Mechanochemical Synthesis: A Tool to Tune Cation Site Disorder and Ionic Transport Properties of Li₃MCl₆ (M = Y, Er) Superionic Conductors

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The lithium-conducting, rare-earth halides, Li₃MX₆ (M = Y, Er; X = Cl, Br), have garnered significantly rising interest recently, as they have been reported to have oxidative stability and high ionic conductivities. However, while a multitude of materials exhibit a superionic conductivity close to 1 mS cm⁻¹, the exact design strategies to further improve the ionic transport properties have not been established yet. Here, the influence of the employed synthesis method of mechano-chemical milling, compared to subsequent crystallization routines as well as classic solid-state syntheses on the structure and resulting transport behavior of Li₃ErCl₆ and Li₃YCl₆ are explored. Using a combination of X-ray diffraction, pair distribution function analysis, density functional theory, and impedance spectroscopy, insights into the average and local structural features that influence the underlying transport are provided. The existence of a cation defect within the structure in which Er/Y are disordered to a new position strongly benefits the transport properties. A synthetically tuned, increasing degree of this disordering leads to a decreasing activation energy and increasing ionic conductivity. This work sheds light on the possible synthesis strategies and helps to systematically understand and further improve the properties of this class of materials.

1. Introduction

The steadily rising demand for energy storage has led to an increased interest in the field of all solid-state batteries and the field of fast ion-conducting solid electrolytes.[1-2] While the liquid electrolytes that are commonly used in conventional Li-ion batteries contain organic easily flammable solvents, recent progress on solid-electrolyte-based batteries offers the opportunity to explore a safer and similar performing alternative.[3] Prominent representatives are the lithium-conducting garnets such as Li₅La₃Zr₂O₁₂,[4-7] thiophosphate-based Li₁₀GeP₂S₁₂,[8-12] and halide argyrodites Li₃PS₄X (X = Cl, Br, and I),[13-16] as well as amorphous phases within the Li₅S-P₂S₅ system.[17-22] While these solid electrolytes are being used in solid-state batteries, the interface behavior in contact to different electrode materials and the need for large-scale processability remain a challenge.[21-27] Nevertheless, despite their higher sensitivity to decomposition in atmosphere and at higher oxidative potentials,[28] thiophosphates have shown promising solid-state battery performance because of their mechanically soft nature and improved processability.[12,29,30]

Challenged by the oxidative instability of the thiophosphate-based electrolyte, recently, the rare-earth halides Li₃YM₆ (X = Cl, Br) have attracted interest as they exhibit high ionic conductivity on the order of 1 mS cm⁻¹ and have been reported to exhibit an enhanced oxidative stability to higher potentials.[31,32] In addition, by combining multiple descriptors[33] for fast ionic motion along with the need for high stability, LiₓErCl₆,[31] LiₓLaI₆,[34] and LiₓInCl₆[35] were found to exhibit a high ionic conductivity. However, none of these materials are novel in itself as the work on the AₓInCl₆ (A = Na, K, Ag, Tl) systems dates back as far as 1967.[36] The rare earth analogue containing yttrium (Y) gained interest in 1992,[37] when Steiner et al. identified AₓMCl₆ (A = Li, Na, Ag, M = In, Y) to be good ionic conductors with an ionic conductivity of around 0.2 S cm⁻¹ at 300 °C for LiₓInCl₆.

