A family of air-stable chalcogenide solid electrolytes in Li₂BMQ₄ (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems

Huican Mao[1, 2#], Xiang Zhu[2#], Guangmao Li[3#], Jie Pang[2], Junfeng Hao[2], Liqi Wang[2], Hailong Yu[2], Youguo Shi[2], Fan Wu[2*], Shilie Pan[3*], Ruijuan Xiao[2*], Hong Li[2*], Liquan Chen[2]

1. Department of Energy Storage Science and Engineering, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

2. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, 100190, Beijing, China.

3. Research Center for Crystal Materials, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, China.

E-mail: fwu@iphy.ac.cn, slpan@ms.xjb.ac.cn, rjxiao@iphy.ac.cn, hli@iphy.ac.cn

Abstract

Combining high-throughput first-principles calculations and experimental measurements, we have identified a novel family of fast lithium-ion chalcogenide conductors in Li_2BMQ_4 (2114, B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems. Our calculations demonstrate that most of the thermodynamically and kinetically stable sulfides and selenides in this new system exhibit ultralow Li^+ ion migration activation energy (0.16 eV ~ 0.56 eV) and considerable bandgaps varying between ~ 2 eV and 3.5 eV. We have successfully synthesized Li_2BaSnS_4 and Li_2SrSiS_4, and they exhibit excellent moisture stability through H_2S gas measurements. Electrochemical impedance measurements indicate 2114 systems show the typical features of solid ionic conductors, with a room-temperature Li^+ conductivity close to 5×10^{-4} mS/cm aligning with our molecular dynamics simulations. Furthermore, we have theoretically investigated the substitution of Cl^- at S^{2-} site. The doped compounds display significantly higher conductivity, with an increase of about three orders of magnitude (up to a maximum of 0.72 mS/cm) compared to the undoped compounds. These findings offer valuable insights for the further exploration of potential chalcogenide solid electrolyte materials with robust air stability and enhanced ionic conductivity for practical applications in lithium-ion batteries.

Introduction

In the race to decarbonize the global economy, all-solid-state battery (ASSB) technology is emerging as one of the most promising solutions to address the energy/power density and safety problems associated with combustible liquid electrolytes in lithium-ion batteries (LIBs) [1-6]. Solid electrolytes (SEs) with fast ionic transport, outstanding deformability and improved air stability are critical components in the development of next-generation ASSBs [7-9]. Despite significant research efforts, only a limited number of inorganic materials out of tens of thousands of known inorganic materials for LIBs, such as oxide-based SEs ($Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$[10], $Li_{6.55}La_3Zr_2Ga_{0.15}O_{12}$[11], $Li_{0.34}La_{0.51}TiO_{2.94}$ [12] etc.), sulfide-based SEs ($Li_{10}GeP_2S_{12}$[13], $Li_7P_3S_{11}$[14], Li_3PS_4 [15], Li_6PS_5Cl [16], Li_4SnS_4 [17] etc.) and halide-based SEs (Li_3InCl_6 [18] etc.), have been identified as fast ionic conductors. However, these above fast ionic conductors still suffer from various challenges, such as inflexibility and expensive large-scale production of oxides, moisture sensitivity and poor compatibility with cathode materials for sulfides, and vulnerability to moisture and low oxidation voltage for halides [19]. Among them, air stability could be a common issue for oxide-, sulfide- and halide-based SEs [20-23]. For example, when oxide-based SEs are exposed to humid air, the sluggish exchange between Li^+ and H^+ could form $LiOH$ and Li_2CO_3, increasing interfacial resistance [24, 25]. For Halide-based SEs, such as Li_3InCl_6, it is easy to absorb water, and first becomes a crystalline hydrate, then partially decomposes to $InCl_3$, $LiCl$ and In_2O_3 [26]. Furthermore, except for the reduction of ionic conductivity and hydrolysis evolution, sulfide-based SEs are prone to release toxic gas H_2S and result in structure/performance degradation [27-29], which severely limits the practical application of chalcogenide-based ASSBs.

Although sulfide-based SEs suffer from the most deadly and well-known drawback of poor air stability, they have been recognized as one of the most promising SEs due to their exceptional superionic conductivity and excellent deformability [13, 30, 31]. To enhance the air stability of sulfide-based SEs, a few promising strategies were employed including partial substitution of P/S by softer acids/O, and designing new

materials with softer acids as central cations [20-23] based on the hard and soft acids and bases theory (HSAB). For example, Xu et al. synthesized $Li_{6.25}PS_4O_{1.25}Cl_{0.75}$ by partial oxygen substitution at both S and Cl sites, achieving high stability toward moist air [32]. The substitution of P with softer acid Sb in $Li_{10}GeP_2S_{12}$ electrolyte system leads to the formation of robust bond Sb-S, which exhibits an effective suppression for H_2S gas generation [29]. In 2012, Kaib et al first synthesized a novel fast ionic conductor Li_4SnS_4, which shows good moisture stability [33].

While elemental substitution is an effective approach to improve air stability of sulfide SEs, partial substitution of P/S with softer acids/O may cause irreversible structural degradation or the reduction of ionic conductivity [29, 32]. Based on HSAB theory, complete substitution of P with softer acids (e.g., Sn, Sb, Ge) may provide the ideal configuration for enhanced significantly air stability. After decades of research, so far, only Li-Sn/Sb-S system demonstrating superior air stability has been discovered as the new materials of sulfide-based SEs with softer acids as central cations [28, 33, 34]. Hence, further investigations into novel compositions/structures of sulfide SEs with outstanding air stability and ionic conductivity are required to diversify the range of sulfides SEs and facilitate the development of next-generation high-performance, safe and sustainable sulfide-based ASSBs.

In this work, we combine materials database with bond valence (BV) and density functional theory (DFT) calculations to build up the high-throughput screening platform for searching for promising chalcogenide-based SEs. Based on this high-throughput calculations, we find a novel family of air-stable fast lithium-ion chalcogenide conductors in Li_2BMQ_4 (2114, B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems, which possess ultralow Li^+ migration energy barrier (0.16 ~ 0.56 eV) and considerable bandgap between ~2.0 and 3.5 eV for sulfides and selenides (**Table S2**). The experimentally synthesized Li_2BaSnS_4 and Li_2SrSiS_4 display exceptional air stability by total H_2S experiment and a promising room-temperature ionic conductivity around $5×10^{-4}$ mS/cm by impedance spectroscopy measurements, which aligns with our calculations. More importantly, the introduction of Li vacancy by substituting S^{2-} with Cl^- could enhance ionic conductivity by three orders of

magnitude based on first-principles molecular dynamics (FPMD) simulations.

