Supplementary Information

Element selection for crystalline inorganic solid discovery guided by unsupervised machine learning of experimentally explored chemistry

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Supplementary Methods

Machine Learning methodology

We treat the problem of detecting phase fields that contain stable compounds as an instance of the inlier/outlier detection problem, which is tightly connected to anomaly and novelty detection tasks as well. The overview of deep learning approaches for this problem is given in 1. In our case, inliers (or normal data) are phase fields containing stable compounds, and outliers (or anomalous data) are the phase fields without them. We assume that the outliers are not available to us at all and that we need to rely only on inliers to build a model, bringing us into the unsupervised learning setting. As described in the Section Machine learning models, we select an autoencoder for this task from a range of potential machine learning approaches.

Autoencoders are a class of non-linear dimensionality reduction techniques that are used in an unsupervised manner. An autoencoder trained on normal data should fail to reconstruct the anomalous data samples and produce large reconstruction errors for them. In addition, the variational autoencoder learns a probability distribution from the input normal data, improving its description. We use reconstruction errors to rank unseen phase fields by their closeness to the normal data.

In order to avoid overfitting, we employ the following strategy discussed in detail in the Section Model Validation. We hold-out a portion of our normal data prior to training and compare the distributions of reconstruction errors on the training and hold-out sets after fitting the model. Generalizability is deemed to be good when the resulting distributions are very similar to each other. In our case, we compare a simple statistic of these reconstruction errors. In general, validation of anomaly detection methods without access to a small sample of outliers is a subject of ongoing research2.
In our case, we prefer models with a relatively broad distribution of reconstruction errors, when both average reconstruction errors and validation metrics are comparable. We expect such models to produce a ranking that is more discriminative and stable.

Training data and its representation are discussed in the Section Training set for the Variational Autoencoder Configuration.

**Machine learning models**

We studied different computationally undemanding machine learning methods\(^3\) for phase field ranking. Each of these methods provides a method-specific metric of dissimilarity between the sample and normal data – the outlier score, which can be used to rank the phase fields. Since these algorithms are stochastic in nature, their outlier scores vary considerably depending on the initialization conditions, e.g., random seed number. In order to alleviate that, we take the mean value of scores across multiple runs as the final score, which requires a large number of iterations to achieve convergence (Supplementary Fig. 1). Noting that the more computationally involved neural-network-based approaches account for statistical variations by considering multiple models in a large network and a dropout\(^4\), yielding converged results in every iteration, we employ a neural-network-based Variational Autoencoder (VAE), which uses the autoencoder’s reconstruction error as a metric, in our study.
Supplementary Figure 1. Convergence of the different methods’ scores with the number of models used. ML methods used for phase field ranking are histogram-based (HBOS), isolation forest (Iforest), cluster-based (CBLOF), minimum covariance (MCD), connectivity-based (COD)\(^3\). Unlike the Variational Autoencoder neural network, accounting for statistical variations, up to 1000 iterations (models) are required to achieve convergence with these approaches.

Training set for the Variational Autoencoder Configuration

The open-source software (implementation of VAE and Phase Field Ranking method) developed for this study is available at https://www.github.com/lrcfmd/PhaseFieldRanking.

The training set contains all quaternary M-M’-A-A’ phase fields containing the \(M_xM'_yA_zA'_t\) phases reported in ICSD-v1 2017 where:

- \(M, M'\) span all cations: all species of the periodic table with positive oxidation states
- \(A, A'\) are anions \{N\(^3-\), P\(^3-\), As\(^3-\), Sb\(^3-\), O\(^2-\), S\(^2-\), Se\(^2-\), Te\(^2-\), F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\}\}
- \(x, y, z, t\) are positive values and stand for stoichiometric coefficients
- There are reported phases in ICSD, where both M (positive oxidation state) and A
(negative oxidation state) are represented by the same element, e.g., phases containing both $S^{6+}$, $S^{2-}$. Such phases are not used in the training set.

The training process, in which reconstruction error (RE) and Kullback-Leibler (KL) divergence of the probability distribution - the two components of the VAE loss function - are minimized, depends on the size of the dataset: for the original dataset (2021 entries) the neural network is overparametrized and requires many computationally expensive epochs of training to converge the loss function with “Adam” optimization. Representation of a phase field in the elemental vector space $(M, M', A, A')$ enables us to augment the training data 24-fold by elemental permutations. Indeed, 24 different vector representations, e.g., $(M, M', A, A')$, $(A', M, M', A)$, $(A, A', M, M')$ etc., are mathematically inequivalent, yet denote the same phase field. This enhances machine learning of the latent vector representation by improving the ratio of parameters to the number of entries, alleviating the risk of overfitting and decreasing the number of epochs required for convergence (Supplementary Fig. 2). Elemental permutations reflect that phase fields are sets that are order-invariant, allowing additional verification of the model that is required to produce identical results for permutations.
Supplementary Figure 2. VAE training mean square error (MSE) vs epoch for the original and augmented data. a Reconstruction error (RE) loss and Kullback-Leibler (KL) divergence loss in training of VAE on the augmented dataset via elemental permutations (48744 data points). Both losses converge within 15 epochs. b RE and KL divergence losses in training of VAE on 2021 data points. With the smaller training dataset, RE converges to the value in (a) (MSE = 0.976) in over 200 epochs, KL does not converge and oscillates with a small variance (MSE ~0.02).

In this paper, we use the VAE to learn the similarities between unexplored phase fields and the reported phase fields in ICSD. This is conducted by learning the multi-dimensional representations of the phase fields and their hidden features in the latent space with a dimensionality of choice in the way that best reconstructs the training data (RE and KL divergence are minimized). There is a small difference in distributions of RE between 2- and 4-dimensional latent space, and a robust distribution of RE that persists in choices of 4, 8, 16 dimensions for the latent space. Thus, we choose 4-dimensional latent space for the model used.

Model validation

We perform 5-fold cross validation. In each of the five iterations, we hold out a different 20% of
the training data and train the model on the remaining 80%. We then apply the VAE model to the validation data (the separate 20%), and check that the distribution of scores of the validation set follows the distribution of the training set, ensuring the width, position and distribution of RE around the peak are within the same range – broadly analogous to the cohesion and separation methods for internal validation of unsupervised learning⁸.

To simplify the comparison of RE for different data points, we use the normalised RE, calculated as \( \frac{\text{RE} - \text{RE}_{\text{min}}}{\text{RE}_{\text{max}} - \text{RE}_{\text{min}}} \). The validation error is calculated as the percentage of the validation set that is distributed in the second half of the training distribution (i.e., the number of phase fields from the validation set which have the normalised RE higher than the threshold value of 0.5). The validation errors for different subsets (the separate 20%) of data chosen for validation are: 24.3, 20.1, 19.8, 26.2, 13.4%, demonstrating a comparable performance of the VAE to the state-of-the-art unsupervised machine learning techniques for various datasets²,⁹,¹⁰. The average validation error across the subsets is 20.76%, demonstrating an expected distribution of the RE in comparison to the training dataset.

Comparison of the distributions in the datasets of different sizes (in our case, ICSD training data - 2021 entries, testing data – 303 entries) can be addressed by methods in statistics for nonparametric density estimation¹¹, where the bin size, \( w \), depends on the number of data entries, \( N \), as follows:

\[
  w = \frac{2 \times \text{IQR}}{\sqrt[3]{N}}
\]

(Supplementary Equation 1)

where \( \text{IQR} \) is the interquartile range. These data size-adapted bins, with widths 0.04 for training and 0.077 for testing data respectively, allow size-independent comparison of RE distribution in the
training and testing data (Figure 2a in the main text and Supplementary Fig. 3). Such data
distribution results in ten data entries located in the first bin of testing data.

Supplementary Figure 3. A histogram of normalised RE (scores) in ICSD and testing datasets. The width of the bins depends on the number of entries in the two datasets, according to Supplementary Equation 1. The scores distributions demonstrate that the patterns for the majority of the data entries are well-recognised by the model (normalised RE < 0.5) with a few outliers.

Feature space

We study different basis sets of features for description of atomic elements built from 39 elemental features\textsuperscript{12,13} (source https://bitbucket.org/wolverton/magpie/src/master/) plus the modified Pettifor number\textsuperscript{14} of each element. Among the multitude of elemental features in the literature, we choose this set because the values are reported for all of the considered chemical elements, ensuring that there are no missing values in Supplementary Table 1.
Supplementary Table 1. Elemental features - values of atomic characteristics selected from\textsuperscript{12-14}

| Atomic number | Bcc band gap | Ground state (GS) band gap | Number of unfilled d-orbitals |
|---------------|--------------|-----------------------------|------------------------------|
| Atomic volume | Bcc effective lattice constant | GS effective lattice constant | Number of valence electrons in d-orbitals |
| Atomic weight | Bcc energy difference | GS energy per atom | Number of unfilled f-orbitals |
| First ionization radius | Bcc energy per atom | GS estimated bcc lattice constant | Number of valence electrons in f-orbitals |
| Covalent radius | Bcc magnetic moment | GS estimated fcc lattice constant | Number of unfilled p-orbitals |
| Density | Bcc volume per atom | GS magnetic moment | Number of valence electrons in p-orbitals |
| Electronegativity | Bcc volume per atom difference | GS volume per atom | Number of unfilled s-orbitals |
| Boiling temperature | Bcc Fermi energy | ICSD volume | Number of valence electrons in s-orbitals |
| Melting temperature | Periodic Table Group (column) | Periodic Table Period (row) | Total number of unfilled orbitals |
| Polarizability | Number on the modified Pettifor scale\textsuperscript{14} | Total number of valence electrons | Mendeleev number |

As different combinations of features may have different efficiencies for phase field description. 9
and resulting precision of the model, we study individual features’ contributions to the
reconstruction error of the phase fields in ICSD as well as the feature reconstruction error (FRE) -
the relative change between the original and the reconstructed values of a feature averaged over all
the phase fields that each element takes part in. For all the studied combinations of features
discussed in this and the next paragraphs, we build a series of VAE models and examine their
performance in terms of the validation error and the width of the score distributions. We begin with
a set of all 40 features. In Supplementary Fig. 4 the average FRE is demonstrated for each element,
enabling quantitative comparison of the effects of different features on the model’s accuracy.

