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# Synergic effect of $\text{CaI}_2$ and $\text{LiI}$ on ionic conductivity of solution-based synthesized $\text{Li}_7\text{P}_3\text{S}_{11}$ solid electrolyte†

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$\text{Li}_7\text{P}_3\text{S}_{11}$  doped with  $\text{CaX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{LiI}$  solid electrolytes were successfully prepared by liquid-phase synthesis using acetonitrile as the reaction medium. Their structure was investigated using XRD, Raman spectroscopy and SEM-EDS. The data obtained from complex impedance spectroscopy was analyzed to study the ionic conductivity and relaxation dynamics in the prepared samples. The XRD results suggested that a part of  $\text{CaX}_2$  and  $\text{LiI}$  incorporated into the structure of  $\text{Li}_7\text{P}_3\text{S}_{11}$ , while the remaining part existed at the grain boundary of the  $\text{Li}_7\text{P}_3\text{S}_{11}$  particle. The Raman peak positions of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  ions in samples  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2$  and  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  had shifted as compared to the  $\text{Li}_7\text{P}_3\text{S}_{11}$  sample, showing that  $\text{CaI}_2$  addition affected the vibration of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  ions. EDS results indicated that  $\text{CaI}_2$  and  $\text{LiI}$  were well dispersed in the prepared powder sample. The ionic conductivity at 25 °C of sample  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  reached a very high value of  $3.1 \text{ mS cm}^{-1}$  due to the improvement of Li-ion movement at the grain boundary and structural improvement upon  $\text{CaI}_2$  and  $\text{LiI}$  doping. This study encouraged the application of  $\text{Li}_7\text{P}_3\text{S}_{11}$  in all-solid-state Li-ion batteries.

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## 1. Introduction

Sulfide-based solid electrolytes (SE) have high potential for application in all-solid-state batteries because of their relatively high ionic conductivity and suitable mechanical properties compared with oxide-based and polymer-based SEs.<sup>1,2</sup>  $\text{Li}_7\text{P}_3\text{S}_{11}$ ,  $\text{Li}_{9.54}\text{Si}_{1.74}\text{P}_{1.44}\text{S}_{11.7}\text{Cl}_{0.3}$ ,  $\text{Li}_{5.35}\text{Ca}_{0.1}\text{PS}_{4.5}\text{Cl}_{1.55}$  and  $\text{Li}_{10.1}\text{P}_{2.95}\text{Sb}_{0.05}\text{S}_{12}\text{I}$  exhibited excellent ionic conductivities of about 17, 25, 10.2 and  $5.9 \text{ mS cm}^{-1}$  at 25 °C, respectively.<sup>3-6</sup> Among them,  $\text{Li}_7\text{P}_3\text{S}_{11}$  has been thoroughly studied since it was invented.<sup>7</sup>  $\text{Li}_7\text{P}_3\text{S}_{11}$  is usually prepared by solid-state reaction and achieves a highest ionic conductivity of about  $17 \text{ mS cm}^{-1}$  at 25 °C.<sup>8</sup> Researchers have studied the effects of many different substances such as  $\text{Li}_3\text{PO}_4$ ,  $\text{Li}_3\text{BO}_3$ ,  $\text{Li}_2\text{ZrO}_3$  and  $\text{P}_2\text{O}_5$  on the ionic conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$ .<sup>9-12</sup> Murakami *et al.* studied <sup>6/7</sup>Li and <sup>31</sup>P solid-state NMR to investigate the origin of high ionic conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$  and found that the significant motion fluctuation of the  $\text{P}_2\text{S}_7$  tetrahedral unit above 310 K facilitated the Li-ion movement, resulting in high

ionic conductivity.<sup>13</sup> Seino *et al.* found that  $\text{Li}_7\text{P}_3\text{S}_{11}$  glass ceramic with the crystallinity ranging from 50% to 80% reached its highest ionic conductivity.<sup>14</sup>