Results and Discussion

Fig.1 The schematic diagram of crystal structures in Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) system. (a) The crystal structure of Li_2BMQ_4 with a 2D Li-Q layer is plotted in the blue dashed rectangle. Some of Li_2BMQ_4 structures are obtained from the substitution of Li at Ag site in Ag_2BMQ_4 systems. **(b)** The 2D layer is composed of the linking LiQ_4 units by sharing corners. **(c)** The BQ_8 dodecahedra connects to each other by edge-sharing MQ_4/corner-sharing BQ_8 units.

Crystal Structure

We first obtain the potential lithium conductors Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems (**Fig.1**) by high-throughput screening platform combining BV and DFT calculations. The majority of 2114 compounds crystallize in the $I\bar{4}2m$ space group as shown in **Figs.1a-c**, and their specific atomic positions can be found in **Table S1**. For these structures, distorted LiQ_4 tetrahedra with

two different Q-Li-Q bond angles are interconnected by sharing corners (**Fig.1b**), resulting in the formation of two-dimensional (2D) layers. These layers are further bonded with segregated MQ_4 units, ultimately creating a three-dimensional (3D) tunnel structure within which the B cations are positioned. The BQ_8 dodecahedron, featuring two types of similar bond lengths of B-Q, could be visualized as the combination of two interpenetrating tetrahedra. When viewed along the a-axis, the structure reveals that the BQ_8 dodecahedra are stacked up by edge-sharing MQ_4/corner-sharing BQ_8 units.

In order to check the thermodynamic and kinetic stability of Li_2BMQ_4, we evaluated their decomposition reaction energies and phonon spectra as shown in **Table S2** and **Fig.S2**. Combining calculated decomposition energies (with positive/marginally-negative value), phonon spectra (with the absence of imaginary frequency modes) and previous experimental reports (some of 2114 compounds have been synthesized and used as promising optical materials) [35-37], we have observed that the mostly Li_2BMQ_4 compounds exhibit thermodynamic and kinetic stability in the $I\bar{4}2m$ space group. Based on this, we will further conduct detailed analysis of moisture stability, electronic structures and ionic transport properties for these stable 2114 compounds.

Fig.2 The moisture stability of multiple sulfide solid electrolytes including Li₃PS₄, Li₆PS₅Cl, Li₂BaSnS₄ and Li₂SrSiS₄. (a) The calculated hydrolysis reaction energies of four sulfides. **(b)** The total H_2S generation amount of four sulfides as a function of exposure time. **(c)** The generation rate of H_2S of the four sulfides, i.e., the first order derivative of curves in **Fig.2b**.

Assessing Air Stability

As is widely recognized that the significant hurdle in the large-scale production of sulfide SEs is their poor stability against moisture in the air, hence it is crucial to evaluate the moisture stability of the novel 2114 chalcogenide systems. We firstly perform thermodynamic analyses and focus on hydrolysis reactions of generating H_2S/H_2Se to examine the moisture stability of all sulfides and selenides. The calculation scheme for possibly representative hydrolysis reactions and reaction energy are detailed in **Table S3**. The positive reaction energy indicates that almost all sulfides and selenides are stable under humid air, which is consistent with the qualitative results reported in

previous experiments (some of 2114 compounds are regarded as promising optical materials) [35-37].

Aiming to further quantitatively assess the moisture stability of the 2114 systems as SE materials, we take Li_2BaSnS_4 and Li_2SrSiS_4 as examples and compare them with common sulfide SEs, namely Li_3PS_4 and Li_6PS_5Cl. As shown in **Fig.2a**, Li_2BaSnS_4 and Li_2SrSiS_4 exhibits good moisture stability based on positive reaction energy, while Li_3PS_4 and Li_6PS_5Cl, having highly thermodynamically favorable reaction, demonstrate poor moisture stability. Furthermore, we successfully synthesized Li_2BaSnS_4 and Li_2SrSiS_4 by high temperature solid-state method [35-37], and characterize their structures by X-ray diffraction. Their crystal structures crystallized in the $I\overline{4}2m$ space group (**Fig.S3**), corresponding to previous experiments [35-37]. In addition, the total generation amount and rate of H_2S are measured by gas-detection experiments [38] for these four sulfide SEs. By the end of the 300-minute exposure period, the cumulative H_2S generation for Li_3PS_4, Li_6PS_5Cl, Li_2BaSnS_4 and Li_2SrSiS_4 are 94.949, 57.085, 15.080 and 26.938 cm^3/g respectively, in the order of L_3PS_4 **>** Li_6PS_5Cl **>** Li_2SrSiS_4 **>** Li_2BaSnS_4. The comparative analysis demonstrates that 2114 chalcogenide SEs exhibit greater moisture stability (even comparable to Li_4SnS_4 [38]) than Li_3PS_4 and Li_6PS_5Cl, suggesting the introduction of elemental combinations Sr^{2+}-Si^{4+}/Ba^{2+}-Sn^{4+} inhibits the generation of H_2S for 2114 SEs. This finding aligns with the empirical HSAB theory and calculations reported by Zhu and Mo [39], indicating that Sr^{2+}-Si^{4+}/Ba^{2+}-Sn^{4+} are more resistant to moisture than P^{5+}. By calculating the first order derivative of total generation amount of H_2S to time, the H_2S generation rate can be obtained, as shown in **Fig.2c**. The H_2S generation rate of Li_3PS_4, Li_6PS_5Cl and Li_2BaSnS_4 increases and reaches the maximum at exposure time $\approx$25 min, 5 min, 2 min respectively and then continuously decreases. In contrast, the H_2S generation rate of Li_2SrSiS_4 start to rise only within the first $\approx$30 min, followed by a slow increase continuing until reaching the maximum at time $\approx$120 min, indicating that it begins to react with water only after 30 minutes. In general, Li_2BaSnS_4 and Li_2SrSiS_4 show the most robust moisture stability among these four sulfide SEs, implying the air stability

feature within the 2114 systems.

Fig.3 The calculated Li$^+$ migration kinetic properties of Li$_2$BMQ$_4$ systems. (a) The continuous Li$^+$ migration channels determined by BV method, (b) the energy barrier simulated by NEB method for Li$_2$CaSiS$_4$. (c) The formation energy of Li$^+$ vacancies and the activation energy of Li ions for 2114 compounds thermodynamically and kinetically stabilized in the I$\overline{4}$2m space group.