Using single-crystal diffraction data, Steiner et al.[37] proposed an orthorhombic unit cell for LiₓYCl₆, while recent studies suggest a trigonal unit cell for LiₓYCl₆ and the...
The structures of $\text{Li}_3\text{MCl}_6$ ($\text{M} = \text{Y, Er};$ space group $\text{P}3\text{m}1$) can be described as $\text{MCl}_6^{3−}$ octahedra forming a trigonal lattice (Figure 1), where the Wyckoff position 1a are occupied by $\text{M}$. In addition, two $\text{M}2$ atoms occupy the Wyckoff 2d position located in the (002) plane (Figure 1b) and also form $\text{MCl}_6^{3−}$ octahedra. In the fully ordered structure the occupancy of $\text{M}2$ would be equal to 100%. However, suggested by Asano et al.\cite{31} and previously shown in single-crystal X-ray diffraction,\cite{38} there seems to exist a site disorder, in which some previous $\text{M}2$ cations are located on another $\text{M}3$ position. This new $\text{M}3$ site can be regarded as the $\text{M}2$-equivalent position in the (001) plane, i.e., translated by half a unit cell in the $z$-direction (see Figure 1). The existence of this $\text{M}2$–$\text{M}3$ disorder can be viewed as chains of face-sharing $\text{MCl}_6^{3−}$ octahedra perpendicular to the (002) plane (Figure 1c), however, a neighboring occupancy of erbium or yttrium is unlikely due to strong repulsion. Recent experimental work on $\text{Li}_3\text{YCl}_6^{\text{3−}}$ and $\text{Li}_3\text{ErCl}_6^{\text{3−}}$ suggests an influence of the synthesis procedure on the site disorder and with a higher disorder a beneficial influence on the ionic transport.\cite{31,33} In contrast, theoretical work suggests that disorder, in this case antisite disorder, is detrimental to the ionic conductivity.\cite{32} However, whereas the experimental work suggests $\text{M}2$–$\text{M}3$ site disorder, the influence of antisite $\text{M}$–$\text{Li}$ disorder on the ionic conductivity was explored theoretically and represents a defect model with a blockage of the lithium-diffusion channels.

Within the structure, lithium ions occupy the octahedral voids (Wyckoff 6g and 6h) that are formed by the halide ions. Each $\text{MCl}_6^{3−}$ octahedron is surrounded by six lithium ions that form a honeycomb lattice of edge-sharing $\text{LiCl}_6^{5−}$ octahedra in the $a$–$b$ plane (Figure 1c,d). In addition, based on X-ray diffraction data, it seems that the Li positions on 6g within the (001) plane are fully occupied with a partial occupancy of $\text{Li}_2$ on 6h within the (002) plane, suggesting a prevalent diffusion pathway within the (002) plane and along the face-sharing octahedra in the $z$-direction.

Inspired by the fast ion transport,\cite{31,35} the clear but not yet understood influence of the synthesis methods on the ionic transport,\cite{33} and the open question of $\text{Y}$/$\text{Er}$ site disorder,\cite{31,33} here we investigate the influence of the synthesis on the local structure and with it the resulting ionic transport properties. Using a combination of X-ray diffraction, X-ray pair distribution function (PDF) analysis, impedance spectroscopy, and density functional theory (DFT), we show the direct influence of the synthesis methods on the local structure and transport properties. While mechanochemical synthesis leads to a high $\text{M}2$–$\text{M}3$ site disorder up to an almost complete site inversion between the $\text{M}2$ and $\text{M}3$ site, the classic ampoule syntheses only lead to a low degree of this site disorder. By employing different crystallization times, the $\text{M}2$–$\text{M}3$ site disorder is further engineered to affect the lithium-ion transport. This work shows that the synthesis approach affects the local structure, local cationic ordering, and ultimately the ionic transport in these halide-based ionic conductors $\text{Li}_3\text{MCl}_6$ ($\text{M} = \text{Y, Er}$).
2. Results

2.1. Influence of Synthesis on the Structure and Disorder

In order to study the influence of the preparation technique on the resulting transport properties, multiple samples of Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ were synthesized by either a classic solid-state reaction in a quartz ampoule or a mechanochemical approach in a planetary ball mill. In addition, the milled samples were subjected to a subsequent crystallization step with two different crystallization times of 1 min and 1 h for Li$_3$ErCl$_6$. In the case of Li$_3$YCl$_6$, a longer crystallization time of 5 min was needed to crystallize the materials (see Figure S1, Supporting Information). As Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ are isostructural and the ionic radii of Er (89 pm) and Y (90 pm) are nearly identical,[39] the following discussion will only involve the data collected for Li$_3$ErCl$_6$ unless indicated otherwise. All results for Li$_3$YCl$_6$ are shown complementary in the Supporting Information.