The liquid phase synthesis of  $\text{Li}_7\text{P}_3\text{S}_{11}$  has been recently introduced and takes the advantage of electrode composite preparation.<sup>15,16</sup> Dimethoxy ethane was the first solvent ever used to prepared  $\text{Li}_7\text{P}_3\text{S}_{11}$ .<sup>17</sup> Ethyl acetate was recently employed to synthesize  $\text{Li}_7\text{P}_3\text{S}_{11}$  which exhibited high ionic conductivity of  $1.05 \text{ mS cm}^{-1}$  at 25 °C.<sup>18</sup> Among of the solvents that has been employed in  $\text{Li}_7\text{P}_3\text{S}_{11}$ , acetonitrile (ACN) is the most common one because the prepared SEs exhibited relatively high ionic conductivity at 25 °C, ranging from 0.8 to  $1.2 \text{ mS cm}^{-1}$ .<sup>15,19,20</sup> The solvent-based synthesis of  $\text{Li}_7\text{P}_3\text{S}_{11}$  is complicated and could be described as dissolution-evaporation process. It was found that  $\text{Li}_2\text{S}$  reacts with  $\text{P}_2\text{S}_5$  in ACN to form soluble  $\text{Li}_4\text{P}_2\text{S}_7$  and  $\text{Li}_3\text{PS}_4$  precipitate at a molar ratio of 1 : 1. The residue obtained after solvent removal are  $\text{Li}_4\text{P}_2\text{S}_7 \cdot \text{ACN}$  and  $\text{Li}_3\text{PS}_4 \cdot \text{ACN}$ .  $\text{Li}_7\text{P}_3\text{S}_{11}$  was formed simultaneously with ACN removal from these phases during heat treatment at high temperature. There are many studies on how to increase the ionic conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$  produced by solid-phase reaction methods, such as using doping substances or creating defects in the crystal lattice.<sup>21-23</sup> However, there are still lack of the information about the method to improve the ionic conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$  prepared using liquid-phase synthesis. It was reported that  $\text{CaI}_2$  and  $\text{CaS}$  addition enhanced the conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$ .<sup>16,24</sup>  $\text{Li}_7\text{P}_3\text{S}_{11}$  prepared

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using a mixture of  $\text{Li}_2\text{S}$ ,  $\text{P}_2\text{S}_5$ , and excess elemental sulfur in a mixed solvent of acetonitrile, tetrahydrofuran, and ethanol also exhibited high ionic conductivity of about  $1.2 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ .<sup>25</sup>

In this study, the ionic conductivity of  $\text{Li}_7\text{P}_3\text{S}_{11}$  prepared using ACN was enhanced by  $\text{CaX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and LiI doping. The  $95\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2$  solid electrolyte exhibited the ionic conductivity of about  $1.0 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ . The

$90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  solid electrolyte showed high ionic conductivity of about  $3.1 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$ , which was comparable to those prepared by solid-state reaction. The data obtained from AC impedance spectroscopy was interpreted in terms of conductivity isotherms, dielectric constant and dielectric loss. It was found that  $\text{CaI}_2$  and LiI doping enhanced the Li-ion movement at grain boundary and  $\text{P}_2\text{S}_7^{4-}$  ion motion, thus improved ionic conductivity.

