Insights into the lithium substructure of the superionic conductors Li_3YCl_6 and Li_3YBr_6

Roman Schlem^a, Ananya Banik^a, Saneyuki Ohno^b, Emmanuelle Suard^c, Wolfgang G. Zeier^{*a}

*^aInstitute for Inorganic and Analytical Chemistry, University of Muenster,
Correnstr. 30, 48149 Münster, Germany.*

*^bDepartment of Applied Chemistry, Graduate School of Engineering, Kyushu
University, 744 Motoooka, Nishi-ku, 819-0395 Fukuoka, Japan*

*^cInstitut Laue-Langevin, 71 avenue des Martyrs,
38042 Grenoble, Cedex 9 - France*

**wzeier@uni-muenster.de*

Abstract: The recent interest in the halide-based solid electrolytes Li_3MX_6 ($\text{M} = \text{Y}, \text{Er}, \text{In}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) shows these materials to be promising candidates for solid-state battery application, due to high ionic conductivity and large electrochemical stability window. However, almost nothing is known about the underlying lithium sub-structure within those compounds. Here, we investigate the lithium sub-structure of Li_3YCl_6 and Li_3YBr_6 using temperature-dependent neutron diffraction. We compare compounds prepared by classic solid-state syntheses with a mechanochemical synthesis to shed light on the influence of the synthetic approach on the reported yttrium disorder and the resulting surrounding lithium sub-structure. This work provides a better understanding of the strong differences in ionic transport depending on the synthesis procedure of Li_3MX_6 .

Keywords: superionic conductor, lithium rare-earth halide, ionic conductivity, solid electrolyte, neutron diffraction study, lithium sub-structure

1. Introduction

The search for material components for all-solid-state batteries has gained increasing momentum in the last years as they are expected to replace lithium-ion batteries in the near future.^{1,2} Whereas currently, sulfidic solid electrolytes are mostly used to construct solid-state batteries, a few drawbacks in terms of instability have been observed.³ Therefore, the requirement of highly conducting, mechanically and electrochemically stable electrolytes has motivated an increased search for novel solid electrolytes.⁴⁻⁷

This ongoing search has led to the rediscovery of a multitude of inorganic compounds that can satisfy the requirements. One of these materials classes is the halide-based lithium and sodium ternary halides A_3MX_6 ($A = \text{Li, Na}$; $M = \text{Y, Er, In}$; $X = \text{Cl, Br, I}$).^{4,6-11} Until now, solid-state battery designs mainly employed the halide-based materials as solid electrolyte catholytes, showing large stability windows of around 4 V against Li^+/Li .^{4,6,7}

The ionic conductivity in the different halide compounds can vary over orders of magnitude, especially when also comparing lithium^{6,9} to sodium-based rare-earth halides.⁵ Na_3ErCl_6 , for example, has a low ionic conductivity of $10^{-6} \text{ mScm}^{-1}$, which can be increased by four orders of magnitude up to 0.035 mScm^{-1} by aliovalent substitution of Er^{3+} with Zr^{4+} .⁵ Li_3YCl_6 has a conductivity of $\sim 0.05 \text{ mScm}^{-1}$ that can be increased by one order of magnitude up to $\sim 1 \text{ mScm}^{-1}$ using a similar substitution.⁴ An aliovalent substitution can often significantly influence the conductivity and activation barrier, by either providing increased amounts of free interstitial positions,¹² an increased amount of charge carriers or a geometric consideration by widening diffusion pathways.¹³⁻¹⁹

Besides the typical optimization strategies, the transport properties of the rare-earth halides have been shown to be heavily dependent on the synthesis procedure.^{6,7,9,10} For instance, in $\text{Li}_3(\text{Er/Y})\text{Cl}_6$ it has been shown that an erbium/yttrium disorder between two positions within the structure exists, resulting in local distortions and altered transport.⁹ The recent theoretical work indeed shows a tremendous influence of the cation sublattice on the lithium substructure.²⁰ However, the underlying lithium sub-structures are still elusive.

Inspired by the missing information about the details of lithium sub-structure in lithium-conducting halides, this work reports on the temperature-dependent neutron diffraction of Li_3YCl_6 and Li_3YBr_6 . Comparing different synthesis procedures will show how the synthesis affects the local cationic ordering and with it the ionic transport in this class of materials. Both compounds show differences in the local polyhedra that appears to be driven by expanding lithium octahedra due to changing cationic ordering. This distortion and expansion, together with the disorder, lead to differences in the thermal displacement parameters when comparing

both synthesis routes indicate the underlying changes and deviations in the transport properties observed.