Ion Transport Mechanisms and Performance

Currently, we have confirmed the thermodynamic, kinetic and moisture stability of these sulfides and selenides for 2114 systems, the subsequent focus will be on investigating their lithium-ion diffusion properties. Li$_2$CaSiS$_4$ is selected for detailed research by combing BV method and DFT simulation in addition with the Nudged Elastic Band (NEB) method. First, we use quasi-empirical BV method to acquire the possible ionic transportation channels and interstitial sites, where the iso-surfaces of potential energies (marked by yellow belts in **Fig.3a**) are regarded as the continuous network for Li$^+$ ion transport. An interstitial 8h site (0, 0.5, z=0.5) related to Li$^+$

migration is signed with blue dotted circles, which is located in the continuous Li^+ migration pathway and connected to mobile Li^+ ions between two adjacent Li-S layers along c axis. The favorite Li^+ ion migration pathway suggests one-dimensional transportation behavior should be expected in these compounds and the fast ionic conducting channel is along the c-axis of the crystal structure.

In order to understand the kinetic properties revealed by the BV method, NEB calculations are carried out to obtain activation energy for the Li^+ ion hopping pathway. For Li_2CaSiS_4, the calculated activation energy E_a with a value of 0.25 eV and corresponding barrier shape is shown in **Fig.3b**. In addition, we also calculate the activation energy for all other 2114 compounds stabilized in the $I\bar{4}2m$ space group using NEB method. As shown in **Fig.3c**, the calculated activation energies of all sulfide- and selenide-based compounds are between 0.16 eV and 0.56 eV, which are considerably comparable to the generally lithium superior conductors such as $Li_{10}GeP_2S_{12}$ (LGPS, 0.24 eV) [13], garnet $Li_7La_3Zr_2O_{12}$ (0.31 eV) [40], whereas all 2114 oxides have a higher activation energy ~ 1.0 eV. With an ultralow energy barrier (0.16 ~ 0.56 eV), these 2114 sulfides and selenides are highly expected to be prominent fast ionic conductors. To achieve high ionic conductivity, a low activation energy and a high concentration of mobile ion carriers (such as vacancies or interstitials) are essential [41]. Furthermore, we have assessed the formation energy of Li vacancies in all thermodynamically and kinetically stable 2114 compounds, revealing a range of 2.7 to 4.8 eV, which is much higher than activation energies. This implies that the elevated Li vacancy formation energy may impede the overall Li^+ conductivity, which will be discussed in the following section.

Fig.4 The ionic conductivity of lithium ion for 2114 compounds. (a) The calculated Arrhenius plots of Li^+ diffusivity D as a function of temperature T in Li_2CaSiS_4, Li_2SrSiS_4, Li_2BaSnS_4, $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$ (Li_2CaSiS_4-Cl) and $Li_{1.75}SrSiS_{3.75}Cl_{0.25}$ (Li_2SrSiS_4-Cl). **(b)** The experimentally measured impedance plots of the conductivity at room temperature 300 K for Li_2BaSnS_4 and Li_2SrSiS_4. The FPMD-estimated/measured activation energies E_a and the ionic conductivity at room temperature σ_T are listed in the Table. The 'Cal.' and 'Exp.' represent FPMD Calculations and Experiments.

To characterize the total Li^+ conductivity of 2114 compounds, First-principles molecular dynamics simulations at different temperatures T (1300 K ~ 1750 K) are carried out to obtain the Arrhenius relation of Li^+ diffusivity as a function of T, which can be used to estimate the total activation energy and ionic conductivity. We take Li_2CaSiS_4, Li_2BaSnS_4 and Li_2SrSiS_4 as examples. The linear MSD-Δt dependence (**Fig.S5**) is utilized to apply the Einstein relation for inferring the diffusivity, while the Arrhenius equation is employed for linearly fitting log(D) against 1/T to derive the total activation energy and ionic conductivity. As shown in **Fig.4**, the fitted activation energy E_a and extrapolated Li^+ conductivity σ_T at 300 K is about 0.5 eV and 10^{-5}~10^{-4} mS/cm for Li_2CaSiS_4, Li_2BaSnS_4 and Li_2SrSiS_4 respectively. Noting that the determined activation energy by FPMD calculations for Li_2CaSiS_4 and Li_2SrSiS_4 is approximately

0.2 eV higher than that obtained from NEB calculations, whereas the activation energy of Li_2BaSnS_4 determined by FPMD and NEB calculations is roughly similar (**Fig.3** and **Fig.4**).

It is generally recognized that low activation energy and an abundant presence of mobile ion carriers, such as vacancies or interstitials, are crucial to achieve high ionic conductivity [41]. FPMD simulations provide a dynamic and temperature-dependent view of the activation barrier, capturing the full complexity of diffusion events, i.e., mobile ion carriers and mobile ion hops [42]. In contrast, the NEB calculations offer a more straightforward and computationally efficient approach to determine the activation barrier by directly searching for the minimum energy path on the potential energy surface [43]. For Li_2CaSiS_4 and Li_2SrSiS_4, the higher Li^+ vacancy formation energy (~3.3 eV in **Fig.3c**) makes it difficult to generate Li vacancy carrier, resulting in a lower concentration of vacancy carriers and reduced ionic conductivity in these two systems. Consequently, the activation energy barrier evaluated by FPMD calculations is about 0.2 eV lower than that calculated by NEB calculations. In addition, typical FPMD simulations are usually limited to a system size of a few hundred atoms and a total physical time duration of tens to hundreds of picoseconds, resulting in a limited number of diffusion events. As a result, the estimated ionic conductivity σ_T at 300 K usually has an error bound within one order of magnitude [42]. This also explains why the FPMD-extrapolated ionic conductivity of Li_2SrSiS_4 (with formation energy ~3.3 eV and NEB-activation energy 0.34 eV) is about an order of magnitude lower than that of Li_2BaSnS_4 (with formation energy ~3.4 eV and NEB-activation energy 0.56 eV). The improved simulation approach will be discussed in the 'Discussion' section for our future work.

In order to validate the Li^+ conductivity capability of the 2114 compounds, we conduct electrochemical impedance spectroscopy measurements on Li_2BaSnS_4 and Li_2SrSiS_4 at room temperature, as shown in **Fig.4b**. The Nyquist plots show the typical features of solid fast ionic conductors, with one semi-circle and a Warburg-like tail, which is ascribed to the contribution of bulk/grain boundary resistance and the solid-state diffusion of the lithium-ion in electrode respectively. According to the total

resistance obtained from the intercept on real axis or the intersection between semi-circle and Warburg-like tail, the total ionic conductivity at room temperature is estimated to be $\sim 5 \times 10^{-4}$ mS/cm at room temperature for both compounds, slightly higher or similar to the values obtained from FPMD calculations.