X-ray diffraction data were measured to gain insight into the average structure (see Figure 2a). As expected, ball milling leads to a strong broadening of the reflections related to an occurring amorphization. Rietveld refinements of all the crystalline compounds are possible and a representative diffraction pattern of Li$_3$ErCl$_6$ crystallized in 1 h can be found in Figure 2c. The obtained refinement results (lattice parameters and site occupancies) for Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ are given in the Supporting Information. The Rietveld refinement results against the X-ray diffraction data show Er2–Er3 disorder that is the lowest with 2.5(1)% for the classic solid-state synthesis and is significantly higher 9.9(2)% in the ball-milled sample with a subsequent crystallization time of 1 min. Whereas a M$_2$–M$_3$ site disorder can be found here, any refinement models that include antisite disorder between M and Li do not lead to a significant fraction of electron density of Er on the Li positions and antisite disorder can be excluded in the here-investigated materials.

The pair distribution functions $G(r)$ of all samples can be found in Figure 2b for Li$_3$ErCl$_6$ along with a representative refinement after a 1 h crystallization time in Figure 2d. When comparing the pair distribution functions, a decaying peak intensity in the ball-milled (as prepared) $G(r)$ can be found,

![Figure 2. a) Collected X-ray diffraction data and b) calculated pair distribution function $G(r)$ for differently prepared Li$_3$ErCl$_6$ samples. c) Additionally, an example Rietveld refinement against the collected X-ray diffraction data and d) fit for the corresponding, calculated $G(r)$ are shown. While the as-prepared sample shows broad reflections indicating a strong amorphization during ball milling, a seemingly complete crystallization of the ball-milled sample can be achieved within 1 min as observable in the diffraction data and respective $G(r)$.](image)
indicating a lower coherence range in comparison to the annealed samples, further corroborating a lower crystallinity of the materials. However, even within a low r-range up to 8 Å, the peak positions in the G(r) suggest that locally Li₃ErCl₆ has already been formed during the milling process, explaining how a short crystallization time of 1 min can even lead to a fully crystalline material. However, a certain phase fraction of the precursor ErCl₃ can still be found (see Table S1, Supporting Information). Exceeding the range of 8 Å, the remaining, more crystalline precursor ErCl₃ dominates the G(r) due to the low coherence length of the locally formed Li₃ErCl₆. This rapid crystallization within 1 min after mechanochemical milling, while surprising, was recently found to also occur in Li₆PS₅Br,[40] providing further evidence that mechanochemical milling already acts as a primary synthesis step leading to low coherency products and possible preequilibrium clusters.

When considering the G(r) at a low r-range some interesting trends can be found. The peak corresponding to the Er1–Er2 distance of around 7.1 Å is not yet present in the ball-milled (as prepared) sample, while the distance at around 6.5 Å corresponding to the Er1–Er3 distance shows higher intensity compared to the annealed samples (Figure 3a). Qualitatively, these changes in the intensities may be correlated to a M2–M3 site disorder from the aforementioned Er2 to the Er3 site during the ball-milling process. Quantitatively, the refinements of the G(r) show similar trends as the Rietveld refinements above. A site disorder between Er2–Er3 of different percentages can be observed for all samples corroborating that the site disorder is strongly dependent on the crystallization time and synthesis procedure. The varying degree of the ordering is shown in Figure 3b, with all exact values provided in Table S2 (Supporting Information). In addition to the changing disorder, annealing leads to a certain degree of microstructural relaxation as indicated by the reduction of the slope in the Williamson–Hall plots in Figure S2 (Supporting Information).

Overall, the structural analyses via Rietveld refinements and pair distribution function analyses show that with increasing annealing time, the Er2–Er3 site disorder decreases from having an almost full disorder after milling. Hence, by applying elevated temperatures, the degree of disorder changes over time and relaxes into a more, but not yet fully ordered structure.

2.2. The Influence of Synthesis on the Polyhedral Pathways

In addition to the changing site disorder, local distortions of the polyhedra can be found using the pair distribution function analyses. These distortions can be visualized using the triangular transition areas that correspond to the bottleneck for lithium diffusion (shown in Figure 4a) assuming jumps from one polyhedron to the next. The lithium positions and occupancies remain unknown due to the lack of neutron diffraction data and these triangular transition areas are based on the Er and Cl positions that will influence the resulting lithium diffusion behavior.

