ion conducting solid electrolytes is also attracting attention in order to develop of high temperature lithium batteries.

Recently, there has been considerable interest in rare earth based solid electrolytes for their high ionic conductivities at higher temperatures. New classes of lithium ion conductors formulated by LiLnSiO_4 (Ln = rare earths)

prepared by solid-state reaction method were reported by Nakayama and Sakamoto [2] and Sato et al. [3,4]. They reported that these electrolytes exhibiting higher conductivities at high temperatures. They also reported that the conductivity of lithium lanthanoid silicates depend primarily on the crystal type, i.e. the compounds in the hexagonal system have much higher conductivity than the orthorhombic ones. The compounds with large lanthanoid ions, from La to Dy, belongs to hexagonal and those with the small ions compared with several lanthanoids are orthorhombic. Different structural types of Lithium lanthanoid silicates were reported by Blasse [5].

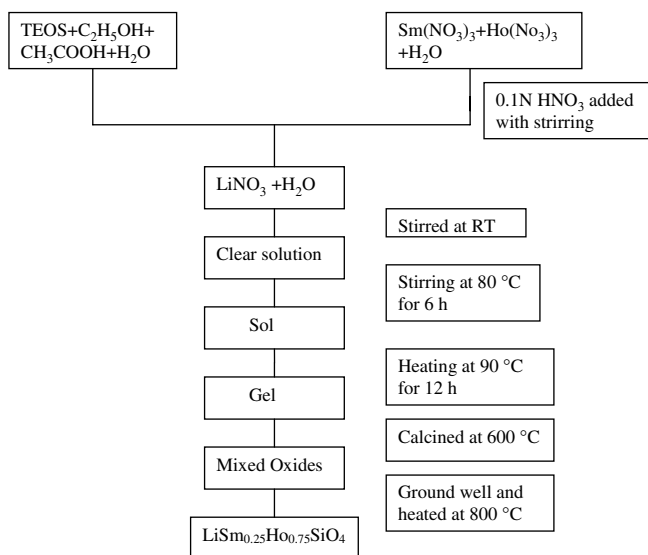
There has been much work published on the characterization of lithium ion conducting solid electrolytes at lower temperatures. However, a very little research has been focused on the characterization of lithium ion conducting rare earth based solid electrolytes at higher temperatures, and this study will be highly desirable from the application point of view especially in high temperature lithium batteries designed for military applications. This manuscript reports the synthesis of a new solid electrolyte $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ by sol–gel method, its characterization and ionic conductivity.

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2. Experimental

2.1. Powder synthesis

Lithium samarium holmium silicate ($\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$) was prepared by sol–gel method. In this method, stoichiometric amounts of lithium nitrate, samarium nitrate and holmium nitrate were dissolved in 0.1 N nitric acid. This was mixed with appropriate amounts of ethanol, acetic acid, tetraethoxysilane (TEOS) and water, stirred at room temperature till it becomes a clear solution. A clear sol was formed after stirring the mixture at 80 °C for about 6 h. The sol transformed to gel after heating at 90 °C for 12 h. The gel was calcined at 600 °C first to get mixed oxides. The resulting compound was ground well and pure $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ was obtained by calcining the powders at 800 °C for 24 h. The flow chart for the preparation of $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ is given below:



2.2. Sample characterization

Thermal decomposition behavior of the dried precursor was examined in air using STA 1500 TG/DTA analyzer from room temperature to 900 °C at 20 °C/min. The pure $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ sample obtained after calcining, was crushed into fine powder and spread in a die. A pressure around 4000 kg/cm² was applied to form pellets of 0.1 cm thickness and 1.5 cm diameter. These pellets are sintered at 800 °C for 24 h. X-ray diffraction analysis has been taken to confirm the formation of $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ by using X-ray diffractometer (JEOL-JDX 8030 X-ray diffractometer, $\lambda = 1.5406 \text{ \AA}$ using nickel filtered Cu $k\alpha$). FTIR spectra of the sample, prepared by sol–gel method, was recorded with Perkin–Elmer Paragon-500 FTIR spectrophotometer in the region 400–4000 cm^{−1}. SEM observations were carried out using Hitachi S-3000 H Scanning electron microscope. For impedance measurements the pellets are placed in between two discs made of gold-coated stainless steel and this set up was placed inside a muffle furnace. AC impedance measurements were made isothermally in the temperature range 25–850 °C. An impedance analyzer (Autolab PGstat 30) controlled by a computer was used to obtain the experimental data.