By comparing the results from FPMD calculations, NEB calculations and Electrochemical impedance spectroscopy measurements, we find that lithium vacancy formation energy plays a crucial role in determining the total Li^+ conductivity. Aiming to mitigate the inhibition of Li vacancy formation, we adopt element doping with low-valence anions to intentionally create lithium vacancies. By substituting S^{2-} with Cl^- in Li_2CaSiS_4 and Li_2SrSiS_4, we form $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$ and $Li_{1.75}SrSiS_{3.75}Cl_{0.25}$, and perform FPMD simulations from 900 K to 1350 K (**Fig.4**). Combining Einstein and Arrhenius relations, we deduce that the activation energy of Cl-doped compounds has been reduced by approximately 0.2 eV, resulting in a three-order-of-magnitude increase of Li^+ conductivity at room temperature, reaching 0.016~0.72 mS/cm. This suggests that the introduction of lithium vacancies via element doping is a highly effective approach for significantly enhancing Li^+ conductivity. The absence of experimental measurements for $Li_2CaSiS_{3.75}Cl_{0.25}$ and $Li_2SrSiS_{3.75}Cl_{0.25}$ will be discussed below.

Discussion

To the best of our knowledge, commonly used solid electrolytes in lithium-ion batteries, such as $Li_{10}GeP_2S_{12}$, $Li_7La_3Zr_2O_{12}$, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$, were typically derived from element doping on their respective parent materials, including Li_4GeS_4-Li_3PS_4, $Li_5La_3M_2O_{12}$ (M = Nb, Ta) and $LiTi_2(PO_4)_3$ [45]. These doped SEs usually exhibit an enhanced Li^+ conductivity that is about 1-3 orders of magnitude higher than their parent materials. This is primarily attributed to the broadening ion migration channels and/or increasing the concentration of mobile ions (from element doping). Moreover, improved synthesis techniques such as solid-state reactions, sol-gel methods, etc. could further augment the ionic conductivity by mitigating grain-boundary resistance. The Li_2BMQ_4 series exhibit the typical features of solid fast ionic conductors,

with considerable Li$^+$ ionic conductivity ~10^{-4} mS/cm at room temperature. Therefore, further tailoring of the compositions by appropriate chemical substitutions and modifying synthesizing methods are crucial for the potential application of this new 2114 family of solid electrolytes in practical lithium-ion batteries. In addition to the substitution of Cl$^-$ at S^{2-} site, Al^{3+}, Ga^{3+} and As^{5+} ions can also be used to replace B and M sites respectively to enhance lithium-ion conductivity as shown in **Fig.S6** of Supplementary Materials.

In this work, we aim to present the novel crystal structure of 2114 chalcogenide SEs that exhibit air stability and potentially can be used as fast ionic conductors, which have been confirmed by Electrochemical impedance spectroscopy measurements. The FPMD simulations on configurations Li$_{1.75}$CaSiS$_{3.75}$Cl$_{0.25}$ and Li$_{1.75}$SrSiS$_{3.75}$Cl$_{0.25}$ are intended to illustrate the similarity of 2114 systems to other common fast ionic conductors, which have potential for further improvement in ionic conductivity through approaches such as element doping. For configurations Li$_{1.75}$CaSiS$_{3.75}$Cl$_{0.25}$ and Li$_{1.75}$SrSiS$_{3.75}$Cl$_{0.25}$, the selection of doping elements and concentrations was currently determined through a small range of element screening and concentration testing. Beyond employing Cl element for anion doping, the possibility of cation doping and even simultaneous co-doping of both anions and cations could also be explored in the future. Managing multiple doping scenarios requires not only careful selection of element types and their concentration distributions but also consideration of element occupancy, including lattice and interstitial sites (such as 8h site), to modulate parameters such as the size of ion transport channels and the concentration of charge carriers. To achieve above goals, the simulation approach that integrates first-principles calculations with classical molecular dynamics, leveraging accelerated machine learning techniques [44], needs to be used next. It is important to note that while enhancing ionic conductivity through element doping, attention must also be paid to the air stability of the materials to achieve solid electrolytes with excellent overall performance. All in all, more efforts in experiments and calculations for the exploration of higher ionic conductivity in Li$_2$BMQ$_4$ systems are demanded.

Conclusion

In summary, the Li$_2$BMQ$_4$ series (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) represent a novel class of solid-state lithium-ion conductors characterized by a unique crystal structure (I$\bar{4}$2m space group). With low diffusion activation energy, robust moisture stability, considerable bandgaps and ionic conductivity, this new family closely rivals promising fast ionic conductors. Leveraging past successes in regulating chemical compositions and improving synthesis methods for fast ionic conductors, similar adjustment approaches are anticipated to be applied to the Li$_2$BMQ$_4$ systems to achieve even higher ionic conductivity. The new family of sulfide- and selenide-based solid electrolyte shows significant potential in simultaneously possessing exceptional moisture stability and excellent ionic conductivity.

Experimental Section

Calculational Methods

In this work, we constructed crystal structures (including lattice constants, atomic coordinate and Wyckoff positions) of Li_2BMQ_4 (2114, B = Ca, Sr and Ba; M = Si, Ge and Sn; and Q = O, S and Se) compounds based on references [35-37, 46]. Some of Li_2BMQ_4 structures were obtained from the substitution of Li at Ag site in Ag_2BMQ_4 systems. All the calculations were carried out using Vienna Ab-initio Simulation Package (VASP) code based on density functional theory [47, 48]. In the standard DFT calculations, the exchange-correlation potential is described via the generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) form [49]. The calculations employed 4×4×3 k-mesh grid and energy cutoff of 520 eV. Ions were relaxed in the optimization with the energy and force convergence criterion of 10^{-5} eV and 0.01 eV/Å.

Calculational Methods--Electronic structures

In the electronic band structure calculations, Perdew-Burke-Ernzerhof (PBE) is well-known to underestimate the bandgaps of semiconductors and insulators, whereas the modified Becke-Johnson (MBJ) exchange potential [50, 51] are known to evaluate bandgaps with an accuracy similar to hybrid functional or many-body perturbation (GW) methods, but computationally less expensive. Therefore, the MBJ exchange potential was adopted for density of states (DOS) calculations, in order to yield more accurate bandgaps.