There are four different jumps possible for diffusion among connected polyhedra: 1) jumps along the z-direction of face-sharing LiCl₆⁵⁻ octahedra, denoted as O₆ (6h)–O₆ (6g) jump. Two possible jumps within the a–b plane in which the LiCl₆⁵⁻ octahedra are connected via edges and jumps need to occur via a tetrahedral transition state.[41] 2) Jumps are possible in the (002) plane which will include the jump from 6h to 6h, here denoted as O₆ (6h)–T₂–O₆ (6h) jump, as well as 3) in the (001) plane which will include the jump from 6g to 6g, here denoted as O₆ (6g)–T₂–O₆ (6g) jump. 4) A fourth jump from T₂–T₂ is possible, but improbable as it corresponds to a jump from one transition state to another. While a full occupancy of the 6g makes O₆ (6g)–T₂–O₆ (6g) unfavorable and unlikely, faster anisotropic diffusion might occur via O₆ (6g)–O₆ (6h) and O₆ (6h)–T₂–O₆ (6h).[32]

Figure 4b shows the four different possible polyhedral transition areas as a function of the obtained Er2–Er3 site disorder and corresponding synthesis methods. While the transition areas between the two tetrahedral sites (T₂–T₂) and the two possible octahedral lithium sites (O₆–O₆, 6h–6g) show no visible change for the annealed samples, a large increase of the areas can be observed for the ball-milled (as-prepared) sample. In addition, the transition areas along the a–b plane...
(O₆–Tₐ–O₆) change significantly with the employed synthesis method. Whereas the transition area of the jump O₆ (6g)–Tₐ–O₆ (6g) decreases with increasing annealing time, the area along O₆ (6h)–Tₐ–O₆ (6h) increases. The large difference between the polyhedra around Wyckoff 6h and 6g in the ball-milled samples suggests that Er disordering leads to strong local distortions, which in turn will likely affect the lithium occupancies due to Coulombic repulsion. Whereas this relationship becomes clear for Li₃ErCl₆, an assessment of the local polyhedral changes in Li₃YCl₆ is not possible due to a large fluorescence-like behavior (see the Experimental Section).

2.3. Energetics of Various Defect Models

Density functional theory was used to assess the thermodynamic possibility of site disorder. Figure 5 shows four possible defect models in a 1 × 1 × 2 supercell with different Er₂–Er₃ disorder and their corresponding energies. The structural models are as follows: structural model 1 corresponds to a Li₃ErCl₆ with Er₁ and Er₂ fully occupied and resembles the fully ordered structure. Disorder model 2 corresponds to a complete site inversion between Er₂ and Er₃ leading to a fully occupied Er₃ site and a fully vacant Er₂ site. Although this

Figure 4. a) Different transition areas for possible lithium diffusion and b) preparation method induced local deformation of structural features. A clear correlation of the obtained Er₂–Er₃ site disorder can be observed for each of the transition areas. Mechanochemical milling introduces local distortions of the structure that can be visualized using the triangular polyhedral-transition areas, which are ultimately related to the lithium diffusion pathway.

Figure 5. Density functional theory calculated defect models for a 1 × 1 × 2 supercell of Li₃ErCl₆. a,b) Fully occupied Er₂ and Er₃ sites, fully ordered and fully disordered, respectively, result in a comparable DFT energy and therefore stability for both structures. Although the same holds for (c), the local symmetry reduction for the rotation-inversion center makes this defect model less likely. A mixed defect model including local face-sharing ErCl₆⁻ octahedra yields the highest energy and lowest stability, possibly related to the resulting strong electrostatic Er₂–Er₃ repulsion.
model can also be regarded as fully ordered, here, it will be described as fully disordered, respective to the fully ordered model 1. Defect model 3 includes an alternating full Er2 and Er3 site, respectively, while retaining the mirror plane along the (002) plane. This results in a formal, partial occupancy of 50% for both sites. Defect model 4 includes a random occupancy for the Er2 and Er3 sites, resulting in a further reduction of the symmetry and the existence of face-sharing $\text{ErCl}_6^{3-}$ octahedra. Similar to Li$_3$YCl$_6$ shown by Wang et al.,[32] here density functional theory corroborates that even a structure with full site inversion from Er2 to Er3 (Figure 5a,b) can exhibit similar energies and stabilities as the fully ordered structure. The same holds true for an alternating model 3, with full Er2–Er3 occupancies (Figure 5c). While this structure would result in a strong local symmetry reduction that cannot be captured here experimentally, it clearly shows the possibility of mixed site occupancies. Figure 5d shows model 4 which includes local face-sharing $\text{ErCl}_6^{3-}$ octahedra due to the random Er2–Er3 configuration. This model shows the highest energy and therefore lowest stability, likely related to the stronger repulsion of Er2–Er3 as a result of their reduced distance in this configuration. Overall, the similar energies for the disordered structures support the local structural motives obtained from the pair distribution function analysis in which site disorder seems to be prevalent.