Supplementary Figure 4. Comparison of elemental features via feature reconstruction errors (FRE). FRE averaged
for all atoms. 40 features are studied, and 3 features with high FRE (melting temperature, boiling temperature and density)
are removed for the final model.
In the next model, we discard the most poorly reconstructed features (boiling temperature, melting temperature and density) to arrive at the basis of 37 features. In this basis, the phase fields are represented by concatenation of all the elemental descriptors of constituent atoms into 148-dimensional vectors. We also compare correlation (Pearson’s correlation) of FRE of different features in Supplementary Fig. 5a. This reveals some strongly positively and negatively correlated pairs of atomic descriptors, including some well-known relations (e.g., density and atomic weight, reverse correlations between covalent radius and first ionisation energy, polarisability and electronegativity\textsuperscript{15}, etc.). Supplementary Fig. 5b, however, demonstrates that FRE practically do not correlate with the total RE, suggesting the importance of maximizing the number of well-reconstructed elemental descriptors for detailed representation of the phase fields. We also confirm that in general, maximization of the number of features enhances the dispersion of the total RE between the data points in the model by increasing the width of the RE distribution, thereby improving the precision in discrimination between the phase fields and identification of the best candidates (Supplementary Fig. 5c).

We validate this elemental feature basis set by developing a Monte-Carlo (MC) approach, in which at every step a basis set of features is augmented or decreased with a randomly selected feature – a move that can be accepted or discarded depending on the VAE validation error produced with this basis (Supplementary Fig. 5d). The MC-derived basis set produces outcomes that are similar to but less effective than the set above (larger validation error, smaller distribution width), supporting the use of the set discussed above in the model.
Supplementary Figure 5. Feature correlation, total RE and model precision and dispersion. **a** Pearson’s correlation between pairs of individual feature reconstruction errors (FRE); **b** Averaged Pearson’s correlation between individual FRE and total RE for quaternary compounds in ICSD, suggesting a strong non-linear dependence; **c** An increasing width of the distributions of RE for quaternaries in ICSD, when described with 3, 12, 40 elemental features improves discrimination between the RE of similar phase fields; **d** Different sets of elemental features representing quaternary phase fields found in the Monte-Carlo (MC) approach: the size and the colour of a circle corresponds to the number of elemental features in a set, its location on the x-axis corresponds to the resulting VAE validation error, when quaternary phase fields in ICSD are described with this set of features, while the y-axis corresponds to the width of the corresponding RE distribution attainable with this set. The best compromise between the range of RE and a low validation error found with MC is the set of 34 features (circled in red); the set of 37 features selected for the final model used is circled in black.

**Synthesis**

Samples with composition LiSnS_{2.33}Cl_{0.33} (#1), Li_3SnS_3Cl (#2), Li_{1.5}SnS_{1.5}Cl_{2.5} (#3), Li_8SnS_4Cl_4 (#4), Li_{1.67}SnS_{0.33}Cl_5 (#5), Li_{11}SnS_3Cl_9 (#6), Li_{3.6}SnS_{3.6}Cl_{0.4} as well as the purified Li_{3.3}SnS_{3.3}Cl_{0.7}
new phase were all synthesized by solid state reaction in alumina crucibles contained in evacuated sealed quartz tubes using the same procedure as described in the method section of the main text. Stoichiometric amounts of Li$_2$S (Merck, 99.98 %), SnS (Alfa Aesar, 99+ %), LiCl (Merck, 99.99 %), S (Merck, 99.98 %), SnCl$_2$ (Merck, >99.99 %) and SnCl$_4$ (Merck, 99.995 %) precursors were weighed in order to yield a total mass of powder of approximately 300 mg (the exact amount of precursors for each sample are given in Supplementary Table 2). Powders were combined and mixed thoroughly with an agate pestle and mortar for 15 min (except for the SnCl$_4$ containing sample for which powder precursor were simply poured into liquid SnCl$_4$), transferred into an alumina crucible and then sealed in a quartz tube under a pressure of 10$^{-4}$ mbar. The ampoule containing the sample was heated to 700 °C at a ramp rate of 5 °C min$^{-1}$, held at 700 °C for 12 hours, and then cooled to room temperature at a ramp rate of 5 °C min$^{-1}$. The resulting powder was then manually ground in order to obtain a fine powder. Precursors and resulting powders were handled in an Ar-filled glovebox (O$_2$ < 1 ppm).

**Supplementary Table 2. Quantities of precursors weighed for each sample made in the Li-Sn-S-Cl phase field.**

| Sample code | Composition       | Precursor weight (mg) |
|-------------|-------------------|-----------------------|
| #1          | LiSnS$_{2.33}$Cl$_{0.33}$ | Li$_2$S 23, SnS 226.2, S 48.1, LiCl 21.2 |
| #2          | Li$_3$SnS$_3$Cl  | Li$_2$S 51.7, SnS 169.6, S 36.1, LiCl 47.7 |
| #3          | Li$_{1.5}$SnS$_{1.5}$Cl$_{2.5}$ | SnCl$_2$ 107, SnS 85.1, S 36.2, LiCl 71.8 |
| #4          | Li$_8$SnS$_4$Cl$_4$ | Li$_2$S 70.3, SnS 115.3, S 24.5, LiCl 129.7 |
| #5          | Li$_{1.67}$SnS$_{0.33}$Cl$_5$ | SnCl$_4$ 205.2 |
|   | Formula          | Element | Concentration |
|---|------------------|---------|---------------|
| #6 | Li$_{11}$Sn$_3$S$_7$Cl$_9$ | SnS    | 23.5          |
|    |                  | S      | 5             |
|    |                  | LiCl   | 66.4          |
| #7 | Li$_{3.6}$Sn$_{3.6}$Cl$_{0.4}$ | Li$_2$S | 23           |
|    |                  | SnS    | 75.4          |
|    |                  | S      | 16            |
|    |                  | LiCl   | 190.8         |
| Phase A | Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ | Li$_2$S | 85.5         |
|    |                  | SnS    | 175.3         |
|    |                  | S      | 37.3          |
|    |                  | LiCl   | 19.7          |
|    |                  | Li$_2$S | 73.5         |
|    |                  | SnS    | 180.9         |
|    |                  | S      | 38.5          |
|    |                  | LiCl   | 33.9          |

**Elemental analysis**

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Elemental analysis of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ was performed by Mikroanalytisches Labor Pascher at Remagen-Bandorf, Germany, to determine Li, Sn, S and Cl content. Samples were handled under inert atmosphere.

WDX analysis. Wavelength dispersive X-ray spectroscopy (WDX) measurements were performed in order to determine the Cl content and further validate Sn and S contents. This was done using a TESCAN S8000 scanning electron microscope (SEM) equipped with a WAVE WDX detector from Oxford Instruments. A pellet of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ was transferred from an argon filled glovebox to the instrument using a vacuum transfer holder from Quorum. The pellet was coated with a thin layer of platinum with a Quorum sputter coater in order to minimize the effects of charging. Measurements and quantifications were performed using the software INCA from Oxford Instruments. For accurate quantification, data were also collected from standard materials (SnO$_2$, Bi$_2$S$_3$, NaCl standards supplied by the manufacturer) for each element.
**Diffraction and refinement**

Routine analysis of phase purity and lattice parameters were performed on a Bruker D8 Advance diffractometer with a monochromated Cu source (K\(\alpha_1\), \(\lambda = 1.54060\) Å) in powder transmission Debye Scherrer geometry (capillary) with sample rotation.

The structural models were refined by the Rietveld method as implemented in the Fullprof suite\(^{16}\). For the sake of realism, all uncertainties were increased by Berar’s factor (4.5, 3.2 and 3.9 for SXRD, NPD Bank 4 and NPD Bank 5, respectively according to FullProf).

The program FullProf was used to obtain information about the microstructure, following the method described by Rodriguez-Carvajal et al\(^{16,17}\). This model uses the Scherrer formula, which considers that the size broadening can be written as a linear combination of spherical harmonics. Peak shapes were modelled using the spherical harmonics expansions in a hexagonal material with Laue class 6/mmm.