Calculational Methods—thermodynamic/kinetic/air stability

To identify the thermodynamic stability of most 2114 sulfides and selenides, we calculated the total energy of 2114 compounds and corresponding decomposition products in Table S2. The positive/negative decomposition reaction energy indicates it is possible to be thermodynamically stable/unstable and can/cannot be synthesized for this compound. To confirm the kinetic stability of 2114 compounds that were not

reported experimentally, the phonon dispersion curves were calculated using the phonopy package [52] based on 2×2×2 supercell containing 128 atoms and 2×2×2 k-mesh. The kinetic stability was evaluated by the existence or absence of imaginary frequency modes in the phonon dispersion curves. In addition, we also calculated the hydrolysis reaction energies of most 2114 compounds to assess their air stability.

Calculational Methods—Li-ion diffusion

We used the quasiempirical bond-valence (BV) method [53, 54] to obtain the possible ionic transportation channels and interstitial sites of these new structures. Based on the favorite Li-ion migration channel, the migration barrier of Li ion was acquired by the nudged elastic band (NEB) method as implemented in VASP [43] based on 2×2×2 supercell. Furthermore, the first-principles molecular dynamics (FPMD) was also carried out on the 2×2×2 supercell with the temperature of 900 −1750 K, lasting for 55000 steps with a time step of 1 fs. The first 6 ps are used to equilibrate the system at the temperature, and the mean-squared displacement (MSD) was calculated from the last 50 ps. Based on FPMD tests with different doping elements and doping concentrations in **Fig.S6**, we selected Cl-doped $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$ and $Li_{1.75}SrSiS_{3.75}Cl_{0.25}$ for FPMD calculations at different temperatures. For the Cl-doping configurations in Li_2CaSiS_4 and Li_2SrSiS_4, we employed the enumlib program [55] to eliminate duplicate configurations, thus identifying the irreducible configurations. Through energy calculations conducted on these configurations, we ultimately pinpointed the most stable configuration with the lowest energy.

Experimental Methods – Synthesis and Characterization

The Li_2BaSnS_4 and Li_2SrSiS_4 compounds were synthesized by solid-state reaction method described in reference [35-37, 46]. Powder X-ray diffraction (XRD) patterns were collected on a Bruker D2 X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å) at room temperature by covering the scattering angle 2θ range 10-70 degrees. The XRD patterns identify the crystal structure of these two compounds with $I\bar{4}2m$ space group, in consistent with what was reported in reference [35-37].

Experimental Methods –Ionic conductivity and Air stability measurements

The Li_2BaSnS_4 and Li_2SrSiS_4 powder was pressed into a pellet (diameter 10 mm; thickness 0.5 mm). The ionic conductivity of the prepared sulfides was measured by the electrochemical impedance spectroscopy (EIS) method. EIS measurements were conducted in the frequency range of 1 Hz to 8 MHz and the amplitude of 50 mV by a Zennium Pro Electrochemical Workstation. In addition, the moisture stability was measured by the specially designed equipment described in reference [39].

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

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Supplementary Materials for "A family of air-stable chalcogenide solid electrolytes in Li₂BMQ₄ (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems"

Huican Mao[1, 2#], Xiang Zhu[2#], Guangmao Li[3#], Jie Pang[2], Junfeng Hao[2], Liqi Wang[2], Hailong Yu[2], Youguo Shi[2], Fan Wu[2*], Shilie Pan[3*], Ruijuan Xiao[2*], Hong Li[2*], Liquan Chen[2]

1. Department of Energy Storage Science and Engineering, School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

2. Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, 100190, Beijing, China.

3. Research Center for Crystal Materials, Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, China.

To explore the thermodynamic stability of Li_2BMQ_4 (2114, B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems, decomposition reaction energies are carried out for all sulfides and selenides. The decomposition reaction equations and decomposition reaction energies are demonstrated in **Table S2**, in which the positive/small negative value of decomposition energies indicate that these compounds can exist as stable/metastable (or be stabilized by entropic effects) structures, verifying the thermodynamic stability of these new structures. We also assessed the kinetic stability by phonon spectrum calculations for all 2114 compounds except for those experimentally reported compounds marked by small white circles inside larger brown filled shapes (diamond, triangle and pentagon) and small white circles inside larger yellow filled shapes in **Fig.S1**, which represent the compounds that have been synthesized experimentally with $I\overline{4}2m$ space group and other space groups ($P6_3cm$, $P3_121$, etc) respectively. The absence of imaginary frequency modes in the Brillouin zone (**Fig.S2**) confirms the kinetic stability of these compounds, denoted by brown filled shapes. In addition, those kinetically unstable structures, with imaginary frequency modes in phonon dispersion, are marked by white unfilled shapes. In the Li_2BMQ_4 systems, only five of them (Li_2SrSiO_4, Li_2BaSiO_4, Li_2CaSnO_4, Li_2CaSnS_4 and $Li_2CaSnSe_4$) are not crystallized/stable in $I\overline{4}2m$ space group, which may be attributed to the special combinations between smallest Ca^{2+} and largest Sn^{4+} ionic radii, smallest $Si^{4+}/O^{2-}$and larger Sr^{2+} and Ba^{2+} ionic radii within the same main group, further leading to the deviation from the structural tolerance factors with $I\overline{4}2m$ symmetry [1].

Table S1 Take Li_2SrSiS_4 as an example to show the lattice constants, atomic coordinates, equivalent isotropic displacement parameters for Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) systems with $I\bar{4}2m$ space group.

Li_2SrSiS_4	Space group		a	c
	$I\bar{4}2m$		6.5133	7.8170
Atoms	Wyckoff positions	x	y	z
Li	4d	0.00	0.50	0.25
Sr	2a	0.00	0.00	0.00
Si	2b	0.00	0.00	0.50
S	8i	0.1905	0.1905	0.3429

Table S2 The crystal structures, experimental synthesis, phonon spectra, bandgap (obtained from the density of states in **Fig.S4**) and activation energies for all Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) compounds. The positive/negative decomposition reaction energy (E_d) indicates it is possible to be thermodynamically stable/unstable and can/cannot be synthesized for this compound. Although the decomposition reaction energies of several Ca-based compounds are negative, the relatively small negative values imply that they can exist as a metastable structure or be stabilized by entropic effects. The absence/existence of imaginary frequency modes in the phonon dispersion curves represents that the phonon spectrum is 'Stable/Unstable'. The calculations of decomposition reaction energy (phonon spectrum) are performed for 2114 sulfides and selenides (for those compounds that are not synthesized experimentally).