2.4. The Influence of Synthesis on the Ionic Transport

In order to determine the influence of the observed local disorder and local distortions on the ionic diffusion behavior, temperature-dependent impedance spectroscopy was used to assess the ionic transport properties of the differently prepared samples. Figure 6a shows a representative Nyquist plot of the ball-milled Li$_3$ErCl$_6$ after a subsequent annealing time of 1 h. The data can be fit with an equivalent circuit consisting of one parallel constant phase element (CPE)/resistor in series with a CPE, representing the gold-blocking electrodes. The resolvable impedance spectra exhibit $\alpha$-values of >0.9, representing the ideality of the CPE,[42] and geometric capacitances around $48 \times 10^{-12}$ F cm$^{-2}$. Bulk and grain boundary contributions cannot be deconvoluted; however, the obtained ideality of the semicircle and capacitances corresponds well with bulk transport.[43]

Due to the significant differences in the ionic conductivity, a comparison of all acquired room-temperature impedance responses for the differently prepared samples is best shown.
in double logarithmic Nyquist plots, normalized to the pellet thickness for better comparison (see Figure 6b). The obtained Arrhenius diagrams can be found in Figure 6c with the calculated activation energies for ion migration and the corresponding room temperature ionic conductivities in Figure 6d. The linear behavior of the Arrhenius plots, as well as the low uncertainty for the transport property values corroborate a good fit quality. With increasing annealing time, an increase of the activation energy can be observed that coincides with a decrease of the ionic conductivity. The ionic conductivity for these chemically identical compounds can range from $1.7(1) \times 10^{-5} \text{S cm}^{-1}$ (ampoule synthesis) to $3.1(5) \times 10^{-4} \text{S cm}^{-1}$ (ball-milled, as-prepared sample), showing the importance and influence of the employed synthesis method.

2.5. Cation-Disorder-Dependent Ion Conductivity

The above-shown data clearly show a significant influence of the synthesis procedure on the ordering of erbium in the structure, along with strong distortions in the polyhedral pathways and changes in the ionic transport. The following structure–transport correlations may be inferred:

1) During the harsh mechanochemical synthesis (ball-milling) a site disorder of Er2 and Er3 can be found, which decreases with increasing annealing time. Density functional calculations show that the disordering has similar thermodynamic stabilities and the experimental data show that the annealing always leads to a high Er2 occupation (Supporting Information). It remains to be seen if changes in the annealing temperatures and times can influence the disorder further.

2) A direct correlation of the Er2–Er3 site disorder on the ionic conductivity can be seen as shown in Figure 7a. With increasing disorder, the conductivity increases. It is likely that this stems from an induced lithium reordering due to the Coulombic repulsion with the disordered erbium as suggested in Figure 7c. The reordering would change the effective carrier density in both planes and significantly affect the transport mechanism. Temperature-dependent neutron diffraction data and extensive ab initio molecular dynamics simulation are necessary to locate the lithium positions and changing occupancies between the different synthesis methods in order to probe the influence of cation disorder on the lithium migration pathways.