**Maximum Entropy Method Analysis of Diffraction Data**

The maximum entropy method (MEM) applied to diffraction data consists of optimizing the reconstruction of the scattering density from the observed structure factors by finding the maximum of the informational entropy under several constraints through an iterative procedure\(^{18}\). MEM applied to crystallography is a powerful tool for reconstructing scattering density from incomplete and/or noisy data systems and limits termination effects obtained through usual Fourier synthesis, particularly important in disordered systems\(^{19}\). The maximum entropy method (MEM) applied to neutron diffraction data is useful to shed light on the positions of light elements, such as Li, poorly visible with X-rays, but presenting large enough neutron scattering length. This method was recently used to describe conduction pathways in several ionic conductors of lithium\(^{20,21}\) and
oxygen in particular.

Because the $^7$Li scattering length is negative ($b_{Li} = -2.22$ fm), visualisation of negative levels is performed to observe Li positions within the structure. The background level was set as the maximum value of the nuclear density obtained in regions where no atoms are expected (surroundings of the S site): 0.001 fm Å$^{-3}$.

**DC polarisation measurements**

For DC polarization measurements, a cylindrical pellet of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ with a thickness of 1.75(9) mm and a surface area of 0.18(9) cm$^2$ was used. An Au|Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$|Au ion-blocking electrode was subjected to different DC bias voltages (0.1 to 1V) at room temperature. The current was recorded as a function of time. The steady state current corresponds to the electronic current. Prior to the DC polarization, the AC impedance was collected from 3 MHz to 1 mHz with a voltage amplitude of 100 mV using a Biologic VSP-300 potentiostat/galvanostat.

**Electrochemical Li plating/stripping**

Symmetrical Li|Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$|Li cells were assembled inside an Ar-filled glovebox ($O_2$, $H_2O \leq 0.1$ ppm). Two-electrode Swagelok cells were used with PEEK-insulated body and uniform spring-loaded compression (Micro Plas Mouldings Ltd.). Lithium ribbon (99.9%, 0.38 mm thick, Sigma) was scraped to remove surface layers, then finely polished to achieve a shiny mirrored surface and punched into discs. Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ pellet (ca. 1.5 mm thickness) was sandwiched between two pieces of Li discs and carefully aligned inside the cell. The cell was sealed hermetically under compression before being transferred to a temperature chamber (Memmert). Li plating/stripping was measured by galvanostatic cycling at 0.01 mA cm$^{-2}$ at 303, 323 and 343 K for 1 h per half-cycle.
using an MPG2 workstation (Biologic). The cell was allowed to thermally equilibrate for a minimum of 1 h between the temperature steps. EIS measurements were performed in 50 cycle intervals using an SP-300 potentiostat (Biologic) with a 20 mV sinusoidal perturbation between 7 MHz and 100 mHz at open circuit potential.

**Ex-situ Raman microscopy and XRD after Li plating/stripping**

After completing Li plating/stripping measurements, the symmetric cell was disassembled inside the Ar-filled glovebox. The pellet material was collected and sealed inside a custom-built stainless-steel holder with a CaF2 window. Raman spectra of the cycled and pristine solid electrolyte were collected using a Renishaw In-Via Rama spectrometer equipped with an inverted microscope to provide spatial sensitivity and the ability to focus on individual particles. Spectra were collected with 785 nm wavelength laser at room temperature. Laboratory XRD patterns were collected for material extracted from the bulk of the cycled pellet, and powder scraped from the Li|Li3.3SnS3.3Cl0.7 interfacial region. This interfacial powder was mixed with amorphous boron and sealed in a 0.5 mm diameter borosilicate capillary for measurement.

**Nuclear Magnetic Resonance (NMR)**

SLR rates in the laboratory frame (T1⁻¹) were obtained using a saturation recovery pulse sequence and the data were fitted to a stretch exponential function of the form:

\[ 1 - \exp\left[-\left(\tau / T_1\right)\alpha\right] \]  

(Supplementary Equation 2)

where \(\tau\) are the variable delays and \(\alpha\) is the stretch exponential (values between 0.4 and 1).

SLR rates in the rotating frame (T1ρ⁻¹) were recorded using a standard spin-lock pulse sequence at frequencies of \(\omega/2\pi\) (\(^7\)Li) = 15, 45, and 80 kHz, and data were fitted to a stretch exponential
function of the form:

\[ \exp[-(\tau/T_{1p}^{-1})^\beta] \]  

(Supplementary Equation 3)

where \( \beta \) values are between 0.3 and 1.

Temperature calibrations were performed using the chemical shift thermometers \( \text{Pb(NO}_3\text{)}_2, \text{CuI} \) and \( \text{CuBr} \) using \( ^{207}\text{Pb} \) and \( ^{63}\text{Cu} \) NMR.\(^{23-26}\) The errors associated with this method were calculated using the broadening of the isotropic peak and ranged from 5 - 20 K.

**Supplementary Discussion**

**Ranking of the quaternary unexplored Li-M-A-A’ phase fields**

For the ranking, we calculated reconstruction errors (RE) of all phase fields of interest as the Euclidean distance between an original 148-dimensional vector, \( p \), and its 148-dimensional image vector, \( p' \), decoded by the VAE, presented in Supplementary Table 3. For the ease of comparison, we also normalise the RE (Norm. RE) by scaling them with the width of the distribution (\( R_{\text{max}} - R_{\text{min}} \)) and presenting all scores from 0 to 1.