Compounds	Space group	Synthesized experimentally	Phonon spectrum	E_d (meV/ atom)	Bandgap (eV)	Activation energy (eV)
Li_2CaSiO_4	$I\bar{4}2m$	Yes[2]	--	--	7.1	0.99
Li_2CaSiS_4	$I\bar{4}2m$	No	Stable	-1.7	3.3	0.25

$Li_2CaSiSe_4$	$I\bar{4}2m$	No	Stable	1.7	2.3	0.16
Li_2CaGeO_4	$I\bar{4}2m$	Yes[3]	--	--	5.7	1.06
Li_2CaGeS_4	$I\bar{4}2m$	No	Stable	-12.7	2.9	0.25
$Li_2CaGeSe_4$	$I\bar{4}2m$	No	Stable	-2.5	1.7	0.17
Li_2CaSnO_4	Uncertain	Yes[4]	--	--	--	--
Li_2CaSnS_4	--	No	Unstable	--	--	--
$Li_2CaSnSe_4$	--	No	Unstable	--	--	--
Li_2SrSiO_4	$P3_121$	Yes[2]	--	--	--	--
Li_2SrSiS_4	$I\bar{4}2m$	Yes[5]	--	40.0	3.5	0.34
$Li_2SrSiSe_4$	$I\bar{4}2m$	No	Stable	41.9	2.4	0.24
Li_2SrGeO_4	$I\bar{4}2m$	Yes[6]	--	--	5.6	1.04
Li_2SrGeS_4	$I\bar{4}2m$	Yes[7]	--	27.2	3.0	0.37
$Li_2SrGeSe_4$	$I\bar{4}2m$	No	Stable	41.4	1.8	0.25
Li_2SrSnO_4	$I\bar{4}2m$	No	Stable	--	4.0	1.18
Li_2SrSnS_4	$I\bar{4}2m$	Yes[7]	--	33.4	3.1	0.45
$Li_2SrSnSe_4$	$I\bar{4}2m$	No	Stable	29.5	2.1	0.32
Li_2BaSiO_4	$P6_3cm$	Yes[2]	--	--	--	--
Li_2BaSiS_4	$I\bar{4}2m$	No	Stable	26.5	3.5	0.44
$Li_2BaSiSe_4$	$I\bar{4}2m$	Yes[8]	--	38.7	2.5	0.33
Li_2BaGeO_4	$I\bar{4}2m$	No	Stable	--	5.2	1.09
Li_2BaGeS_4	$I\bar{4}2m$	Yes[9]	--	21.7	3.1	0.47
$Li_2BaGeSe_4$	$I\bar{4}2m$	Yes[9]	--	42.4	2.0	0.36
Li_2BaSnO_4	$I\bar{4}2m$	No	Stable	--	3.8	1.27
Li_2BaSnS_4	$I\bar{4}2m$	Yes[9]	--	43.9	3.2	0.56
$Li_2BaSnSe_4$	$I\bar{4}2m$	Yes[9]	--	42.3	2.1	0.43

Decomposition reaction equations:

$Li_2CaSiS_4 = CaS + Li_2SiS_3$

$Li_2CaGeS_4 = CaS + Li_2GeS_3$

$Li_2CaGeSe_4 = CaSe + GeSe_2 + Li_2Se$

2 Li$_2$SrSiS$_4$ = Li$_2$S + Li$_2$SiS$_3$ + Sr$_2$SiS$_4$

2 Li$_2$SrSiSe$_4$ = SiSe$_2$ + 2 Li$_2$Se + Sr$_2$SiSe$_4$

2 Li$_2$SrGeS$_4$ = Li$_4$GeS$_4$ + Sr$_2$GeS$_4$

2 Li$_2$SrGeSe$_4$ = GeSe$_2$ + 2 Li$_2$Se + Sr$_2$GeSe$_4$

Li$_2$SrSnS$_4$ = Li$_2$SnS$_3$ + SrS

Li$_2$SrSnSe$_4$ = Li$_2$Se + SrSe + SnSe$_2$

2 Li$_2$BaSiS$_4$ = Ba$_2$SiS$_4$ + Li2S + Li$_2$SiS$_3$

2 Li$_2$BaSiSe$_4$ = Ba$_2$SiSe$_4$ + 2 Li$_2$Se + SiSe$_2$

2 Li$_2$BaGeS$_4$ = Ba$_2$GeS$_4$ + Li$_4$GeS$_4$

2 Li$_2$BaGeSe$_4$ = Ba$_2$GeSe$_4$ + 2 Li$_2$Se + GeSe$_2$

2 Li$_2$BaSnS$_4$ = Ba$_2$SnS$_4$ + Li$_2$S + Li$_2$SnS$_3$

2 Li$_2$BaSnSe$_4$ = Ba$_2$SnSe$_4$ + 2 Li$_2$Se + SnSe$_2$

Fig.S1 The schematic diagram of the structure stability for Li$_2$BMQ$_4$ (B = Ca, Sr and Ba; M = Si, Ge and Sn; Q = O, S and Se) compounds. Small white circles inside the larger brown filled shapes (diamond, triangle and pentagon) and small white circles inside the larger yellow filled shapes indicate that the compounds have been synthesized experimentally with I$\overline{4}$2m space group and other space groups (P6$_3$cm, P3$_1$21, etc.), respectively. Brown filled shapes and white unfilled shapes represent the compounds that are not synthesized experimentally, where the imaginary frequency

mode is absent in the calculated phonon dispersion curves for the materials denoted by brown filled shapes while the compounds marked by white unfilled diamond behave in an opposite manner.

Fig.S2 The calculated phonon dispersion curves in Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn and Q = O, S and Se) systems except for those experimentally synthesized and phonon-unstable compounds. The absence of imaginary frequency modes suggests these compounds are kinetically stable.

Table S3 The hydrolysis reaction energies of 2114 chalcogenides solid electrolytes (SEs) evaluated by DFT methods. More-negative reaction energy indicates worse moisture stability (moisture sensitive), whereas more-positive reaction energy indicative better moisture stability (moisture stable).