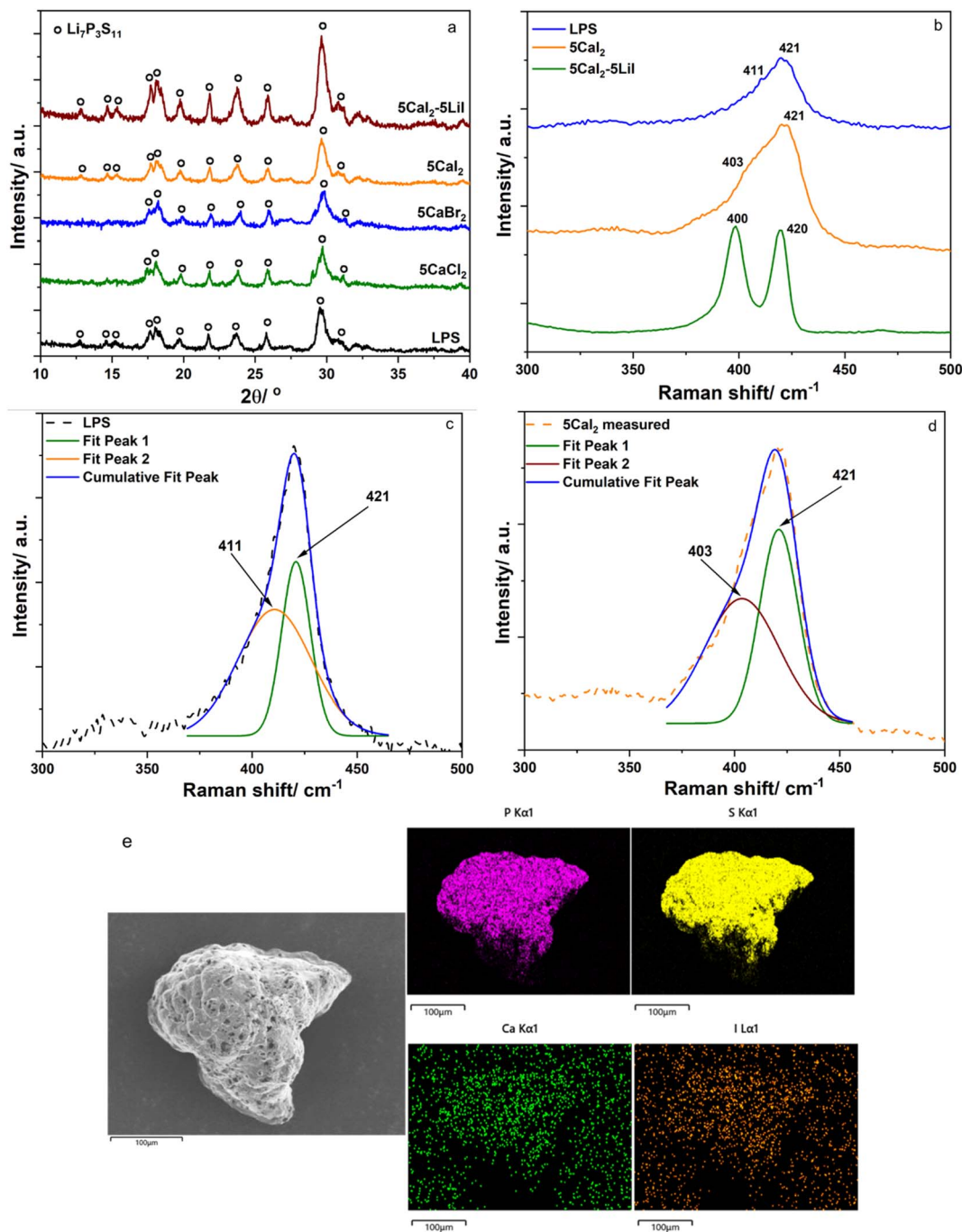


Fig. 1 Structural characterization of the prepared samples. (a) XRD patterns of  $\text{Li}_7\text{P}_3\text{S}_{11}$  (LPS),  $95\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaX}_2$  ( $5\text{CaX}_2$ ) and  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  ( $5\text{CaI}_2-5\text{LiI}$ ) solid electrolytes; (b) Raman spectra of LPS,  $5\text{CaI}_2$  and  $5\text{CaI}_2-5\text{LiI}$ ; (c and d) deconvolution of the main Raman peaks of LPS and  $5\text{CaI}_2$ , respectively; (e) SEM-EDS results of  $5\text{CaI}_2-5\text{LiI}$ .



## 2. Experimental

### Chemicals

$\text{Li}_2\text{S}$  (99.9%, Macklin),  $\text{P}_2\text{S}_5$  (99%, Macklin),  $\text{CaCl}_2$  (99.99%, Macklin),  $\text{CaBr}_2$  (99.99%, Aladin),  $\text{CaI}_2$  (99.999%, Macklin),  $\text{LiI}$  (99.999%, Macklin) and super dehydrated acetonitrile (Aldrich) were used as-received without any further treatment.

### Liquid-phase synthesis of $\text{Li}_7\text{P}_3\text{S}_{11}$

1.5 g of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  (7 : 3 in molar ratio) was weighted and put into a three-necked flask together with 40 ml of ACN. The mixture was stirred at 300 rpm and 50 °C for 24 h, the solvent was then evaporated at 80 °C under low pressure. The residue was carefully grounded using agate mortar prior to be heat treated at 270 °C for 2 h in Ar atmosphere to obtain  $\text{Li}_7\text{P}_3\text{S}_{11}$  solid electrolyte (hereafter denote as LPS).

### Liquid-phase synthesis of $95\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaX}_2$ (X = Cl, Br, I)

1.5 g of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  (7 : 3 in molar ratio) and appropriate amount of  $\text{CaX}_2$  to form  $95\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaX}_2$  (molar ratio) was put into a three-necked flask together with 40 ml of ACN. The mixture was stirred at 300 rpm and 50 °C for 24 h, the solvent was then evaporated at 80 °C under low pressure. The residue was carefully grounded using agate mortar prior to be heat treated at 270 °C for 2 h in Ar atmosphere to obtain  $95\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaX}_2$  solid electrolytes (hereafter denote as  $5\text{CaX}_2$ ).