**Supplementary Table 3. Ranking of 303 Li-M-A-A’ phase fields.**

| Phase fields | RE  | Norm. RE | Phase fields | RE  | Norm. RE | Phase fields | RE  | Norm. RE |
|--------------|-----|----------|--------------|-----|----------|--------------|-----|----------|
| Li Si S Cl   | 9.782 | 0        | Li Zr S I    | 11.402 | 0.269    | Li Zr N O    | 12.481 | 0.448    |
| Li Zn S Cl   | 9.931 | 0.025    | Li Al O F    | 11.402 | 0.269    | Li Ta S I    | 12.513 | 0.453    |
| Li Al S Cl   | 10.041 | 0.043   | Li Mg N Cl   | 11.408 | 0.27     | Li Ta I Cl   | 12.57 | 0.463    |
| Li Mg S Cl   | 10.05 | 0.044    | Li Mg O F    | 11.41 | 0.27     | Li Sr O Br   | 12.573 | 0.463    |
| Li Sn S Cl   | 10.095 | 0.052   | Li Ca Br Cl  | 11.424 | 0.272    | Li La O Br   | 12.574 | 0.463    |
| Li Si S Br   | 10.115 | 0.055    | Li N P Br    | 11.441 | 0.275    | Li Ca N Br   | 12.579 | 0.464    |
| Compound       | Mass   | Error | Compound       | Mass   | Error |
|----------------|--------|-------|----------------|--------|-------|
| Li P Br Cl     | 10.158 | 0.062 | Li Ca S O      | 11.442 | 0.275 |
| Li P S O       | 10.177 | 0.066 | Li B O Br      | 11.447 | 0.276 |
| Li Si Br Cl    | 10.185 | 0.067 | Li Sn N Cl     | 11.448 | 0.276 |
| Li Si S O      | 10.205 | 0.07  | Li Sn O F      | 11.45  | 0.277 |
| Li Zn S Br     | 10.259 | 0.079 | Li Zn I F      | 11.453 | 0.277 |
| Li Si O Cl     | 10.275 | 0.082 | Li Zr I Cl     | 11.464 | 0.279 |
| Li Zn Br Cl    | 10.328 | 0.091 | Li Si N Br     | 11.465 | 0.279 |
| Li Zn S O      | 10.348 | 0.094 | Li Y S Cl      | 11.485 | 0.282 |
| Li Al S Br     | 10.365 | 0.097 | Li Ca O Cl     | 11.504 | 0.286 |
| Li Si S I      | 10.368 | 0.097 | Li Al I F      | 11.548 | 0.293 |
| Li Mg S Br     | 10.374 | 0.098 | Li Mg I F      | 11.556 | 0.294 |
| Li P I Cl      | 10.41  | 0.104 | Li B S F       | 11.568 | 0.296 |
| Li Zn O Cl     | 10.417 | 0.105 | Li Ca S I      | 11.588 | 0.299 |
| Li Sn S Br     | 10.418 | 0.105 | Li B I Br      | 11.592 | 0.3   |
| Li Al Br Cl    | 10.434 | 0.108 | Li Zn N Br     | 11.593 | 0.3   |
| Li Si I Cl     | 10.437 | 0.109 | Li Sn I F      | 11.596 | 0.301 |
| Li Mg Br Cl    | 10.443 | 0.11  | Li Zr O Br     | 11.606 | 0.302 |
| Li Al S O      | 10.453 | 0.111 | Li B Cl F      | 11.63  | 0.307 |
| Li Mg S O      | 10.462 | 0.113 | Li Ca I Cl     | 11.649 | 0.31  |
| Li Sn Br Cl    | 10.486 | 0.117 | Li N P I       | 11.665 | 0.312 |
| Li Sn S O      | 10.506 | 0.12  | Li B O I       | 11.671 | 0.313 |
| Li Zn S I      | 10.509 | 0.121 | Li Zn N O      | 11.671 | 0.313 |
| Li Al O Cl     | 10.521 | 0.123 | Li Al N Br     | 11.687 | 0.316 |
| Li Mg O Cl     | 10.53  | 0.124 | Li Si N I      | 11.69  | 0.316 |
| Li Sn O Cl     | 10.573 | 0.131 | Li Mg N Br     | 11.695 | 0.317 |
| Li Zn I Cl     | 10.577 | 0.132 | Li Zr S F      | 11.726 | 0.322 |
| Li Si O Br     | 10.592 | 0.134 | Li Sn N Br     | 11.734 | 0.324 |
| Compound       | Atomic Number | Bond Length | Bond Angle | Force Constant | Force Constant Angle |
|----------------|---------------|-------------|------------|----------------|----------------------|
| Li Al S I      | 10.612        | 0.138       | Li Zr I Br | 11.749         | 0.326                | Li Sr N S            | 13.011                | 0.536                |
| Li Mg S I      | 10.621        | 0.139       | Li Al N O  | 11.765         | 0.329                | Li La N S            | 13.012                | 0.536                |
| Li Sn S I      | 10.664        | 0.146       | Li Y S Br  | 11.769         | 0.33                  | Li Y N O             | 13.019                | 0.537                |
| Li Al I Cl     | 10.68         | 0.149       | Li Mg N O  | 11.773         | 0.33                  | Li Sr N Cl           | 13.066                | 0.545                |
| Li Mg I Cl     | 10.688        | 0.15        | Li Zr Cl F | 11.787         | 0.332                 | Li La N Cl           | 13.067                | 0.545                |
| Li P S F       | 10.697        | 0.152       | Li Ca O Br | 11.789         | 0.333                 | Li Sr O F            | 13.068                | 0.545                |
| Li B S Cl      | 10.702        | 0.153       | Li Sn N O  | 11.812         | 0.337                 | Li La O F            | 13.069                | 0.545                |
| Li P I Br      | 10.723        | 0.156       | Li Zn N I  | 11.814         | 0.337                 | Li Ca N F            | 13.073                | 0.546                |
| Li Si S F      | 10.724        | 0.156       | Li Zr O I  | 11.827         | 0.339                 | Li Ta Br F           | 13.12                 | 0.554                |
| Li Zn O Br     | 10.73         | 0.157       | Li Y Br Cl | 11.83          | 0.34                  | Li Ta N S            | 13.134                | 0.556                |
| Li Sn I Cl     | 10.731        | 0.157       | Li Y S O   | 11.847         | 0.342                 | Li Y N I             | 13.147                | 0.558                |
| Li Si I Br     | 10.749        | 0.16        | Li Sr S Cl | 11.899         | 0.351                 | Li Ba S Br           | 13.156                | 0.56                 |
| Li P Cl F      | 10.764        | 0.163       | Li La S Cl | 11.9          | 0.351                | Li Ta N Cl           | 13.188                | 0.565                |
| Li Si Cl F     | 10.79         | 0.167       | Li Al N I  | 11.907         | 0.352                 | Li Sr I F            | 13.196                | 0.566                |
| Li P O I       | 10.808        | 0.17        | Li Ca S F  | 11.907         | 0.352                 | Li La I F            | 13.197                | 0.566                |
| Li Al O Br     | 10.831        | 0.174       | Li Y O Cl  | 11.907         | 0.352                 | Li Ba Br Cl          | 13.21                 | 0.569                |
| Li Si O I      | 10.834        | 0.175       | Li B Br F  | 11.911         | 0.353                 | Li Ba S O            | 13.225                | 0.571                |
| Li Mg O Br     | 10.84         | 0.175       | Li Mg N I  | 11.915         | 0.354                 | Li Ba O Cl           | 13.279                | 0.58                 |
| Li Zn S F      | 10.859        | 0.179       | Li B N S   | 11.926         | 0.356                 | Li Ta I F            | 13.316                | 0.586                |
| Li Zr S Cl     | 10.871        | 0.181       | Li Ca I Br | 11.93          | 0.356                 | Li Sr N Br           | 13.317                | 0.586                |
| Li Sn O Br     | 10.882        | 0.182       | Li Sn N I  | 11.953         | 0.36                  | Li La N Br           | 13.318                | 0.587                |
| Li Zn I Br     | 10.885        | 0.183       | Li Ca Cl F | 11.967         | 0.362                 | Li Ba S I            | 13.352                | 0.592                |
| Li Zn Cl F     | 10.925        | 0.19        | Li N P F   | 11.982         | 0.365                 | Li Sr N O            | 13.386                | 0.598                |
| Li Al S F      | 10.96         | 0.195       | Li B N Cl  | 11.986         | 0.366                 | Li La N O            | 13.387                | 0.598                |
| Li Mg S F      | 10.968        | 0.197       | Li Y S I   | 11.988         | 0.366                 | Li Ba I Cl           | 13.405                | 0.601                |
| Li Zn O I      | 10.969        | 0.197       | Li Si N F  | 12.006         | 0.369                 | Li Y N F             | 13.429                | 0.605                |
| Li Al I Br     | 10.985        | 0.2         | Li Ca O I  | 12.007         | 0.369                 | Li Ta N Br           | 13.437                | 0.606                |
| Compound            | Value 1 | Value 2 | ... | Value 9 | Value 10 |
|---------------------|---------|---------|-----|---------|----------|
| Li Mg I Br          | 10.994  | 0.201   |     | Li Sr N I | 13.511   |
| Li B S Br           | 11.006  | 0.203   |     | Li La N I | 13.511   |
| Li Sn S F           | 11.01   | 0.204   |     | Li Ba O Br | 13.526   |
| Li Al Cl F          | 11.025  | 0.206   |     | Li Ta N I | 13.628   |
| Li Mg Cl F          | 11.033  | 0.208   |     | Li Ba S F | 13.629   |
| Li Sn I Br          | 11.035  | 0.208   |     | Li Ba I Br | 13.65    |
| Li Ca S Cl          | 11.066  | 0.213   |     | Li Ba Cl F | 13.682   |
| Li P Br F           | 11.067  | 0.213   |     | Li Ba O I | 13.717   |
| Li Al O I           | 11.068  | 0.213   |     | Li La S Br | 13.785   |
| Li B Br Cl          | 11.071  | 0.214   |     | Li La N F | 13.786   |
| Li Sn Cl F          | 11.075  | 0.214   |     | Li Ta N F | 13.901   |
| Li Mg O I           | 11.077  | 0.215   |     | Li Ba Br F | 13.922   |
| Li N P S            | 11.083  | 0.216   |     | Li Ba N S | 13.934   |
| Li B S O            | 11.089  | 0.217   |     | Li Ba N Cl | 13.986   |
| Li Si Br F          | 11.093  | 0.217   |     | Li Ba O F | 13.987   |
| Li Si N S           | 11.109  | 0.22    |     | Li Ba I F | 14.107   |
| Li Sn O I           | 11.118  | 0.222   |     | Li La S O | 12.25    |
| Li N P Cl           | 11.148  | 0.227   |     | Li Ca N S | 12.255   |
| Li P O F            | 11.15   | 0.227   |     | Li Ba N O | 14.285   |
| Li Zr S Br          | 11.172  | 0.23    |     | Li Ba N I | 14.402   |
| Li Si N Cl          | 11.173  | 0.231   |     | Li Zr I F | 12.277   |
| Li Si O F           | 11.175  | 0.231   |     | Li Y S F | 12.296   |
| Li Zn Br F          | 11.224  | 0.239   |     | Li Zr O Cl | 13.07    |
| Li Zr Br Cl         | 11.236  | 0.241   |     | Li Sr O Cl | 13.07    |
| Li B S I            | 11.24   | 0.242   |     | Li La O Cl | 12.308   |
| Li Zn N S           | 11.24   | 0.242   |     | Li Ca N Cl | 12.313   |
| Li Zr S O           | 11.253  | 0.244   |     | Li Ca O F | 12.315   |

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| Compound              | Conductivity (S·cm⁻¹)                      | Reference          |
|-----------------------|---------------------------------------------|--------------------|
| Li₂SiS₃               | 2 × 10⁻⁶ (25°C)                             | Ahn et al.²⁷       |
| Li₄SiS₄               | 5 × 10⁻⁸ (25°C)                             | Ahn et al.²⁷       |
| Li₂ZnCl₄              | 8.1 × 10⁻⁹ (200°C)                          | Lutz et al.²⁸      |
| Li₂MgCl₄              | ~10⁻⁵ (25°C)                               | Kanno et al.²⁹     |
| Li₃AlS₃               | 1.3 × 10⁻⁸ (25°C)                           | Gamon et al.³⁰     |
| Li₃AlS₄               | 9.7 × 10⁻⁹ (25°C)                           | Lim et al.³¹       |
| Li₄SnS₄ orthorhombic  | 7.0 × 10⁻⁵ (25°C)                           | Kaib et al.³²      |
| Li₄SnS₄ hexagonal     | 1.1 × 10⁻⁴ (25°C)                           | Kanazawa et al.³³  |
| Li₀₈Sn₉₈S₂             | 1.5 × 10⁻² (25°C)                           | Holtzmann et al.³⁴ |
| Li₂SnS₃               | 1.5 × 10⁻⁵ (25°C)                           | Brant et al.³⁵     |
Experimental phase diagram evaluation

Using the results from experiments #2 and #6, the composition of Phase A can be averaged considering the molar ratio of impurities present in each sample (#2: Li_{0.8}Sn_{0.8}S_{2}/LiCl = 0.9; #6: SnS_{2}/LiCl ~ 0.05), determined by the Rietveld method. The relative weight fractions of impurities derived from Rietveld refinement on these two samples were used to form a system of equations and determine the subsequent composition to make. The intersection of the two lines derived from equations: Li_{3}SnS_{3}Cl – x \times (0.9 \times Li_{0.8}Sn_{0.8}S_{2} + LiCl) and Li_{11}SnS_{3}Cl_{9} – x \times (0.05 \times SnS_{2} + LiCl) (short and long yellow lines, respectively, on Figure 2b) gives a composition close to Li_{3.6}SnS_{3.6}Cl_{0.4}.