3. Results and discussion

3.1. Thermal analysis

To determine the formation temperature of the compound and the decomposition temperature of the organic components, $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ gels were subjected to thermal analysis and the result is shown in Fig. 1. From the figure it is observed that TG curve shows four regions. First region up to 101 °C is due to the evaporation of water; second region up to 295 °C is attributed to the decomposition of organics. Later are due to the

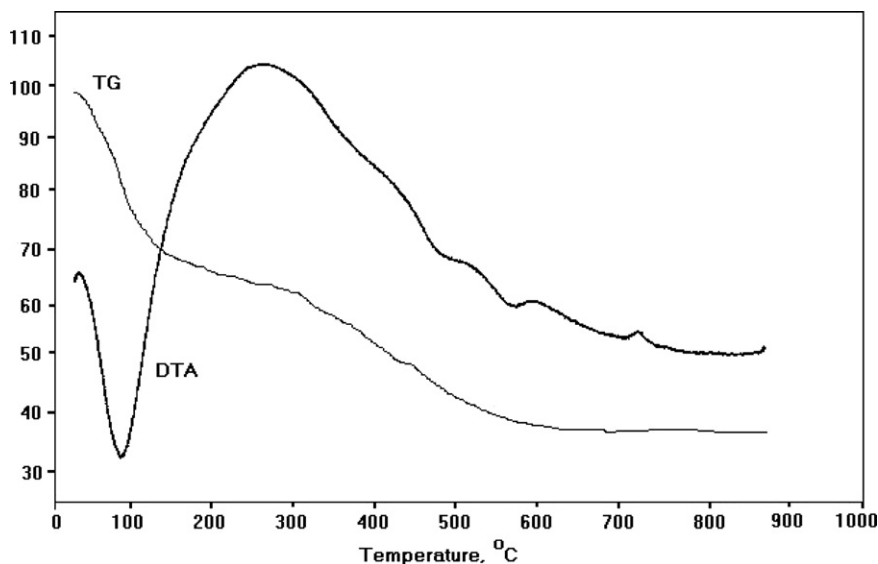


Fig. 1. TG/DTA for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$.

evaporation of nitrates and other components. From 574.99 °C, negligible weight loss is observed which indicates the formation temperature of this compound. DTA analysis of the precursor shows endothermic peaks at 83.26, 477.26, 562.11 and 742.55 °C. The peak at 83.26 °C is due to the removal of water whereas at other temperatures, at 477.26 °C and 562.11 °C the peaks are due to decomposition of TEOS and LiNO_3 . The peak at 742.55 °C is due to the crystallization of the compound.

3.2. X-ray diffraction

Fig. 2 shows the X-ray diffraction pattern of $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$. The diffraction pattern matched with that of hexagonal $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ in accordance with previous

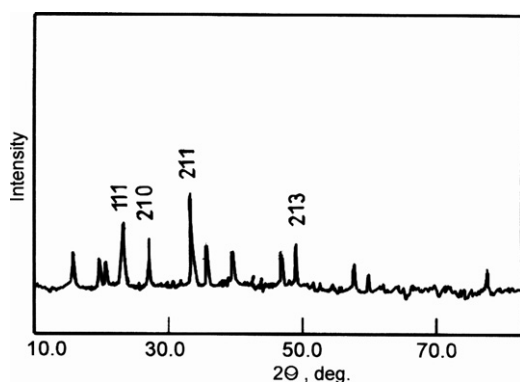


Fig. 2. XRD for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$.

reports [3–6]. The largest peak at $2\theta = 30^\circ$ (JCPDS corresponding to LiLaSiO_4) shifted towards higher angles viz. 32.2° with d spacing of 2.778 in the present case. This may be due to the presence of more holmium content than samarium. Another high intensity peak is obtained at 29.3° with d spacing of 3.046 is in well agreement with the reported values earlier for LiLnSiO_4 [4].

3.3. Infrared spectroscopy

Fig. 3a shows the FTIR spectra for the precursor (LiOH , $\text{Sm}(\text{NO}_3)_2$, $\text{Ho}(\text{NO}_3)_2$, and TEOS) material heated to 90 °C. From the figure, the broad bands in the regions of 3200–3400 and at 1630–1650 cm^{-1} may be attributed to stretching and bending vibrational modes of O–H of molecular water and the Si–OH stretching of surface silanol hydrogen bond to molecular water. The band at 1350–1475 cm^{-1} region corresponds to Sm–O, Ho–O asymmetric stretching vibration in SmO_3 and HoO_3 units. The band in the region of 910–925 cm^{-1} is assigned to Sm–O bond vibration of SmO_4 units. The broad band at 1100–990 and 750 cm^{-1} may be due to stretching mode of broken Si–O[−] bridges. The band at 475 cm^{-1} corresponds to the deformation mode of Si–O–Si [7].