### Liquid-phase synthesis of $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$

1.5 g of  $\text{Li}_2\text{S}$  and  $\text{P}_2\text{S}_5$  (7 : 3 in molar ratio), appropriate amount of  $\text{CaI}_2$  and  $\text{LiI}$  to form  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  (molar ratio) was put into a three-necked flask together with 40 ml of ACN. The mixture was stirred at 300 rpm and 50 °C for 24 h, the solvent was then evaporated at 80 °C under low pressure. The residue was carefully grounded using agate mortar prior to be heat treated at 270 °C for 2 h in Ar atmosphere to obtain  $90\text{Li}_7\text{P}_3\text{S}_{11}-5\text{CaI}_2-5\text{LiI}$  solid electrolyte (hereafter denote as  $5\text{CaI}_2-5\text{LiI}$ ).

### Structural characterization

The structure of the prepared samples was characterized with X-ray diffraction (XRD; X8, Bruker), Raman spectroscopy (Horiba LabRam HR spectrometer, 532 nm) and SEM (S4800, Hitachi) and EDS (ULTIM MAX, Oxford Instrument).

The samples were prepared in an Ar-filled glove box. The prepared sample was loaded into an air-tide sample holder for characterization.

### AC electrochemical impedance spectroscopy

The electrical conductivity measurement was performed on a pellet prepared by uniaxially cold pressing approximately 100 mg of the powder at a pressure of 510 MPa as reported previously.<sup>26</sup> The alternating-current impedance spectroscopy measurement was carried out using a potentiostat (PGSTAT302N, Autolab, Herisau, Switzerland) from 10 MHz to 10 Hz. Since  $5\text{CaI}_2-5\text{LiI}$  exhibited high ionic conductivity at room temperature, a pellet with thickness of about 4.2 mm was prepared to get accurate data.

## 3. Results and discussion

Fig. 1a showed the XRD patterns of LPS,  $5\text{CaX}_2$  and  $5\text{CaI}_2-5\text{LiI}$  solid electrolytes. The patterns of all samples could be assigned to  $\text{Li}_7\text{P}_3\text{S}_{11}$  crystal phase.<sup>7,27</sup> No peaks of  $\text{CaX}_2$  and  $\text{LiI}$  was detected. The position of the most intense peak in the doped samples was almost similar to that of LPS indicating that only a small amount of  $\text{CaX}_2$  incorporated to the crystal structure of  $\text{Li}_7\text{P}_3\text{S}_{11}$ . It was also reported that the full doping amount of  $\text{CaI}_2$  to  $\text{Li}_7\text{P}_3\text{S}_{11}$  was about 3 mol%.<sup>16</sup> Ujiie *et al.* reported that  $\text{LiX}$  (X = F, Cl, Br, I) dissolved into LPS crystal structure at less than 10% molar ratio.<sup>27</sup> Hikima *et al.* found that  $\text{CaS}$  and  $\text{CaI}_2$  mainly remained at the grain boundary of  $\text{Li}_7\text{P}_3\text{S}_{11}$ .<sup>24</sup> Thus, the patterns in Fig. 1a suggested that a part of  $\text{CaX}_2$  and  $\text{LiI}$  incorporated into the structure of LPS, while the remained part existed at the grain boundary of the LPS particle. Fig. 1b showed the Raman spectra of LPS,  $5\text{CaI}_2$  and  $5\text{CaI}_2-5\text{LiI}$ . Fig. 1c and