Supplementary Table 5. Compositions, sample code in Figure 2b (main text) and phases obtained after reaction in a sealed quartz tube at 700 °C for 12 hours identified by XRD.

| Sample code | Composition       | Phases identified by XRD               |
|------------|-------------------|---------------------------------------|
| #1         | LiSnS_{2.33}Cl_{0.33} | Li_{0.8}SnS_{2}                        |
|            |                   | LiCl                                  |
|            |                   | Li_{2}SnS_{3}                        |
| #2         | Li_{3}SnS_{3}Cl    | Phase A                               |
|            |                   | Li_{0.8}Sn_{0.8}S_{2}, LiCl            |
|            |                   | (Li_{0.8}Sn_{0.8}S_{2}/LiCl = 0.9)    |
| #3         | Li_{1.5}SnS_{1.5}Cl_{2.5} | SnS_{2}                              |
|            |                   | LiCl                                  |
| #4         | Li_{8}SnS_{4}Cl_{4} | Li_{3}S                               |
|            |                   | LiCl                                  |
|            |                   | Li_{4}SnS_{4}                        |
| #5         | Li_{1.67}SnS_{0.33}Cl_{5} | SnS_{2}                              |
|            |                   | LiCl                                  |
| #6         | Li_{11}SnS_{3}Cl_{9} | Phase A                               |
|            |                   | LiCl, SnS, S(am)                      |
|            |                   | (SnS_{2}/LiCl = 0.05)                |
Supplementary Figure 6. Laboratory XRD patterns of samples. a #2, b #6 and c #7 made in the Li-Sn-S-Cl phase field (cf. Figure 2b and Supplementary Table 5), synthesized in sealed quartz tubes at 700 °C for 12 h. Known phases are denoted with signs defined in the legend. Phase A is denoted with the “∗” sign.
Crystal structure determination

The observed reflections for the SXRD pattern of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ indicated the presence of a 6$_3$ screw axis and a c glide plane, therefore leaving the possibility for the three space groups $P6_3mc$, $P6\bar{2}c$ and $P6_3/mmc$ (extinction symbol $P-\overline{c}$).$^{36}$ The presence of a minor impurity of orthorhombic Li$_4$SnS$_4$ was identified in the SXRD pattern and this phase was included in the refinement. The final refinement yields no more than 4 wt% of this phase.

A preliminary structural model based on the wurtzite structure (space group $P6_3mc$) in which S and Cl atoms share the anion site in a S/Cl = 3.3/0.7 ratio (site occupancy factor, sof, for S and Cl of 0.825 and 0.175, respectively), and where the cation site is partially occupied by Sn and Li, with sof of 0.25 and 0.75, respectively, was used. The remaining Li atoms were omitted in the first step of the refinement. After refining cationic and anionic positions and isotropic displacement parameters, a good fit against SXRD data was obtained, revealing appropriate positions for the heavier atoms Sn, S/Cl in the Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$ structure.

The screening of the Fourier difference map using the NPD data, revealed the presence of a negative nuclear density in the octahedral interstice of the anion sublattice (Supplementary Fig. 7). A lithium atom was added in this position and its occupancy refined to 0.092(8) while the goodness of fit for the refinement, $\chi^2$, decreased from 9.53 and 6.90 to 5.69 and 1.59 for Banks 4 and 5, respectively.

A Rietveld refinement using a structural model containing a Li atom on the T$^-$ site was envisaged (constraining the overall occupancy of the T$^+$-T$^-$ face shared unit to be less than 1). However, at such low occupancy, the error obtained on the refined sof was too high (sof = 0.01(2)) for this site to be kept in the final structural model. The position, displacement parameters and sof of all atoms were then refined simultaneously constraining the composition to be charge-neutral, with no constraint of full occupancy for the anion site, and this yielded the final model. The outcome of the
refinement is presented in Supplementary Table 6 and Supplementary Table 7.

The final refined composition is \( \text{Li}_{3.41(4)}\text{SnS}_{3.29(3)}\text{Cl}_{0.70(3)} \), close to the measured composition \( \text{Li}_{3.305(14)}\text{Sn}_{1.000(9)}\text{S}_{3.317(44)}\text{Cl}_{0.6269(8)} \) as determined by ICP-AES. Measurements from SEM-WDX (cf. Methods) show that the material is homogeneous and yields a measured elemental ratio of 1.000(6):3.57(4):0.61(4) for Sn:S:Cl which agrees well the expected values of 1:3.3:0.7 and confirming the assumption required for the multiple source refinement of anion occupancies that S and Cl are the only elements occupying the anion sites.

**Supplementary Figure 7.** Fourier difference map from the refinement of the NPD data from Bank 4 of Polaris using: a the wurtzite structural model for \( \text{Li}_{3.3}\text{SnS}_{3.3}\text{Cl}_{0.7} \), showing the negative nuclear density at the octahedral site of the anion sublattice and b Fourier difference map after refining Li occupancy in the octahedral interstice.

**Supplementary Table 6.** Summary of the outcome of the refinement of \( \text{Li}_{3.3}\text{SnS}_{3.3}\text{Cl}_{0.7} \) against synchrotron X-ray powder diffraction (SXRD) and neutron powder diffraction (NPD) data.

| Radiation | NPD Bank 4 | NPD Bank 5 | SXRD |
|-----------|------------|------------|------|
| Refined composition | \( \text{Li}_{3.41(4)}\text{SnS}_{3.29(3)}\text{Cl}_{0.70(3)} \) | | |
| Formula weight (g·mol\(^{-1}\)) | | 272.69 | |
| Space group | | \( P6_3\text{mc} \) | |
| \( Z \) | | 2 | |
| Density (g·cm\(^{-3}\)) | | 2.570 | |
| Temperature (K) | | 298 | |
### Supplementary Table 7. Crystal structure of Li$_3$SnS$_3$Cl$_{0.7}$.

| Site | x | y | z | $B_{iso}$ (Å$^2$) | sof | $\chi^2$ | $\rho_{\text{min./max.}}$ res. (fm/e$^\cdot$Å$^{-3}$) | Wyckoff position |
|------|---|---|---|------------------|-----|---------|---------------------------------|------------------|
| S    | 1/3 | 2/3 | 0.378(3) | 2.5(4) | 0.823(8) | 5.69 | -0.01 / 0.02 | 2b               |
| Cl   | 1/3 | 2/3 | 0.378(3) | 1.2(3) | 0.175(8) | 5.57 | -0.02 / 0.03 | 2b               |
| Sn   | 1/3 | 2/3 | 0 | 2.4(4) | 0.242(3) | 3.72 | -0.87 / 1.19 | 2b               |
| Li1  | 1/3 | 2/3 | -0.013(1) | 3.3(5) | 0.760(3) | 3.72 | -0.87 / 1.19 | 2b               |
| Li2  | 0  | 0  | 0.079(4) | 3.3(5) | 0.092(8) | 0.57379 - 22.61176 | -0.02 / 0.03 | 2b               |

#### Crystal Structure Data

| Angle (°) / Wavelength (Å) | 92.590 | 146.720 | 0.82637 |
|---------------------------|--------|---------|---------|
| $d$ spacing range (Å)     | 0.74043 - 3.66017 | 0.54095 - 2.56047 | 0.57379 - 22.61176 |
| TOF (μsec.) / $2\theta$ range | 1107.354858 - 19937.962891 | 1103.836304 - 19944.859375 | 2.084000 - 92.116005 |
| TOF (μsec.) / $2\theta$ (°) step | 6.5135 | 3.2546 | 0.004000 |
| No. of reflections | 162 | 326 | 220 |
| No. of data | 2893 | 5791 | 22509 |
| No. of refined parameters | 16 (profile) | 18 (profile) |
| $a$ (Å) | 3.9723(3) | 3.9723(3) |
| $b$ (Å) | 6.3524(6) | 6.3524(6) |
| Volume (Å$^3$) | 87.06(2) | 87.06(2) |
| $R_p$ | 9.36 | 10.8 | 17.4 |
| $R_{wp}$ | 8.87 | 10.6 | 15.7 |
| $R_{exp}$ | 3.72 | 8.42 | 2.00 |
| $R_{Bragg}$ | 5.57 | 4.53 | 7.95 |
| $\chi^2$ | 5.69 | 1.59 | 61.8 |
| $\rho_{\text{min./max.}}$ res. (fm/e$^\cdot$Å$^{-3}$) | -0.01 / 0.02 | -0.02 / 0.03 | -0.87 / 1.19 |
Supplementary Table 8. Selected interatomic distances and angles for Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$.