3) A direct correlation of the Er2–Er3 site disorder and the obtained activation barrier for ion migration can be observed in Figure 7b. Due to the milling and the occurring site disorder, severe local distortions can be found that can affect the structural windows of the ion jump, as discussed in Figure 4b. A correlation of the activation barriers with the changing bottleneck sizes along the diffusion pathway in the z-direction in $\text{Li}_3\text{ErCl}_6$ is shown in Figure S13 (Supporting Information). As shown for multiple different material
classes, a changing of the structural bottleneck areas leads to a decreasing activation energy and is related to the lower necessary anion displacement during lithium diffusion from one to another vacant site.\textsuperscript{19,15,44}

3. Conclusion

In this work, we report the influence of the synthetic procedure on the structure and ionic transport properties of Li$_3$ErCl$_6$ and Li$_3$YCl$_6$. Using the highly amorphous phases after mechanochemical synthesis, Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ can be crystallized, within an annealing time of 1 and 5 min, respectively. By monitoring the structural differences via Rietveld refinement against X-ray diffraction data and pair distribution functions analyses the structural differences were explored. A prevalent site disorder can be found between the Er/Y sites alongside other local changes such as LiCl$_6$ octahedral distortion that results in changing polyhedral-transition areas. A large degree of disordering occurs during the mechanochemical synthesis, i.e., an almost complete site inversion from the M2 to the M3 site. The subsequent annealing leads to a crystallization and partial reordering between those sites and an effective temporal dependence of the ordering. This in turn affects the ionic transport, where the disordered and distorted structure as obtained from the mechanochemical synthesis shows significantly enhanced transport properties by expanding bottlenecks for lithium diffusion and a possible reordering of the lithium sublattice corresponding to the M2–M3 disorder. This work highlights the importance of the employed synthesis approach on the ionic transport in lithium-conducting halides, as it shows that differences in the synthetic procedure can severely affect the structure and resulting diffusion pathways in superionic conductors.

4. Experimental Section

Synthesis: The preparation for all compounds was carried out under Ar atmosphere. LiCl (Alfa Aesar, 99.9%), ErCl$_3$ (Sigma Aldrich, 99%), and YCl$_3$ (Alfa Aesar, 99.999%) were used as received. 1 g batches for the classic solid-state synthesis or put into 45 mL ball mill cups filling them into 10 cm long quartz ampoules (10 mm inner diameter) for the mechanochemical synthesis, Li$_3$YCl$_6$ and Li$_3$YCl$_6$. Using the highly amorphous phases after mechanochemical synthesis, Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ can be crystallized, within an annealing time of 1 and 5 min, respectively. By monitoring the structural differences via Rietveld refinement against X-ray diffraction data and pair distribution functions analyses the structural differences were explored. A prevalent site disorder can be found between the Er/Y sites alongside other local changes such as LiCl$_6$ octahedral distortion that results in changing polyhedral-transition areas. A large degree of disordering occurs during the mechanochemical synthesis, i.e., an almost complete site inversion from the M2 to the M3 site. The subsequent annealing leads to a crystallization and partial reordering between those sites and an effective temporal dependence of the ordering. This in turn affects the ionic transport, where the disordered and distorted structure as obtained from the mechanochemical synthesis shows significantly enhanced transport properties by expanding bottlenecks for lithium diffusion and a possible reordering of the lithium sublattice corresponding to the M2–M3 disorder. This work highlights the importance of the employed synthesis approach on the ionic transport in lithium-conducting halides, as it shows that differences in the synthetic procedure can severely affect the structure and resulting diffusion pathways in superionic conductors.

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In this work, we report the influence of the synthetic procedure on the structure and ionic transport properties of Li$_3$ErCl$_6$ and Li$_3$YCl$_6$. Using the highly amorphous phases after mechanochemical synthesis, Li$_3$ErCl$_6$ and Li$_3$YCl$_6$ can be crystallized, within an annealing time of 1 and 5 min, respectively. By monitoring the structural differences via Rietveld refinement against X-ray diffraction data and pair distribution functions analyses the structural differences were explored. A prevalent site disorder can be found between the Er/Y sites alongside other local changes such as LiCl$_6$ octahedral distortion that results in changing polyhedral-transition areas. A large degree of disordering occurs during the mechanochemical synthesis, i.e., an almost complete site inversion from the M2 to the M3 site. The subsequent annealing leads to a crystallization and partial reordering between those sites and an effective temporal dependence of the ordering. This in turn affects the ionic transport, where the disordered and distorted structure as obtained from the mechanochemical synthesis shows significantly enhanced transport properties by expanding bottlenecks for lithium diffusion and a possible reordering of the lithium sublattice corresponding to the M2–M3 disorder. This work highlights the importance of the employed synthesis approach on the ionic transport in lithium-conducting halides, as it shows that differences in the synthetic procedure can severely affect the structure and resulting diffusion pathways in superionic conductors.
function was calculated from the X-ray diffraction pattern, the lithium-related values were not refined. For the crystalline samples, a r-range of 20 Å was refined in the pair distribution function, corresponding to the unit cell diagonal distance.