Fig. 3b shows the FTIR spectra of the synthesized $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$. FTIR spectra showed the disappearance of a band at 1100 cm^{-1} and appearance of a band at 940–999 cm^{-1} , which is associated with the formation of a ring structure of SiO_4 tetrahedral [8] as well as the stretching frequency of Si–O–Sm–Ho and it is especially sig-

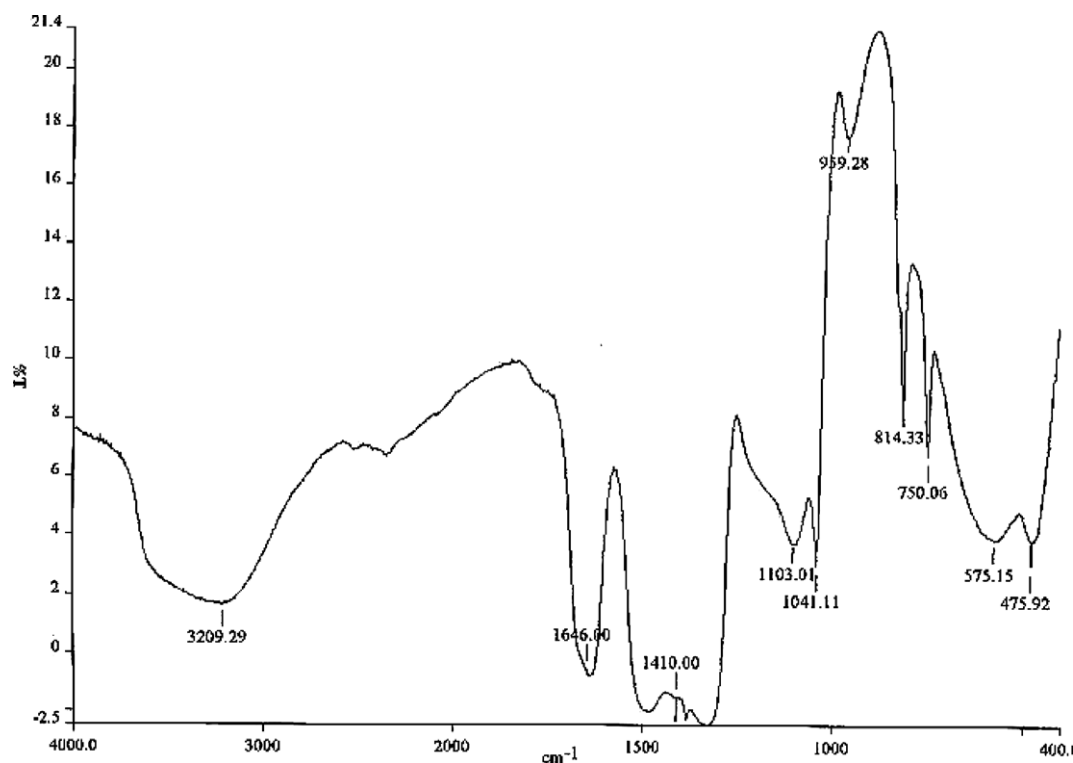


Fig. 3a. FTIR for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ (after heating at 90 °C).