| Atom | Distance around atom (Å) | Angles around atom (°) | Coordination |
|------|--------------------------|------------------------|--------------|
| Sn   | S/Cl 2.4016(3) ×3        | S/Cl Sn S/Cl           | 4            |
| Sn   | S/Cl 2.4207(3)           | S/Cl Sn S/Cl           | 110.27(2) ×3 |
| Li1  | S/Cl 2.3961(3) ×3        | S/Cl Li1 S/Cl          | 4            |
| Li1  | S/Cl 2.4823(3)           | S/Cl Li1 S/Cl          | 111.98(2) ×3 |
| Li2  | S/Cl 2.9781(3) ×3        | S/Cl Li2 S/Cl          | 3            |
| Li2  | S/Cl 2.6246(2) ×3        | S/Cl Li2 S/Cl          | 169.46(2) ×3 |
|      |                          | S/Cl Li2 S/Cl          | 98.35(2) ×3  |

Supplementary Figure 8. Elemental analysis via SEM-WDX and ICP-AES on Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$  

a shows datapoints collected from 15 different areas (black squares) and the expected composition of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ (orange circle) showing that the composition measured by WDX agrees well with that expected and that the composition is homogeneous throughout the material. Analysis by WDX yields an averaged measured ratio of 1.000(6):3.57(4):0.61(4) for Sn:S:Cl close to the expected values of 1:3.3:0.7. The composition of Li$_{3.305(14)}$Sn$_{1.000(9)}$S$_{3.317(44)}$Cl$_{0.6269(8)}$ measured by ICP-AES (blue triangle) also agrees well with the expected values. b shows an example WDX spectrum measured from one of the fifteen areas with peaks observed for Sn, Cl and S.

Li ion dynamics

AC-Impedance spectroscopy

The first shoulder appearing at high frequency on the Nyquist plot on Figure 4a (main text)
corresponds to the contribution of the bulk conductivity whereas the semicircle at lower frequency is characteristic of the grain boundary response to the conductivity. Despite both semicircles not being fully resolved, it is possible to fit the data using an equivalent circuit taking both contributions into account (inset Figure 4a). The estimated capacitances from the value of the admittance of the Constant Phase Element (CPE) using Hsu and Mansfeld’s equation, are $3.2(6) \times 10^{-12}$ F and $1.1(2) \times 10^{-11}$ F, for the first and second semi-circles, respectively, which are consistent with bulk and grain boundary contributions. AC-impedance was measured over the temperature range 30-125 °C and the bulk conductivity was extracted at each temperature in the same way as described above for the room temperature conductivity.

Supplementary Figure 9. AC-impedance response of Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$ from 30 to 125 °C. a Nyquist plots of the impedance response at variable temperature of Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$. b Nyquist plot at 75°C and fit using the equivalent circuit shown in Figure 4a (see Main Text).

The results of these fits are shown in Supplementary Table 9.

Supplementary Table 9. Results of the fits to the impedance data collected in the 30-125 °C temperature range on a cylindrical pellet of Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$ with surface $S = 0.50(5)$ cm$^2$ and thickness $e = 0.10(1)$ cm.

| Temp °C | $\chi^2$ | $R_{\text{bulk}}$/Ω | $Q_{\text{bulk}}$ | $m_{\text{bulk}}$ | $R_{\text{GB}}$/Ω | $Q_{\text{GB}}$ | $n_{\text{GB}}$ |
|--------|---------|----------------|----------------|----------------|----------------|-------------|-------------|
| 110    | $3.59 \times 10^{-5}$ | $8.7(1) \times 10^3$ | -- | -- | $5.28 \times 10^4$ | $5.9(1) \times 10^{-11}$ | 0.859(2) |
Determination of the electronic conductivity through DC polarization measurements

Determination of the electronic conductivity contribution was performed through DC polarization measurements, which consist of applying a steady voltage while measuring the current response as a function of time. The value of the current at \( t = 0 \) accounts for both ionic and electronic conductivities and then it decreases exponentially as the ions polarize at the ion blocking electrode (Supplementary Fig. 10a-e). At \( t = \infty \), all ions are polarized, and only electrons contribute to the conductivity. Changing the value of the steady voltage and recording the value of the current after long enough equilibrium time enables construction of the I-V curve. The value of the electronic conductivity is then extracted through Ohm’s law (Supplementary Fig. 10f). At room temperature, the electronic conductivity is \( \sigma_e = 1.1(1) \times 10^{-8} \text{ S cm}^{-1} \). The electronic conductivity therefore contributes to around 1% of the total conductivity (\( \sigma_{tot} = 12.4(1) \times 10^{-6} \text{ S cm}^{-1} \)) and can be considered negligible.

|   | \( 5.01 \times 10^{-5} \) | \( 1.40(2) \times 10^4 \) | -- | -- | \( 1.14(3) \times 10^4 \) | \( 6.1(2) \times 10^{-11} \) | 0.849(2) |
|---|-----------------------------|----------------------------|---|---|-----------------------------|----------------|----------|
| 90 | \( 1.40 \times 10^{-5} \) | \( 3.13(6) \times 10^4 \) | -- | -- | \( 2.62(7) \times 10^4 \) | \( 5.27(9) \times 10^{-11} \) | 0.853(2) |
| 70 | \( 5.76 \times 10^{-3} \) | \( 9(1) \times 10^4 \) | \( 1.0(2) \times 10^{-10} \) | 0.76(1) | \( 6(2) \times 10^5 \) | \( 4.8(9) \times 10^{-11} \) | 0.85(2) |
| 50 | \( 5.64 \times 10^{-3} \) | \( 1.4(2) \times 10^5 \) | \( 2.8(6) \times 10^{-11} \) | 0.84(2) | \( 1.80 \times 10^6 \) | \( 6.6(1) \times 10^{-11} \) | 0.81(2) |
Supplementary Figure 10. a-e I-t curve measured at different steady applied voltages (value in legend) and f I-V curve of the electronic contribution. A fit using Ohm’s law yields a total electronic conductivity $1.1(1) \times 10^{-8}$ S cm$^{-1}$.

Prior to the DC polarization, EIS measurements were performed at room temperature using a Biologic VSP-300 potentiostat/galvanostat, which enables the collection of the impedance spectra down to a low frequency of 1 mHz, permitting visualization the Warburg tail at low frequency region (Supplementary Fig. 11). Fitting of the data points using a (R-CPE) equivalent electrical circuit yields a total conductivity of $1.0(4) \times 10^{-6}$ S cm$^{-1}$ close to the value obtained using the
Keysight instrument (data collected to 20 Hz, cf. Figure 4, main text).

**Supplementary Figure 11.** EIS of the Au|Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$|Au ion-blocking electrode measured at room temperature from 3 MHz to 1 mHz. The red line corresponds to the fit of the data points using a (R-CPE) parallel equivalent electrical circuit yielding $R = 1.55(2)\ \text{M}\Omega$, $Q = 3.87(7)$ and $n = 0.91(1)$.

**Evidence of ionic conductivity and stability against Li metal through Li plating/stripping in a Li|Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$|Li symmetric cell**

The voltage profile of the Li|Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$|Li symmetric cell upon repeated Li plating/stripping at room temperature, 323 K and 343 K over 400 h, is shown in Figure 4e, and Supplementary Fig. 12a. The transport of Li$^+$ through the Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$ solid-state electrolyte, as well as across the Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$|Li$^0$ interface, can be confirmed. An initial polarization of ±1.28 V was observed at a low current density of 10 µA cm$^{-2}$ at room temperature due to the moderate ionic conductivity of the material. At elevated temperatures, the polarization is largely reduced, confirming improved ionic conductivity. The change in overpotential can be used to evaluate the Li|Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$ interfacial reactions and possible degradation of Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$. During the initial 50 h, the overpotential rises gently, in line with the increased diameter of the semicircle over cycling observed from the EIS (Supplementary Fig. 12), indicating the formation of an interphase layer. Interestingly, the
overpotentials remain constant over the subsequent plating/stripping, suggesting a stable interphase layer is formed. This promising result is in contrast with what has been observed in the Sb- and As-doped Li₄SnS₄ material,³⁹,⁴₀ which showed irregular voltage profiles over 20 h. After galvanostatic stripping and plating, the symmetric cell was disassembled. At the Li|Li₃.₃SnS₃.₃Cl₀.₇ interface, the colour of Li₃.₃SnS₃.₃Cl₀.₇ pellet became darker. XRD measurements of Li₃.₃SnS₃.₃Cl₀.₇ material extracted from the bulk pellet and also from this interfacial region show negligible change when compared against the as-synthesised powder (Supplementary Fig. 13). No difference can be seen from the Raman spectra between the cycled bulk pellet and the pristine Li₃.₃SnS₃.₃Cl₀.₇ (Supplementary Fig. 14). However, the dark colour powders scraped from the Li surface show new Raman bands, which can be tentatively assigned to S-S-S bending (i.e., S₈, 158/215 cm⁻¹),⁴¹ Sn-S (185 cm⁻¹),⁴² and SCl₂/S₃⁻ (~525 cm⁻¹)⁴³ that have been observed at the interface between Li⁰ and sulfide-based solid state electrolytes.⁴¹ The mixed S-Cl anion material enhances stability properties against Li metal compared to the monoanionic sulfide Li₄SnS₄ without degrading the ionic conductivity.