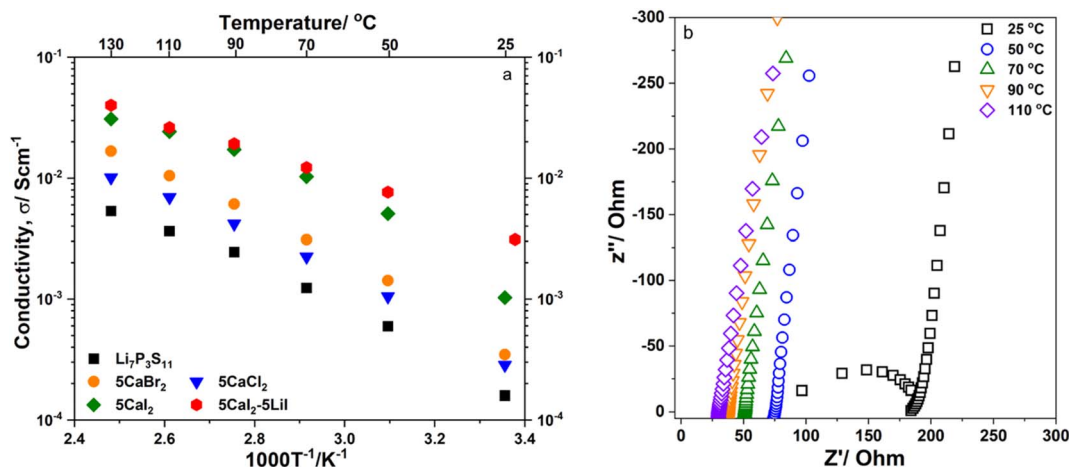


Fig. 2 (a) Temperature dependence of  $\text{Li}_7\text{P}_3\text{S}_{11}$ ,  $5\text{CaX}_2$  (X = Cl, Br, I) and  $5\text{CaI}_2-5\text{LiI}$  solid electrolytes; (b) electrochemical impedance spectra of the prepared  $5\text{CaI}_2-5\text{LiI}$  solid electrolyte.



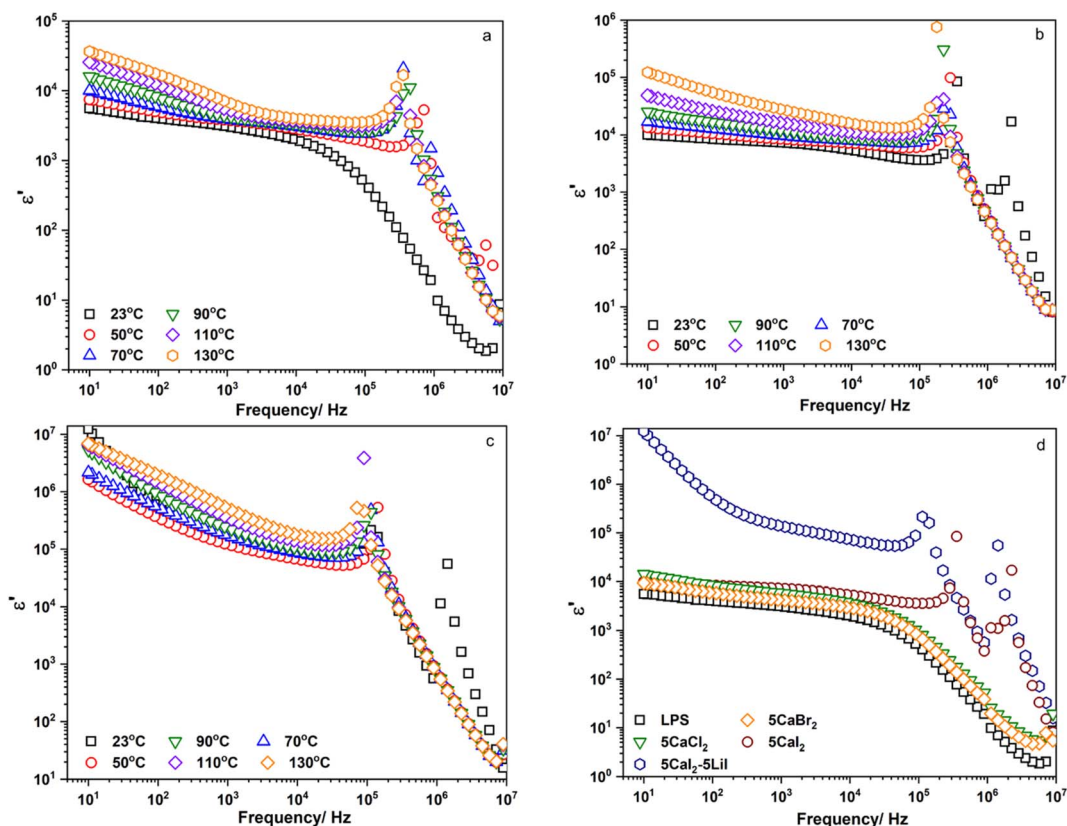
**Table 1** DC activation energy  $E_{a,DC}$ , activation energy  $E_{a,m}$  of ion migration at grain boundary, and characteristic time  $\tau_{0,m}$  of ion migration at grain boundary