Due to its amorphous nature and resulting lower coherence length, two different ranges of 2–8 Å (highly local) and 2–20 Å (more average) were fit for the ball-milled (as-prepared) sample, to gain insight into different features of the of Li3ErCl6 structure. Although a fit for a r-range of 20 Å was also performed and is shown in Figure S4 (Supporting Information), the structure obtained from the lower 8 Å r-range fit was used for the upcoming discussion, to correlate the observed behavior to the highly local structural changes. The experimentally pair distribution function for both ranges was fitted by the sum of a Li3ErCl6 and a precursor ErCl3 contribution. As a starting model, the crystal structures of Li3ErCl6 and ErCl3 as obtained by Rietveld refinements against collected X-ray diffraction data were used. The atomic displacement parameters were refined with PDFgui and set constant in the DiffPy-CMI fit afterward.[50] The correlated motion parameter, occupancy of the Er2/Er3 positions, z-coordinates of the Er2/Er3 atoms, and x,y,z-coordinates of the Cl atoms, constrained to an octahedral geometry respective to the Er center cation, were refined in DiffPy-CMI. The two phases ErCl3 and Li3ErCl6 were each considered in the fit with their own scaling factor (mc1, mc2), while G(r) is the partial pair distribution function of phase $p$, and G(r)$_{total}$ the sum of the two scaled partial PDFs

$$ mc1 \times G(r)_{Li3ErCl6} + mc2 \times G(r)_{ErCl3} = G(r)_{total} $$

The scaling factors for the two phases provide the molar ratio ErCl3:Li3ErCl6. A refinement including the second precursor phase LiCl as a third phase did not result in any observable contributions to the fit, possibly due to a low scattering form factor, and was therefore excluded for the final fits. The scaling factors and calculated molar ratio of both phases can be found in Table S1 (Supporting Information).

Whereas refinements of the G(r) of Li3ErCl6 are possible, a large fluorescence-like behavior was observed for Li3YCl6 that resulted in a bad signal-to-noise ratio and the appearance of termination ripples that cannot be accounted for during fitting (see Figures S1 and S5, Supporting Information). Although the pair distribution function can still be described by the same structure as used for Li3ErCl6, the aforementioned issues result in high fit residuals and therefore no quantitative pair distribution function analysis of Li3YCl6 will be included in the discussion, however, a qualitative comparison is still possible.

**DFT Calculations:** All calculations were performed within the framework of the density functional theory based on the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximations[50] as implemented in the VASP package.[31] The core electrons were treated within the projector augmented wave (PAW) method.[31] A 3 x 3 x 3 Monkhorst-Pack k-point mesh was used on the 1 x 1 x 1 supercell of Li3ErCl6. The lattice parameters were kept at the experimental values while atomic positions are relaxed until the forces on all atoms were smaller than 10$^{-4}$ eV Å$^{-1}$. A 520 eV plane-wave energy cutoff was used for all calculations. To remove partial occupancies on Li and Er sites, the Ewald summation as implemented in Pymatgen package[35] was used to compute the electrostatic energy of different configurations of Li and Er ions in the structure. Ten structures with different symmetries and lowest electrostatic energy were recomputed with DFT to get a more accurate ground-state energy.

**Electrochemical Impedance Spectroscopy (EIS):** Electrical conductivities were measured using AC impedance spectroscopy, using consolidated pellets with a thickness of ~2 mm and a geometric density of >85% packed into argon-filled pouch cells. The pellets (0.79 cm$^2$) were initially hand pressed and afterwad isostastically pressed at ~360 MPa for 45 min. Evaporated gold electrodes (0.53 cm$^2$) were used for contacting. EIS was conducted in the temperature range of −40 to 60 °C using a VMP300 impedance analyzer (BioLogic) at a frequency range of 7 MHz to 100 mHz with an excitation amplitude of 10 mV.

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**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

mechanochemical synthesis, solid electrolyte, solid-state battery, superionic conductor

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