2. Experimental Section.

General synthesis. The syntheses of all samples were carried out under Ar atmosphere in gloveboxes. LiCl (ChemPur, 99.99 %), YCl₃ (Alfa Aesar, anhydrous, 99.9 %), LiBr (ChemPur, 99.99 %, pre-dried at 200 °C for 24 h) and YBr₃ (Alfa Aesar, ultra-dry, 99.9 %) were used with around 10 wt% excess of the rare-earth halide as described elsewhere.⁹ All used ampoules were pre-heated under dynamic vacuum at 800 °C for at least 1.5 hours and ball mill cups were dried for at least 12 h at 60 °C under dynamic vacuum.

Ampoule synthesis. For the ampoule synthesis, hand-ground mixtures were pressed into dense pellets and filled into ~10 cm long quartz ampoules (10 mm inner diameter). The solid-state ampoule synthesis was carried out for a week at 550 °C, followed by a slow cooling step. Three batches of 1 g were mixed and hand-ground together for 15 minutes to homogenize the powder.

Ball mill synthesis. The mechanochemical synthesis was carried out using 45 mL ball mill cups with a 30:1 mass ratio of 3 mm ZrO₂ milling media : precursor-powder and 298 cycles using three subsequent steps of 99 cycles each (a cycle = 5 min milling at 500 rpm, followed by 15 min rest). After each step, the cups were opened under argon in a glovebox and the mixture was homogenized.

Three batches of 1 g were mixed after the mechanochemical synthesis and homogenized in an agate mortar for 15 minutes by hand grinding. The mixed powder was then filled into a quartz ampoule and annealed for 5 minutes at 550 °C and afterwards air-quenched. For the crystallization step, the furnace was pre-heated to 550 °C and equilibrated for at least one hour, before putting the ampoule in the hot furnace. The air quenching was done by removing the ampoule after precisely 5 min from the furnace and placing it inside an upright standing corundum crucible.

Neutron diffraction. Temperature dependent neutron powder diffraction measurements were performed on the D2B high resolution powder diffractometer at the ILL (Grenoble, France). A cryo-furnace was used to regulate the temperature. The selected neutron wavelength was $\lambda=1.594\text{\AA}$, corresponding to the (335) Bragg reflection of a germanium vertically focusing monochromator. A complete diffraction pattern is obtained after about 25 steps of 0.05° in 2 θ , since the 128 ³He counting tubes are spaced at 1.25° intervals. This scan was repeated 10 times at various 2 θ values to improve statistics, therefore, collection of one pattern typically required 4 h.

General rietveld-refinement. Rietveld-refinements were carried out using the TOPAS software package. The refinements included: (1) The wavelength due to the moving detectors, (2) the background and scaling factors for the main and side phase, followed by (3) the peak-shape parameters. For the structural refinement, initially, (4) the halide and yttrium positions were refined, followed by (5) the respective thermal displacement parameters. (6) The values for the yttrium disorder between the possibly yttrium-positions, as identified by the X-ray diffraction analyses were used as starting values, then refined for the room temperature measurement and afterwards set to fixed for all temperatures. (7) The lithium occupancies, positions, and thermal displacement were refined. (8) Disorders in which yttrium occupies vacant octahedral sites and lithium occupies either a free or partially vacant octahedral site or a vacant tetrahedral site were tested.

Li_3YCl_6 refinement. Various disorders of lithium and yttrium were tested separately, including the occupancy of either lithium or yttrium on the (0, 0, 0.5) position, which would result in the existence of additional face-sharing chains of octahedra in *c*-direction. Neither lithium, nor yttrium is found on that site. Furthermore, lithium was tested on partially vacant yttrium sites to account for possible Li-Y disorder, again with no significant occupancy found. Lithium was additionally allowed to occupy tetrahedral positions connecting the edge-sharing octahedra in the *ab*-plane, which also did not result in any observable occupancy. The obtained fits, with the corresponding fit parameters can be found in (Figure S6-Figure S9, Table S2-Table S9 and Table S11-Table S18).

Li_3YBr_6 refinement. Yttrium was tested for an occupancy on free octahedral sites in the (002) plane and on octahedral lithium positions to account for additional disorder. For the tetrahedral sites, the observation for Li_3YBr_6 was more complex. Especially for the room temperature data of the mechanochemically synthesized compound, a tetrahedral position ($x = 0.125$, $y = 0.667$, $z = 0.375$) for example suggested an occupancy of roughly 4 %, but resulted in negative thermal displacement parameters. In a case, in which unreasonable negative values for the thermal displacement parameters were obtained in combination with a low occupancy of below 4 %, the lithium position was discarded and regarded as vacant. Only the here shown tetrahedral position ($x = 0.85$, $y = 0.175$, $z = 0.153$) satisfied a high occupancy with physically reasonable thermal displacement parameters. However, refining the coordinates resulted in a large shift out of the tetrahedra, in high thermal displacement parameters and unreasonable coordination. Therefore, this position was fixed to the the most stable position. The obtained fits, with the corresponding fit parameters can be found in (Figure S6-Figure S9, Table S2-Table S9 and Table S11-Table S18).