Supplementary Figure 12. Galvanostatic Li plating/stripping of a symmetric Li|Li₃.₃SnS₃.₃Cl₀.₇|Li cell. a Enlarged snapshots of voltage profiles at the three studied temperatures. b Electrochemical impedance spectra collected at 50 cycle intervals for the cell shown in Figure 4e.
Supplementary Figure 13. *Ex situ* investigation of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ after galvanostatic Li plating/stripping. Laboratory XRD patterns show comparison between as-synthesized Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$, material extracted from the bulk of the cycled pellet, and powder which was scraped from the interfacial region of the Li|Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$|Li cell. This interfacial powder was mixed with amorphous boron (B) and sealed in a 0.5 mm diameter borosilicate capillary for measurement.

Supplementary Figure 14. *Ex situ* Raman spectra of Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ after galvanostatic Li plating/stripping. Raman microscopy of the as-synthesized pristine Li$_{3.3}$Sn$_{3.3}$Cl$_{0.7}$ (black), the bulk solid electrolyte after cycling (blue), and of the small dark particles within the bulk cycled powder visible under the microscope (red). No peaks were observed in the higher wavenumber regions 700-4000 cm$^{-1}$ for any of the studied materials.
Nuclear Magnetic Resonance Spectroscopy

In static $^7\text{Li}$ solid-state NMR spectra the absence of mobility is displayed through a broadening of the $1/2 \leftrightarrow -1/2$ central transition arising from the strong homonuclear $^7\text{Li}$-$^7\text{Li}$ dipolar coupling interactions. At low temperatures the material is said to be in the rigid lattice regime, in this regime spectra dominated by dipolar broadening are observed. This effect is present at approximately 165 K, where the line width of the central transition is approximately 5.2 kHz for Li$_3$SnS$_3$Cl$_{0.7}$. As the temperature is increased the dipolar interactions are continuously averaged due to the increasing motion of the Li spins causing the spectra to narrow significantly (Supplementary Fig. 9). This effect can be seen by plotting the full width half maximum of the peak in function of the temperature (Figure 4b), where the onset of motional narrowing, $T_{\text{onset}}$ occurs at around 200 K. Using an expression introduced by Waugh and Fedin\textsuperscript{44} relating the onset temperature of motional narrowing with the activation energy of the diffusion process, given by:

$$E_a = 1.67 \times 10^{-3} \ T_{\text{onset}}$$  \hspace{1cm} (Supplementary Equation 4)

an activation energy of approximately 0.3 eV can be estimated for Li$_3$SnS$_3$Cl$_{0.7}$. The peak width decreases significantly as the temperature is increased above $\sim$ 200 K, down to a minimum line width of approximately 750 Hz where the homonuclear dipolar interactions are completely averaged out.

As Li$_3$SnS$_3$Cl$_{0.7}$ appears to be in the fast-motional regime at room temperature, this is a reasonable explanation for the absence of two distinct resonances attributed to the material in the $^6\text{Li}$ MAS NMR spectrum. At room temperature rapid exchange between tetrahedral and octahedral Li sites will occur on the NMR timescale leading to the observation of a single resonance.

The temperature dependence of the $^7\text{Li}$ SLR in the laboratory ($T_1^{-1}$) and rotating frame ($T_{1\rho}^{-1}$)
under static conditions were monitored using the saturation recovery and spin lock pulse sequences. These measurements were performed in order to obtain values for the activation energy, conductivity and dimensionality of the Li diffusion. The SLR $T_{1\rho}^{-1}$ rates are purely induced by diffusion processes initially increasing with temperatures above room temperature before decreasing thereby passing through a maximum at temperatures that are characteristic of the Li correlation rates $\tau^{-1}$ (that is the average Li jump rates $\tau^{-1}$) being equal to the spin-lock frequencies $\omega_1$, i.e. $2\omega_1 \approx \tau^{-1} = \tau^{-1}$. Accessing these maxima at different $\omega_1$ enables different NMR-derived jump rates $\tau^{-1}$ to be obtained at different temperatures (Figure 4c). $\tau^{-1}$ from NMR line narrowing experiments and relaxometry experiments are plotted against reciprocal temperature in Supplementary Fig. 9. Fitting to $\tau^{-1} = \tau_0^{-1} \exp(-E_a/(RT))$ yields an activation barrier of 0.23(6) eV for Li$_3$SnS$_3$Cl$_{0.7}$.

The dimensionality of the Li$^+$ ion diffusion can be accessed from the frequency-dependence of the high temperature limits of the SLR $T_{1\rho}^{-1}$ values and follows characteristic relationships with one, two, and three-dimensional diffusion in solids being proportional to $(\tau/\omega)^{0.5}$, $\tau \ln(1/\omega \tau)$, or $\tau$, respectively (where $\tau$ and $\omega$ are the correlation times and probe frequencies, respectively) for which the corresponding fit is shown at various temperatures in Supplementary Fig. 17. NMR conductivity $\sigma_{NMR}$ can be estimated from the Li jump rates $\tau^{-1}$ using the combined Nernst-Einstein and Einstein-Smoluchowski equations:

$$\sigma_{NMR} = \frac{f}{H_R} \frac{N_{CC}q^2a^2}{N_{NN}k_BT} \frac{1}{\tau}$$

(Supplementary Equation 5)

where $f/H_R$ is the correlation factor and Haven ratio (1 for uncorrelated motion), $N_{CC}/N_{NN}$ is the number of charge carriers per unit cell volume (0.092 Å$^{-3}$), $q$ is the ionic charge of Li, $a$ is the closest Li-Li jump distance at room temperature (2.4 Å), extracted from the crystal structure determined via diffraction experiments.
Supplementary Figure 15. $^7$Li NMR spectra as a function of temperature for Li$_{3.3}$SnS$_{3.3}$Cl$_{0.7}$.

Supplementary Figure 16. Arrhenius plot of Li jump rates $\tau^{-1}$. Data were extracted from the onset of $^7$Li line narrowing of the variable temperature $^7$Li NMR spectra (black circle, Figure 4b) and SLR rates in the rotating frame ($T_1^\rho$) experiments (Figure 4c) at spin lock frequencies $\omega_1/2\pi$ of 15 (red triangle), 45 (green inverted triangle) and 80 kHz (purple diamond), respectively. The black error bar associated with the temperature is calculated from the broadening of the isotropic peak of the chemical shift thermometer Pb(NO$_3$)$_2$ as explained above. Errors in the jump rate $\tau^{-1}$ are within the
Supplementary Figure 17. Frequency dependence of the NMR SLR $T_1^{-1}$ rates at 425, 415, 395 and 385 K for one, two and three-dimensional models, at spin lock frequencies $\omega_1/2\pi$ of 15 (red triangle), 45 (green inverted triangle), 80 kHz (purple diamond), and average Li+ jump times $\tau$ from $T_1^{-1}$ maxima (Figure 4c). The solid lines correspond to linear fits of $(\tau/\omega)^{0.5}$ and $\tau\ln(1/\omega\tau)$ for one and two-dimensional diffusion, respectively. The frequency dependence of the SLR $T_1^{-1}$ rates (also shown in Figure 4c) clearly rules out the possibility of three-dimensional diffusion. Errors in the spin-lock frequencies $\omega_1$ are estimated to be 10% while the errors in the correlation time $\tau$ are extracted from the fit in Supplementary Fig. 16. Errors in $T_1^{-1}$ are obtained from the outputs of the fits to Supplementary Equation 3.

Supplementary Table 10. Previously reported Li pathways in hcp sulphides described in terms of interstitial site occupancy and dimensionality.

| Composition | Interstitial site involvement in the hopping pathway$^{45}$ | Dimensionality | References |
|-------------|----------------------------------------------------------|----------------|------------|
| $\gamma$-Li$_3$PS$_4$ | T – T (in the (ac) plane) | 2D | Pan et al.$^{46}$ |
| Li$_4$GeS$_4$ | O – T – O (along $b$) | 1D | Al-Qawasmeh et al.$^{47}$ |
| Li$_4$SnS$_4$ | T – O – T (along $b$) | 3D | Al-Qawasmeh et al.$^{47}$ |
Exploration of Li-Mg-S-Cl quaternary phase fields

Computational and Experimental Results

Li-Mg-S-Cl is ranked #4 in the list of unexplored phase fields by the variational autoencoder (Supplementary Table 3). Compositions in this phase field were sampled computationally prior to synthesis using a method similar to that described in the main text, identifying a low energy region which lead to the discovery of new compounds (Supplementary Fig. 18). The variational autoencoder identified and ranked highly this series of compounds that had not been discovered in the previous four decades since the initial report of ionic conductivity in Li_2MgCl_4.\textsuperscript{50,51}
Supplementary Figure 18. Computational and experimental exploration of Li-Mg-S-Cl phase field. Contour plot of energy above the convex hull for the computationally explored set of compositions (white squares) in the Li-Mg-S-Cl phase field. The compositions marked by blue squares were successfully synthesized as single-phase powders through a conventional solid-state route, whilst the compositions shown by cyan squares were single-phase only after quenching.