Compounds	Hydrolysis reaction	Reaction energy (eV/H_2O)
Li_2CaSiS_4	$Li_2CaSiS_4 + H_2O = CaO + Li_2SiS_3 + H_2S$	0.52796
	$Li_2CaSiS_4 + 4 H_2O = Li_2SiO_3 + CaO + 4 H_2S$	-0.45626
	$Li_2CaSiS_4 + 3 H_2O = CaS + Li_2SiO_3 + 3 H_2S$	-0.78895
	$Li_2CaSiS_4 + 4 H_2O = 4 H_2S + Li_2CaSiO_4$	-0.53477
$Li_2CaSiSe_4$	$Li_2CaSiSe_4 + H_2O = CaSe + Li_2O + H_2Se + SiSe2$	0.95244
	$Li_2CaSiSe_4 + 5 H_2O = CaO + SiO_2 + 4 H_2Se + 2 LiOH$	-0.22620
	$Li_2CaSiSe_4 + 4 H_2O = CaO + SiO_2 + 4 H_2Se + Li_2O$	0.03631
	$Li_2CaSiSe_4 + 4 H_2O = 4 H_2Se + Li_2CaSiO_4$	-0.37895
Li_2CaGeS_4	$Li_2CaGeS_4 + 4 H_2O = 4 H_2S + Li_2CaGeO_4$	0.05151
	$Li_2CaGeS_4 + 4 H_2O = Li_2GeO_3 + CaO + 4 H_2S$	0.11849
$Li_2CaGeSe_4$	$Li_2CaGeSe_4 + 4 H_2O = 4 H_2Se + Li2CaGeO4$	0.32803
	$Li_2CaGeSe_4 + 5 H_2O = CaO + GeO_2 + 4 H_2Se + 2 LiOH$	0.36674
	$Li_2CaGeSe_4 + 4 H_2O = CaO + GeO_2 + 4 H_2Se + Li_2O$	0.77749
	$Li_2CaGeSe_4 + H_2O = CaSe + Li_2O + H_2Se + GeSe_2$	0.94510
Li_2CaSnS_4	$Li_2CaSnS_4 + 4 H_2O = 4 H_2S + Li_2CaSnO_4$	0.34419
	$Li_2CaSnS_4 + 4 H_2O = Li_2SnO_3 + CaO + 4 H_2S$	0.24295
$Li_2CaSnSe_4$	$Li_2CaSnSe_4 + 4 H_2O = 4 H_2Se + Li_2CaSnO_4$	0.66934
	$Li_2CaSnSe_4 + 4 H_2O = CaO + SnO_2 + 4 H_2Se + Li_2O$	0.76766
Li_2SrSiS_4	$2 Li_2SrSiS_4 + H_2O = Li_2SiS_3 + Sr_2SiS_4 + Li_2O + H_2S$	1.30316
	$2 Li_2SrSiS_4 + 9 H_2O = Li_2SiO_3 + Sr_2SiO_4 + 8 H_2S + 2 LiOH$	-0.41345
	$2 Li_2SrSiS_4 + 8 H_2O = Li_2SiO_3 + Sr_2SiO_4 + 8 H_2S + Li_2O$	-0.30560
	$2 Li_2SrSiS_4 + 4 H_2O = Li_2SiO_3 + Sr_2SiS_4 + Li_2O + 4 H_2S$	-0.26246

	$2\ Li_2SrSiS_4 + 5\ H_2O = Li_2SiS_3 + Sr_2SiO_4 + Li_2O + 5\ H_2S$	-0.01835
	$Li_2SrSiS_4 + 4\ H_2O = 4\ H_2S + Li_2SrSiO_4$	-0.39931
$Li_2SrSiSe_4$	$2\ Li_2SrSiSe_4 + 2\ H_2O = Sr_2SiSe_4 + SiSe_2 + 2\ Li_2O + 2\ H_2Se$	1.27414
	$2\ Li_2SrSiSe_4 + 10\ H_2O = Sr_2SiO_4 + SiO_2 + 8\ H_2Se + 4\ LiOH$	-0.22775
	$2\ Li_2SrSiSe_4 + 8\ H_2O = Sr_2SiO_4 + SiO_2 + 8\ H_2Se + 2\ Li_2O$	0.03438
	$Li_2SrSiSe_4 + 4\ H_2O = 4\ H_2Se + Li_2SrSiO_4$	-0.22771
Li_2SrGeS_4	$Li_2SrGeS_4 + 4\ H_2O = 4\ H_2S + Li_2SrGeO_4$	0.18674
	$2\ Li_2SrGeS_4 + 8\ H_2O = Li_4GeO_4 + Sr_2GeO_4 + 8\ H_2S$	0.23063
	$2\ Li_2SrGeS_4 + 4\ H_2O = Li_4GeO_4 + Sr_2GeS_4 + 4\ H_2S$	0.18689
$Li_2SrGeSe_4$	$Li_2SrGeSe_4 + 4\ H_2O = 4\ H_2Se + Li_2SrGeO_4$	0.47388
	$2\ Li_2SrGeSe_4 + 10\ H_2O = Sr_2GeO_4 + GeO_2 + 8\ H_2Se + 4\ LiOH$	0.36929
	$2\ Li_2SrGeSe_4 + 8\ H_2O = Sr_2GeO_4 + GeO_2 + 8\ H_2Se + 2\ Li_2O$	0.78067
	$2\ Li_2SrGeSe_4 + 2\ H_2O = Sr_2GeSe_4 + GeSe_2 + 2\ Li_2O + 2\ H_2Se$	1.27020
Li_2SrSnS_4	$Li_2SrSnS_4 + 4\ H_2O = 4\ H_2S + Li_2SrSnO_4$	0.48324
	$Li_2SrSnS_4 + 4\ H_2O = Li_2SnO_3 + SrO + 4\ H_2S$	0.46845
	$Li_2SrSnS_4 + H_2O = Li_2SnS_3 + SrO + H_2S$	1.27435
	$Li_2SrSnS_4 + 3\ H_2O = Li_2SnO_3 + SrS + 3\ H_2S$	0.28625
$Li_2SrSnSe_4$	$Li_2SrSnSe_4 + 4\ H_2O = 4\ H_2Se + Li_2SrSnO_4$	0.82683
	$Li_2SrSnSe_4 + 5\ H_2O = SrO + SnO_2 + 4\ H_2Se + 2\ LiOH$	0.55403
	$Li_2SrSnSe_4 + 4\ H_2O = SrO + SnO_2 + 4\ H_2Se + Li_2O$	1.01161
	$Li_2SrSnSe_4 + H_2O = SrSe + SnSe_2 + Li_2O + H_2Se$	1.17463
Li_2BaSiS_4	$2\ Li_2BaSiS_4 + H_2O = Ba_2SiS_4 + Li_2SiS_3 + H_2S + Li_2O$	1.08640