	LPS	5CaCl <sub>2</sub>	5CaBr <sub>2</sub>	5CaI <sub>2</sub>	5CaI <sub>2</sub> -5LiI
$E_{a,DC}/\text{kJ mol}^{-1}$	36	37	36	30	25
$E_{a,m}/\text{kJ mol}^{-1}$	37	38	37	31	19
$\tau_{0,m}/\text{s}$	$5.0 \times 10^{-10}$	$3.4 \times 10^{-10}$	$4.4 \times 10^{-10}$	$6.3 \times 10^{-9}$	$4.1 \times 10^{-7}$

d showed the deconvolution spectra of LPS and 5CaI<sub>2</sub>, respectively. The spectrum of LPS had two peaks at 421 and 411  $\text{cm}^{-1}$ , which corresponded to the vibration of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$ .<sup>28</sup> The spectrum of 5CaI<sub>2</sub> also revealed two peaks of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  located at 421 and 403  $\text{cm}^{-1}$ . The spectrum of 5CaI<sub>2</sub>-5LiI showed two peaks located at 420 and 400  $\text{cm}^{-1}$ , which could be assigned to the local structure unit of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  in  $\text{Li}_7\text{P}_3\text{S}_{11}$ , respectively. The peak positions of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  ions in samples 5CaI<sub>2</sub> and 5CaI<sub>2</sub>-5LiI had shifted as compared to the LPS sample showing that CaI<sub>2</sub> addition affected the vibration of  $\text{PS}_4^{3-}$  and  $\text{P}_2\text{S}_7^{4-}$  ions. The results from Raman spectra demonstrated that a portion of CaI<sub>2</sub> incorporated into the crystal structure of LPS. SEM-EDS results for 5CaI<sub>2</sub>-5LiI is shown in Fig. 1e. The SEs are in the form of particles with a size of several tens of micrometers. EDS results indicated that CaI<sub>2</sub> and LiI were well dispersed in the prepared powder sample. It can be reasonably concluded that  $\text{Ca}^{2+}$  and  $\text{I}^-$  were doped in the

$\text{Li}_7\text{P}_3\text{S}_{11}$  structure based on the experimental results: the disappearance of the peak corresponding to CaI<sub>2</sub> and LiI in the XRD results, the peak shift in the Raman spectrum, Ca and I are also dispersed in the particles as shown in the EDS results.

The temperature dependence of the ionic conductivity of LPS, 5CaX<sub>2</sub> and 5CaI<sub>2</sub>-5LiI solid electrolytes were illustrated in Fig. 2a. The electrochemical impedance spectra of 5CaI<sub>2</sub>-5LiI, which were employed to calculate ionic conductivity, were illustrated in Fig. 2b. Those of LPS and 5CaI<sub>2</sub> were shown in Fig. S1 (ESI).<sup>†</sup> The ionic conductivity at 25 °C of LPS, 5CaCl<sub>2</sub>, 5CaBr<sub>2</sub>, 5CaI<sub>2</sub> and 5CaI<sub>2</sub>-5LiI were 0.15, 0.19, 0.25, 1.0 and 3.1 mS, respectively. At 70 °C, the ionic conductivity of all the samples increased and reached the value of 1.05, 2.0, 2.2, 10.1 and 13 mS for LPS, 5CaCl<sub>2</sub>, 5CaBr<sub>2</sub>, 5CaI<sub>2</sub> and 5CaI<sub>2</sub>-5LiI, respectively. It could be seen that  $\log_{10}(\sigma)$  satisfied an almost linear dependence on inversed temperature and therefore followed Arrhenius equation  $\sigma = \sigma_0 \exp(-E_{a,DC}/(k_B T))$ . The



**Fig. 3** Frequency dependence of the real part of dielectric constant,  $\epsilon'$ , of (a) LPS, (b) 5CaI<sub>2</sub>, (c) 5CaI<sub>2</sub>-5LiI measured at different temperature and (d) frequency dependence of  $\epsilon'$  of LPS, 5CaCl<sub>2</sub>, 5CaBr<sub>2</sub>, 5CaI<sub>2</sub>, 5CaI<sub>2</sub>-5LiI measured at room temperature.



activation energy  $E_{a,DC}$  was then calculated and shown in Table 1. The activation energy  $E_{a,DC}$  of LPS, 5CaI<sub>2</sub>, 5CaCl<sub>2</sub>, 5CaBr<sub>2</sub> and 5CaI<sub>2</sub>-5LiI were 36, 37, 36, 30 and 25 kJ mol<sup>-1</sup>, respectively. The results showed that CaI<sub>2</sub> and LiI addition greatly improved the ionic conductivity and activation energy of LPS.