Electrochemical Impedance spectroscopy. The ionic conductivities were measured using AC impedance spectroscopy. A steel press-cell was used, with the exact setup being described elsewhere.²¹ The powder was pressed uniaxially with a pressure of 382 MPa for 3 minutes and a subsequent slow pressure-release step. The resulting geometrical densities of the pellets were around 90 %. A VMP300 impedance analyzer (Biologic) at a frequency range of 7 MHz to 100 mHz with an amplitude of 10 mV was used in a temperature range of -40 °C to 60 °C.

While the mechanochemical synthesis results in only one semicircle in the Nyquist plot, representing the bulk ionic conductivity, the ampoule syntheses show a significant grain boundary contribution for Li_3YCl_6 and an electrode contribution for Li_3YBr_6 . The separation can be performed by the respective capacitances. For the ampoule synthesized Li_3YCl_6 the capacitances are 36 pF/cm² for the bulk contribution and 6.3 nF/cm² for the grain boundary contribution. For the ampoule synthesized Li_3YBr_6 the capacitances are 64 pF/cm² for the bulk contribution and 0.94 $\mu\text{F}/\text{cm}^2$ for the electrode contribution, which can appear due to non-ideal contact between the electrolyte and current collector or a general electrode roughness.

3. Results and Discussion

Differences in ionic transport. To show the influence of the synthesis procedures on the ionic transport, Figure 1 shows temperature-dependent ionic conductivities for mechanochemically synthesized as well as ampoule synthesized Li_3YCl_6 and Li_3YBr_6 , respectively. The corresponding Nyquist plots of the impedance response can be found in the Supporting Information. While it is often shown that the mechanochemical synthesis yields a higher ionic conductivity and lower activation barrier for $\text{Li}_3(\text{Y/Er})\text{Cl}_6$,^{6,9} this observation is reversed for Li_3YBr_6 .⁶ In addition, the temperature dependency of the conductivity of Li_3YBr_6 shows some deviations from linearity.²² We employ temperature-dependent neutron diffraction data to shed light on the differences in the lithium substructure within differently synthesized Li_3YCl_6 and Li_3YBr_6 .

Figure 1: Comparison of temperature-dependent ionic conductivities of the mechanochemical synthesis with subsequent crystallization step and the ampoule synthesized sample of Li_3YCl_6 (a) and Li_3YBr_6 (b). Whereas mechanochemically synthesized Li_3YCl_6 exhibits higher ionic conductivities compared to the classic solid-state synthesis route, in Li_3YBr_6 the trend is the opposite.

The lithium substructure of Li_3YCl_6 . Although Steiner et al.²³ initially proposed an orthorhombic unit cell for Li_3YCl_6 in 1992, using single crystal diffraction techniques, recent reports suggest a trigonal unit cell^{6,8,9} with the space group $\text{P}\bar{3}\text{m}1$ (see Figure 2). Every cation within the structure is octahedrally coordinated, resulting in the existence of YCl_6^{3-} and LiCl_6^{5-} octahedra. Yttrium occupies two different Wyckoff positions (Figure 2a), namely the Wyckoff $1a$ position, where the YCl_6^{3-} octahedra are isolated from each other and the Wyckoff $2d$ position, on which the YCl_6^{3-} octahedra share a face along the c -direction. While the Wyckoff $1a$ position has been reported to be fully occupied by yttrium, the Wyckoff $2d$ position has been shown to exhibit a significant yttrium-disorder between the positions within the (001) and (002) plane. This yttrium disorder has been shown to depend on the employed synthesis approach and annealing times.⁹ Lithium is found to build face-sharing chains along the c -direction (Figure 2b). These chains are face-sharing along the c -direction and edge-sharing within the ab -plane, thereby creating tetrahedral interstitial sites that likely act as lithium diffusion sites.¹¹ The edge-sharing octahedral arrangement results in the formation of a honeycomb-like arrangement along

the ab -plane (Figure 2c). The two lithium positions Wyckoff 6g and 6h are usually reported with an occupancy of 100 % and 50 %, respectively; however, this distribution needs to be investigated here. The structure can be well understood as a layered structure of honeycomb-like arranged LiCl_6^{5-} octahedra along the c -direction, with YCl_6^{3-} octahedra occupying all voids within the (001) plane and two-third of the voids in the (002) plane (Figure 2d, e, f).

Figure 2: Structure of the Li_3YCl_6 unit-cell (ampoule synthesis). (a) YCl_6^{3-} octahedra are isolated from each other on the corners, but form partially occupied chains of face-sharing octahedra along the c -direction within the structure. (b) Lithium is also found to form these chains, (c) but additionally shows a honeycomb-like arrangement along the ab -plane. (d, e, f) The structure can be regarded as a layered arrangement of edge-sharing octahedra within the ab -plane.