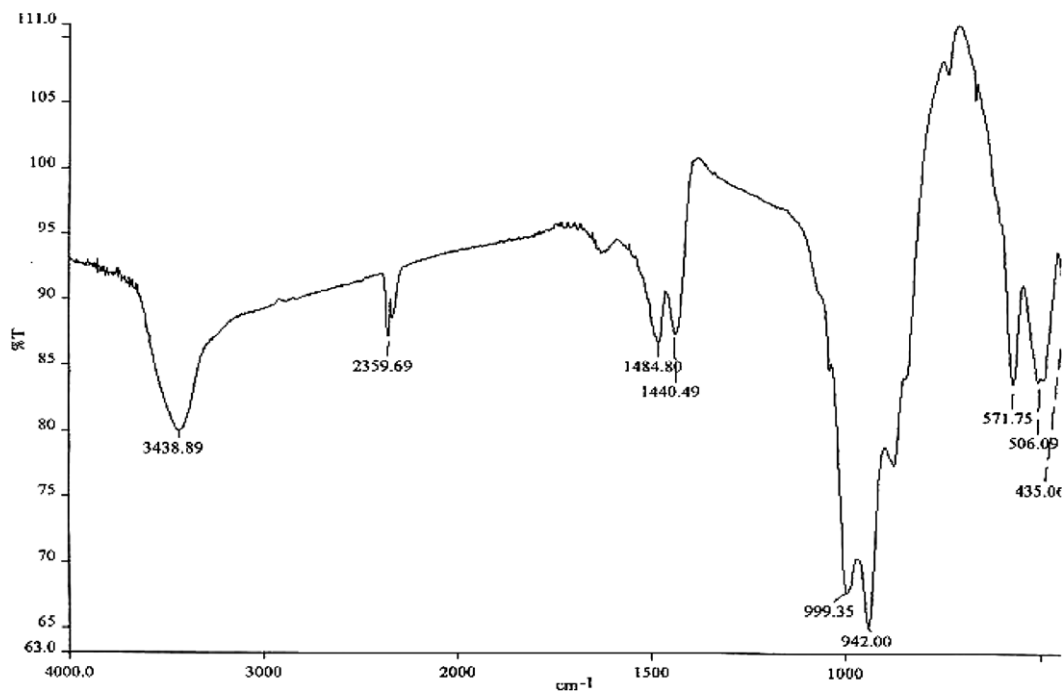


Fig. 3b. FTIR for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ (after heating at 800 °C).

nificant in crystalline phase. A band at $1440\text{--}1485\text{ cm}^{-1}$ is attributed to the formation of samarium–holmium silicate linkage. The crystalline phase formation is confirmed from XRD results for the sample.

3.4. SEM

SEM observation of the sample is given in Fig. 4. From SEM it is evident that the synthesized material displays uniform distribution of the crystals of $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$. It can also be seen from the surface topography that there are distinct grain boundaries between the particles. The particle size of the compound is around $5\text{ }\mu\text{m}$.

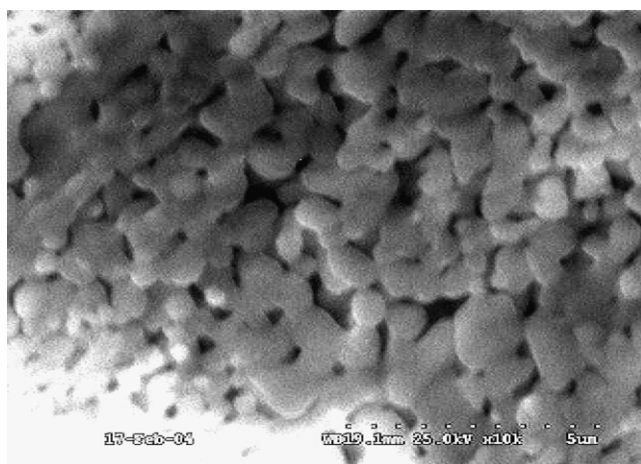


Fig. 4. SEM for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$.

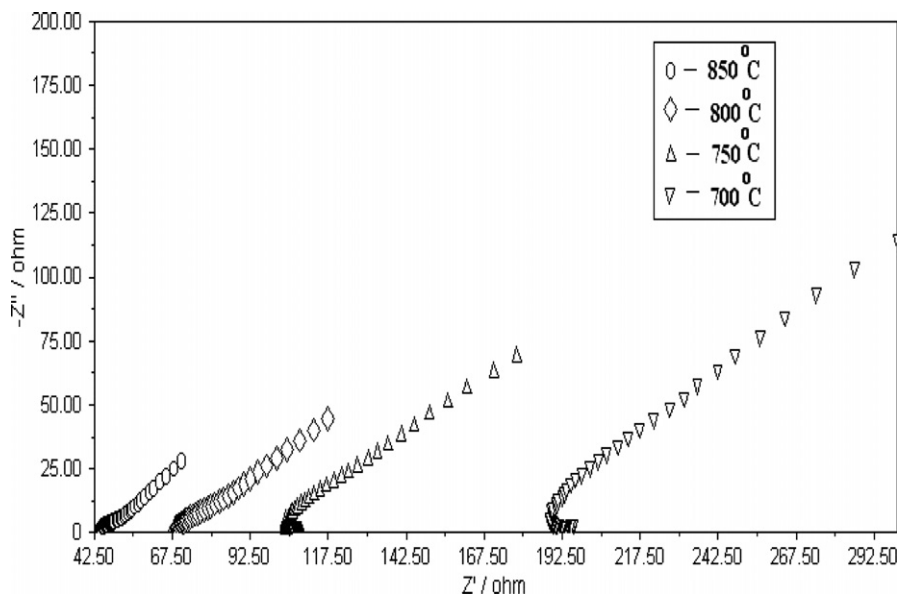
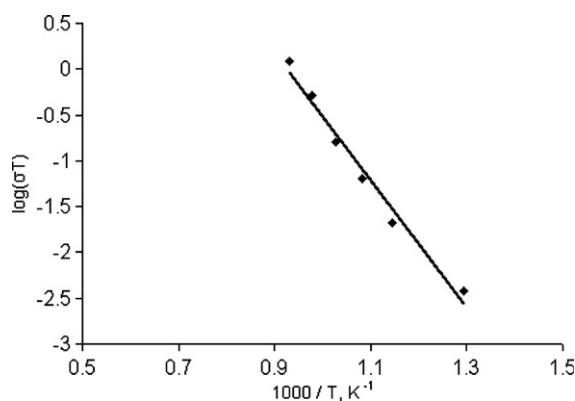
3.5. Impedance and conductivity analysis