The study of dielectric properties provides information on electrical energy decay in materials with alternating electric fields. The real part of the dielectric constant,  $\epsilon'$ , reflects the amount of energy stored in the form of polarization when an electric field is applied.<sup>29</sup> The real part of the permittivity,  $\epsilon'$ , was calculated using the following equation:

$$\epsilon' = -\frac{Z''}{\omega C_0(Z'^2 + Z''^2)}$$

where  $C_0 = \epsilon_0(A/d)$  is the free space capacitance of the cell,  $\epsilon_0$  is the permittivity of the free space ( $8.854 \times 10^{-12}$  F m<sup>-1</sup>), and  $A$  and  $d$  are the surface area and thickness, respectively, of the sample pellet.

Fig. 3 showed the frequency dependence of the real part of dielectric constant,  $\epsilon'$ , of (a) LPS, (b) 5CaI<sub>2</sub>, (c) 5CaI<sub>2</sub>-5LiI measured at different temperature and (d) frequency dependence of  $\epsilon'$  of LPS, 5CaCl<sub>2</sub>, 5CaBr<sub>2</sub>, 5CaI<sub>2</sub>, 5CaI<sub>2</sub>-5LiI measured at room temperature. The observed upturn in all plots at lower frequencies could be attributed to the electrode-electrolyte interface polarization. This is because the accumulation of

charged ions near the electrode leads to the formation of space charge layer, which in turn block the electric field and enhance electrical polarization. As frequency increased, the dielectric constant decreased. This phenomenon is a typical property of ionic conducting materials.<sup>30</sup> An increase in  $\epsilon'$  with an increase in temperature was observed at low and intermediate frequency region in all the samples suggesting that charge carrier movement at grain boundary was thermally activated (Fig. 3 and S2†). The plots of LPS, 5CaCl<sub>2</sub> and 5CaBr<sub>2</sub> at room temperature continuously decreased in intermediate and high frequency region; however, the plots of 5CaI<sub>2</sub> and 5CaI<sub>2</sub>-5LiI at room temperature exhibited a maxima at  $10^5$ - $10^6$  Hz (Fig. 3d). The maxima were observed at  $10^5$ - $10^6$  Hz in all the plots at 50 °C or above (Fig. 3 and S1†). Those observation suggested that CaI<sub>2</sub> and LiI addition enhanced dielectric properties of Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub>. This observation was in agreement with Raman spectra (Fig. 1b) and ionic conductivity at room temperature of the prepared samples (Fig. 2).

Fig. 4a-c showed the frequency dependence of the loss factor,  $\tan \delta$ , of LPS, 5CaI<sub>2</sub> and 5CaI<sub>2</sub>-5LiI, respectively. The plot at room temperature of LPS showed two peaks at low and high frequency, which could be attributed to ion migration at grain boundary and bulk (Fig. 4a). As temperature increased, two peaks appeared at low frequency region. The one at lower frequency was assigned to electrode polarization. The peak at