Experimental syntheses were carried out by grinding LiCl (Merck, 99.99%), Li₂S (Merck, 99.98%) and MgCl₂ (Merck, 99.9%) together with a pestle and mortar before pressing into pellets and sealing in carbon-coated evacuated (<10⁻⁴ mbar) sealed silica ampoules and heating to 600 °C for 12 hrs using heating and cooling rates of 5°C min⁻¹. Powder XRD patterns measured from samples of these low computed energy compositions indicate successful formation of new single-phase materials which can be accessed through Li₂-2xMg₁+x+yCl₄-ySy, where x = 0, 0.125 and 0.25, and y ≤ 0.5. These compositions maintain a total anion content of 4, but introduce cation vacancies up to a maximum content of 0.25 (8.3% of the total number of cations). All of the observed reflections in powder patterns from the new Li₂-2xMg₁+x+yCl₄-ySy series can be indexed to a cubic unit cell with space group symmetry Fd3m (Supplementary Fig. 19).

Supplementary Figure 19. Pawley fit of Li₁.₅Mg₁.₃₇₅Cl₃.₇₅S₀.₂₅. Pawley fit of XRD data measured from Li₁.₅Mg₁.₃₇₅Cl₃.₇₅S₀.₂₅ with Iobs (red dots), Icalc (black line), Iobs - Icalc (blue line), and Bragg reflections (black tick marks).

A solubility limit exists within the new Li₂-2xMg₁+x+yCl₄-ySy series. Six compositions were synthesized using the conditions described above, shown by blue squares in Supplementary Fig.
Synthesis attempts at other compositions (green squares and triangles in Supplementary Fig. 20a) were unsuccessful, resulting in significant amounts of MgS or MgCl$_2$ as secondary phases and no further change in lattice parameter of the majority cubic phase. Quenching of powder samples by placing sealed tubes into a water bath from synthesis temperature, rather than cooling at a controlled rate, was used to promote further solubility of Mg through entropic mechanisms. This enabled the isolation of two further compositions (cyan squares in Supplementary Fig. 20a) increasing the solubility of Mg to Li$_{1.375}$Mg$_{1.5}$Cl$_{3.625}$S$_{0.375}$ or increasing the cation vacancy content $x = 0.25$ in the compound Li$_{1.375}$Mg$_{1.375}$Cl$_{3.875}$S$_{0.125}$. Incorporation of 1.5Mg and 0.25 vacancies per formula unit of Li$_2$MgCl$_4$ is a significant increase compared to a previous study which indicated the solubility limit was Li$_{1.6}$Mg$_{1.2}$Cl$_4$ with 0.2 cation vacancies, and directly results from anion mixing via incorporation for the second anion (S$^{2-}$) originally identified and ranked by the variational autoencoder.

The phase pure Li$_{2-2x}$Mg$_{1+x+y}$Cl$_{4-y}$S$_y$ materials ($x = 0, 0.125$ and $0.25$ and $y \leq 0.5$; Supplementary Table 11) obtained through these synthesis methods all obey Vegard’s law where extracted lattice parameters follow a linear trend as a function of doping. Replacement of Cl$^-$ for S$^{2-}$, Li$^+$ for Mg$^{2+}$ and introduction of cation vacancies all play a role in these behaviours (Supplementary Fig. 20b and c). Monotonic decreases in lattice parameter are observed with increasing $y$ (S content) for samples with the same number of cation vacancies; the effect of substituting Li$^+$ with smaller Mg$^{2+}$ ($r_{Li^+} = 0.76$ Å, $r_{Mg^{2+}} = 0.72$ Å) is more significant that the lattice expansion expected from replacing Cl$^-$ with S$^{2-}$ ($R_{Cl^-} = 1.81$ Å, $r_{S^{2-}} = 1.84$ Å$^2$). A monotonic decrease in lattice parameter is observed with increasing $x$ (cation vacancy content) at fixed $y$ (S content) also, highlighting the impact of cation
vacancies on unit cell size in these materials with a cubic close-packed anion lattice.

Supplementary Figure 20. Solubility limit of Mg in Li_{2-2x}Mg_{1+x+y}Cl_{4-y}S_y and lattice parameters. a Low energy region of Li-Mg-S-Cl computed phase field showing attempted and successful synthesis. Compositions shown as blue squares were synthesized as single-phase powders through a conventional solid-state route, whilst the compositions shown as cyan squares were single-phase only after quenching. Green squares and triangles represent unsuccessful synthesis attempts. Black line represents proposed solubility limit of Mg and cation vacancies in Li_{2-2x}Mg_{1+x+y}Cl_{4-y}S_y accessible through conventional solid-state routes. Labels infer x and y in Li_{2-2x}Mg_{1+x+y}Cl_{4-y}S_y, where 0, 1 and 2 correspond to x values (vacancy content) of 0, 0.125 and 0.25, respectively, while A, B, C, D correspond to y values (S content) of 0.125, 0.25, 0.375 and 0.5. b lattice parameters plotted as a function of y (S content) for compositions with no cation vacancies (circles) and 0.125 cation vacancies (diamonds). c lattice parameters plotted as a function of x (cation vacancy content) for compositions with y = 0.125.

Compositions measured through ICP-AES by Mikroanalytisches Labor Pascher (cf. Methods) for each material in the Li_{2-2x}Mg_{1+x+y}Cl_{4-y}S_y series show reasonable agreement with the nominal compositions (Supplementary Table 11); e.g., an overall composition of Li_{1.506(1)}Mg_{1.392(4)}Cl_{3.763(8)}S_{0.237(2)} is obtained for Li_{1.5}Mg_{1.375}Cl_{3.75}S_{0.25}. Though the sulphur content
for each material is slightly underestimated, likely due to the loss of some sulphur through evolutions of H₂S upon dissolution, the results provide clear evidence for combination of multiple anions (Cl and S) in these materials.

Supplementary Table 11. Nominal and measured compositions for phase-pure materials studied in the Li₂₋₂ₓMg₁₊ₓ₊₁S₀ₓCl₄₋₀ₓSy series obtained through ICP-AES. Values are normalised to a total anion content of 4.

| Nominal composition | Code (Fig. S18) | Li    | Mg    | Cl    | S    | Synthesis |
|---------------------|-----------------|-------|-------|-------|-------|------------|
| Li₂MgCl₄            |                 | 2.141(20) | 0.945(4) | 4.000(8) | -     | Solid-state |
| No cation vacancies; x = 0 |
| Li₁.₈₇₅Mg₁.₁₂₅Cl₃.₈₇₅S₀.₁₂₅ | 0A             | 1.989(5) | 1.139(4) | 3.899(31) | 0.101(6) | Solid-state |
| Li₁.₇₅Mg₁.₂₅Cl₃.₇₅S₀.₂₅  | 0B             | 1.697(8) | 1.279(4) | 3.739(10) | 0.207(2) | Solid-state |
| Li₁.₆₂₅Mg₁.₃₇₅Cl₃.₆₂₅S₀.₃₇₅ | 0C             | 1.568(1) | 1.399(4) | 3.689(10) | 0.311(3) | Solid-state |
| Li₁.₅Mg₁.₅Cl₃.₅S₀.₅   | 0D             | 1.471(5) | 1.523(4) | 3.568(34) | 0.432(2) | Solid-state |
| Cation vacancies; x = 0.125 |
| Li₁.₆₂₅Mg₁.₂₅Cl₃.₈₇₅S₀.₁₂₅ | 1A             | 1.705(2) | 1.218(4) | 3.909(39) | 0.091(3) | Solid-state |
| Li₁.₅Mg₁.₃₇₅Cl₃.₇₅S₀.₂₅  | 1B             | 1.506(1) | 1.392(4) | 3.673(8)  | 0.273(2) | Solid-state |
| Li₁.₃₇₅Mg₁.₅Cl₃.₆₂₅S₀.₃₇₅ | 1C             | 1.385(7) | 1.532(4) | 3.700(5)  | 0.300(2) | Quenching  |
| Cation vacancies; x = 0.25 |
| Li₁.₃₇₅Mg₁.₃₇₅Cl₃.₈₇₅S₀.₁₂₅ | 2A             | 1.395(15)| 1.402(4) | 3.959(5)  | 0.041(2) | Quenching  |

Clear evidence for new quaternary materials in the Li-Mg-S-Cl phase field, ranked highly by the VAE (ranked #4, Supplementary Table 3), is provided by the results of synthetic exploration presented here. The series Li₂₋₂ₓMg₁₊ₓ₊₁S₀ₓCl₄₋₀ₓSy (where x = 0, 0.125 and 0.25 and y ≤ 0.5) is discovered through anion mixing and incorporation of cation vacancies.
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