3.5.1. Impedance

Impedance spectroscopy is a highly useful technique for studying the conductivity of the crystalline materials. Using this technique, one can measure the resistances due to grain interiors, grain boundaries and electrodes independently. From these data and from the knowledge of the sample dimensions, the bulk (or grain interior) and grain boundary conductivities can be estimated in a rather straightforward manner. Thus the synthesized sample is placed in between gold-coated SS plates and heated to different temperatures externally. The temperature is kept $\pm 5\text{ }^\circ\text{C}$ accuracy and the impedance spectra are recorded from 10^6 to 10^{-2} Hz with an AC amplitude of 5 mV using Autolab PGstat 30. From this, conductivity of the lithium samarium holmium silicate prepared by the sol–gel method was calculated. Fig. 5 shows the complex impedance diagrams of the sample at various temperatures. The impedance diagram at 700, 750, 800 and $850\text{ }^\circ\text{C}$ consists of one semicircle, followed by a straight line with an angle of 45° to the real axis. The semicircle in the high frequency region was attributed to the bulk of the grain, while the straight line in the low frequency region is attributed to the Warburg impedance, which may be due to the semi-infinite diffusion of charge carriers. Further, it is observed that as the temperature is increased the enhancement of conductivity is seen by the reduction in the diameter of the circular arcs. From the intercepts of the semicircles with the real axis at low frequencies, resistances are calculated.

3.5.2. Conductivity

The total resistances obtained in the present communication were obtained from the intercept of the semicircles

Fig. 5. Impedance spectroscopy for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$.Fig. 6. Temperature dependency of conductivity for $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$.

with the real axis in the low frequency range. The total ionic conductivity was obtained from these resistances at various temperatures. Conductivities obtained were parameterized by the Arrhenius equation:

$$\sigma = \sigma_0 \exp(-E_a/kT),$$

where σ , σ_0 are conductivity and pre-exponential factor E_a , k and T are activation energy, Boltzmann constant and absolute temperature, respectively. Fig. 6 shows the temperature dependency of conductivity value of the sample $\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$. It is observed that conductivity of $0.8087 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ at 25 °C was obtained, it increases with increasing temperature. The highest conductivity of $0.1095 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ was obtained at 850 °C, which is high compared to the conductivity of LiSmSiO_4 which is 10^{-6} at 430 °C [9] and Lanthanum silicate (10^{-3} at 727 °C) [10]. The activation energy estimated for this compound was 0.421 eV.

4. Conclusions

$\text{LiSm}_{0.25}\text{Ho}_{0.75}\text{SiO}_4$ compound was prepared by using sol–gel method in which a relatively less formation temperature of nearly 600 °C was needed. The advantages of this method are its simplicity and mild operating conditions. The resulting powder exhibited high ionic conductivities at temperatures above 600 °C. This compound exhibited higher conductivities compared to other high temperature lithium ion conductors. The experimental results indicate that lithium samarium holmium silicate is a good lithium ion conductor at higher temperatures which can be used as a solid electrolyte for high temperature lithium batteries used in military and space applications. This result is very promising one in the direction of searching materials with high lithium ion conductivity at high temperatures.

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