	$Li_2BaSiS_4 + 4\ H_2O = 4\ H_2S + Li_2BaSiO_4$	-0.22865
	$2\ Li_2BaSiS_4 + 9\ H_2O = Ba_2SiO_4 + 8\ H_2S + Li_2SiO_3 + 2\ LiOH$	-0.35080
	$2\ Li_2BaSiS_4 + 8\ H_2O = Ba_2SiO_4 + 8\ H_2S + Li_2SiO_3 + Li_2O$	-0.23512
	$2\ Li_2BaSiS_4 + 5\ H_2O = Li_2SiS_3 + Ba_2SiO_4 + Li_2O + 5\ H_2S$	0.09442
	$2\ Li_2BaSiS_4 + 4\ H_2O = Li_2SiO_3 + Ba_2SiS_4 + Li_2O + 4\ H_2S$	-0.31666
$Li_2BaSiSe_4$	$2\ Li_2BaSiSe_4 + 2\ H_2O = Ba_2SiSe_4 + 2\ Li_2O + 2\ H_2Se + SiSe_2$	1.24877
	$2\ Li_2BaSiSe_4 + 10\ H_2O = Ba_2SiO_4 + SiO_2 + 8\ H_2Se + 4\ LiOH$	-0.14684
	$2\ Li_2BaSiSe_4 + 8\ H_2O = Ba_2SiO_4 + SiO_2 + 8\ H_2Se + 2\ Li_2O$	0.13552
	$Li_2BaSiSe_4 + 4\ H_2O = 4\ H_2Se + Li_2BaSiO_4$	-0.02639
Li_2BaGeS_4	$Li_2BaGeS_4 + 4\ H_2O = 4\ H_2S + Li_2BaGeO_4$	0.34437
	$2\ Li_2BaGeS_4 + 8\ H_2O = Ba_2GeO_4 + Li_4GeO_4 + 8\ H_2S$	0.33248
	$2\ Li_2BaGeS_4 + 4\ H_2O = Ba_2GeS_4 + Li_4GeO_4 + 4\ H_2S$	0.16490
	$2\ Li_2BaGeS_4 + 4\ H_2O = Ba_2GeO_4 + Li_4GeS_4 + 4\ H_2S$	0.58690
$Li_2BaGeSe_4$	$Li_2BaGeSe_4 + 4\ H_2O = 4\ H_2Se + Li_2BaGeO_4$	0.66032
	$2\ Li_2BaGeSe_4 + 10\ H_2O = Ba_2GeO_4 + GeO_2 + 8\ H_2Se + 4\ LiOH$	0.47382
	$2\ Li_2BaGeSe_4 + 8\ H_2O = Ba_2GeO_4 + GeO_2 + 8\ H_2Se + 2\ Li_2O$	0.91134
	$2\ Li_2BaGeSe_4 + 2\ H_2O = Ba_2GeSe_4 + 2\ Li_2O + 2\ H_2Se + GeSe_2$	1.27870
Li_2BaSnS_4	$Li_2BaSnS_4 + 4\ H_2O = 4\ H_2S + Li_2BaSnO_4$	0.63734
	$2\ Li_2BaSnS_4 + 9\ H_2O = Ba_2SnO_4 + 8\ H_2S + Li_2SnO_3 +$	0.34673

	2 LiOH	
	$2 Li_2BaSnS_4 + 8 H_2O = Ba_2SnO_4 + 8 H_2S + Li_2SnO_3 + Li_2O$	0.54961
	$2 Li_2BaSnS_4 + H_2O = Ba_2SnS_4 + Li_2O + H_2S + Li_2SnS_3$	1.36508
$Li_2BaSnSe_4$	$Li_2BaSnSe_4 + 4 H_2O = 4 H_2Se + Li_2BaSnO_4$	1.00761
	$2 Li_2BaSnSe_4 + 10 H_2O = Ba_2SnO_4 + SnO_2 + 8 H_2Se + 4 LiOH$	0.56047
	$2 Li_2BaSnSe_4 + 8 H_2O = Ba_2SnO_4 + SnO_2 + 8 H_2Se + 2 Li_2O$	1.01966
	$2 Li_2BaSnSe_4 + 9 H_2O = Ba_2SnO_4 + Li_2SnO_3 + 8 H_2Se + 2 LiOH$	0.67586
	$2 Li_2BaSnSe_4 + 8 H_2O = Ba_2SnO_4 + Li_2SnO_3 + 8 H_2Se + Li_2O$	0.91988
	$2 Li_2BaSnSe_4 + 2 H_2O = Ba_2SnSe_4 + 2 Li_2O + 2 H_2Se + SnSe_2$	1.27748

Fig.S3 Powder X-ray diffraction (XRD) patterns of Li_2BaSnS_4 and Li_2SrSiS_4.

Fig.S4 The calculated density of states by MBJ exchange potential for those compounds that have been synthesized experimentally or are thermodynamically and kinetically stable with $I\bar{4}2m$ space group in Li_2BMQ_4 (B = Ca, Sr and Ba; M = Si, Ge and Sn and Q = O, S and Se) systems.

Fig.S5 The *MSD*(mean-squared displacement)-Δt curves from first-principles molecular dynamics (FPMD) simulations over 50 ps between 900 K and 1750 K for Li_2CaSiS_4, Li_2SrSiS_4, Li_2BaSnS_4, $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$ and $Li_{1.75}SrSiS_{3.75}Cl_{0.25}$. The linear MSD-$\Delta t$ dependence is utilized to apply the Einstein relation $D = \frac{MSD(\Delta t)}{2d\Delta t} + D_{offset}$ for inferring the diffusivity, and the Arrhenius equation $D = D_0 \exp\left(-\frac{E_a}{kT}\right)$ is employed for linearly fitting log(D) against 1/T to derive the total activation energy

and ionic conductivity.

Fig.S6 The MSD-Δt curves from first-principles molecular dynamics tests for Li_2CaSiS_4 and doped Li_2CaSiS_4 (with different doping elements such as Al, Ga, As and Cl at different concentrations) to choose appropriate doping element and doping concentrations. Mostly doped Li_2CaSiS_4 with some lithium vacancies exhibit larger MSD than the parent compound at the same temperature, indicating element doping could enhance Li^+ ionic conductivity. At lower doping concentrations, the enhancement of ionic conductivity is not significant, whereas higher doping concentrations may potentially enhance ionic conductivity better, albeit at the risk of inducing lattice instability. Taking these factors into account, we selected $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$ configuration to perform FPMD with different temperatures aiming at estimating room-temperature ionic conductivity and activation energy, marked in the red box of **Fig.S6b**. The configurations of $Li_{1.75}SrSiS_{3.75}Cl_{0.25}$ is also constructed based on the configuration of $Li_{1.75}CaSiS_{3.75}Cl_{0.25}$.

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