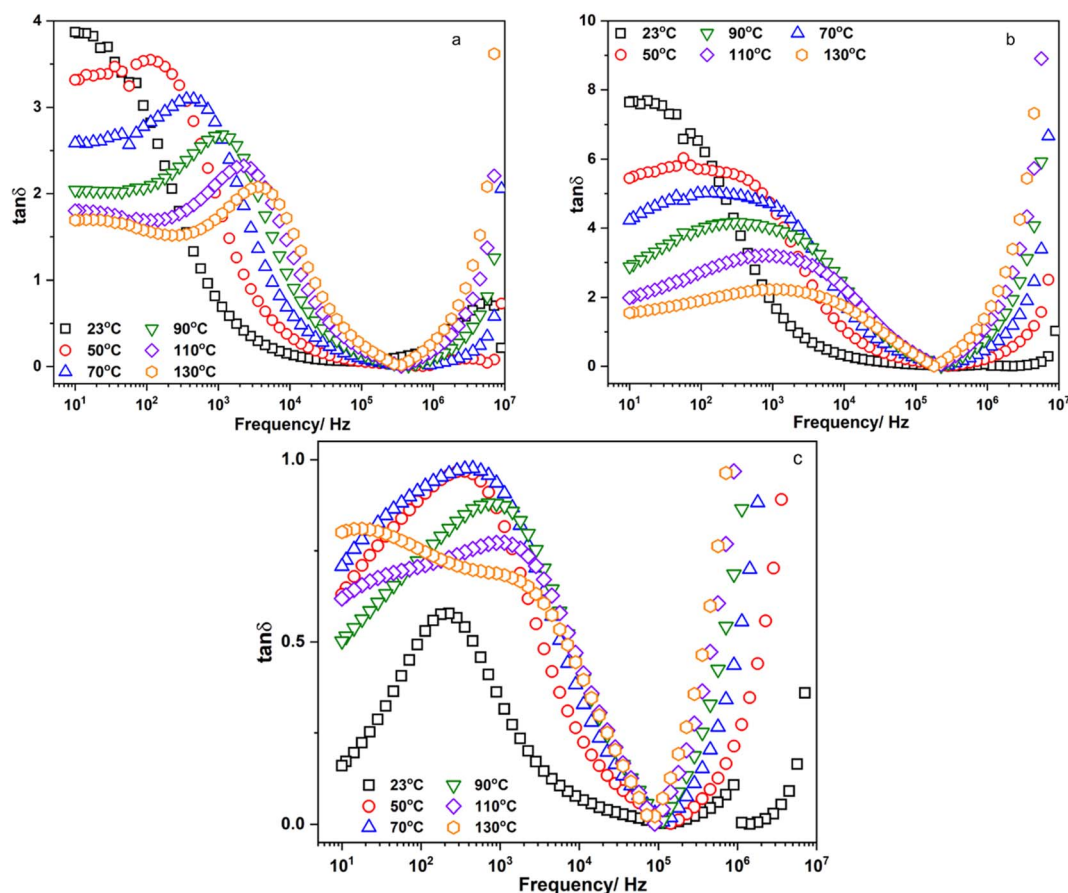


Fig. 4 Frequency dependence of the loss factor,  $\tan \delta$ , of (a) LPS, (b) 5CaI<sub>2</sub> and (c) 5CaI<sub>2</sub>-5LiI.



higher frequency shifted toward high frequency as temperature increased and could be attributed to grain boundary migration. The migration energy  $E_{a,m}$  of the  $\text{Li}^+$  ion moving at grain boundary could be obtained from the temperature dependence of the peak position at low frequency in  $\tan \delta$ . Temperature dependence of the inverse relaxation time ( $\tau_m^{-1} = F_{\max}$ ) was plotted, and the migration characteristic time  $\tau_{0,m}$  was then obtained by numerically fitting the data using the Arrhenius equation:  $\tau_m = \tau_{0,m} \exp(-E_{a,m}/(k_B T))$ . The obtained  $E_{a,m}$  and  $\tau_{0,m}$  were illustrated in Table 1. The migration activation energy at grain boundary  $E_{a,m}$  of the prepared samples were similar to DC activation energy  $E_{a,DC}$ , suggesting that charge carrier moving at grain boundary was the critical process in those samples. The characteristic migration time of LPS,  $5\text{CaCl}_2$  and  $5\text{CaBr}_2$  were  $5.0 \times 10^{-10}$ ,  $3.4 \times 10^{-10}$  and  $4.4 \times 10^{-10}$  s, respectively. The characteristic migration time of  $5\text{CaI}_2$  and  $5\text{CaI}_2-5\text{LiI}$  were  $6.3 \times 10^{-9}$  and  $4.1 \times 10^{-7}$  s, respectively. Therefore, the charge carrier movement at grain boundary was enhanced by  $\text{CaI}_2$  and  $\text{LiI}$  addition; it changed from short range diffusion in LPS to long range diffusion in  $5\text{CaI}_2$  and  $5\text{CaI}_2-5\text{LiI}$ . This phenomenon was also consistent with the article by Tu *et al.*, which reported the influence of  $\text{LiI}$  doping on the impedance at the grain boundary of  $\text{Li}_2\text{S}-\text{AlI}_3$  solid solution.<sup>31</sup>

## 4. Conclusion

$\text{Li}_7\text{P}_3\text{S}_{11}$  solid electrolytes doped with  $\text{CaX}_2$  ( $X = \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{LiI}$  were successfully prepared by liquid-phase synthesis using ACN as reaction medium. Results from XRD, Raman spectroscopy and SEM-EDS proved that  $\text{CaX}_2$  and  $\text{LiI}$  incorporated into the crystal structure of  $\text{Li}_7\text{P}_3\text{S}_{11}$ . Results from AC electrochemical impedance spectroscopy showed that  $\text{CaI}_2$  and  $\text{LiI}$  addition enhanced dielectric properties of  $\text{Li}_7\text{P}_3\text{S}_{11}$ . In addition, the charge carrier movement at grain boundary changed from short range diffusion in LPS to long range diffusion in  $5\text{CaI}_2$  and  $5\text{CaI}_2-5\text{LiI}$ . As a result, very high ionic conductivity of  $3.1 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$  was obtained.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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