In this work, two differently synthesized Li_3YCl_6 samples are investigated, which show Y-disorder of 43 % (mechanochemically synthesized and subsequently crystallized) and 23 % (ampoule synthesis), respectively (See Figure 2a). These data are in line with previous results showing a higher Y-disorder by mechanochemical synthesis.⁹ Here, the disorder refers to the occupancy of the Wyckoff $2d$ position in the (001) plane, being the disorder position, as the Wyckoff $2d$ position within the (002) plane is usually more occupied and regarded as the standard position.^{6,9} Figure 3 shows the thermal expansion of the unit cell. The lattice parameters and lattice volume increase linearly with increasing temperature as expected and a slightly large unit cell volume can be found in the mechanochemically synthesized Li_3YCl_6 that exhibits the higher Y-disorder.

Figure 3: Thermal evolution of lattice parameters a , b , c (a) and the volume (b) for the two differently prepared samples of Li_3YCl_6 (mechanochemical synthesis = purple, ampoule synthesis = black). The lattice shows linear thermal expansion.

In order to explore the structural changes in more detail, Figure 4 shows the thermal evolution of the different polyhedra within the structure, with Figure 4a showing a schematic on how the lithium layers change in dependency of the yttrium-occupancy (Wyckoff $2d$). The following information can be obtained:

- (1) The evolution of the yttrium-related octahedra volume is complex, with each polyhedron on their respective Wyckoff position showing different behavior. This seems to be caused by a slight distortion or angular change of the polyhedra with respect to the lattice axes. A representative distortion for the room temperature measurement of the mechanochemically

synthesized compound is visualized in the Supporting Information (Figure S2). Generally, the Y-octahedra do not appear to change significantly in size (Figure 4b, c), with the largest difference and change in size observed for the octahedra on the Wyckoff $2d$ position within the (002) plane (Figure 4d). This is possibly directly correlated to the observed disorder of yttrium between the Wyckoff $2d$ positions in the (001) and (002) plane.

- (2) When taking lithium into account, it is clear that the layer-size ($6g$ in (001) vs. $6h$ in (002)) is heavily dependent on the synthesis route. Although both lithium related polyhedra increase in size (Figure 4e, f) with increasing temperature, a systematic size difference can be observed when comparing the lithium Wyckoff $6g$ and $6h$ positions. While the lithium octahedra on the Wyckoff $6g$ position ((001) plane) exhibits the larger volume in the ampoule synthesis, this trend is reversed for the lithium octahedra on the Wyckoff $6h$ position ((002) plane). The respective occupancies of yttrium in the (002) plane (Wyckoff $2d$, see Figure 2e) is 57 % (43 % disorder) in the mechanochemical synthesis and 77 % (23 % disorder) in the ampoule synthesis. The smaller sizes of the yttrium and lithium octahedra in the (002) plane (Figure 4d and f, respectively) for the ampoule synthesis lead to the conclusion that the resulting layer size is anti-proportional to the yttrium $2d$ occupancy, despite showing a larger yttrium occupancy in the (002) plane. This may be rationalized by a stronger coulombic attraction of the surrounding halide ions by yttrium due to its higher charge resulting in smaller polyhedra size.

Figure 4: Evolution of polyhedral sizes in the differently prepared Li_3YCl_6 (mechanochemical synthesis = purple, ampoule synthesis = black). Dashed lines act as guides to the eye. (a) Schematic showing overall changes within the layers. A high occupancy of Y within the layer reduces its size, possibly related to a stronger attraction of surrounding halide anions due to the higher charge of yttrium compared to lithium. The two lithium octahedra on the Wyckoff 6g (e) and 6h (f) position both increase in size, following the general unit cell evolution. However, the mechanochemical synthesis yields a smaller LiCl_6^{5-} octahedra on the Wyckoff 6g position, with a reversed trend on the Wyckoff 6h position.

Besides the size of the different polyhedra, the occupancy within the polyhedra is of great importance regarding the diffusion behavior of lithium ions. The evolution of the occupancy and the corresponding thermal displacement parameters of lithium within both octahedra are shown in the Supporting Information (Figure S3). Although the yttrium disorder on the Wyckoff $2d$ position is significantly larger in the mechanochemically synthesized sample (43 % vs. 23 % in the ampoule synthesis), it does not appear to influence the surrounding lithium occupancies. However, the usually reported occupancy of 100 % and 50 % for the Wyckoff $6g$ and $6h$ positions do not appear to match. Both positions appear to be roughly equally occupied, indicating no preference for lithium regarding the layer occupancy. The behavior of the thermal displacement parameters also holds valuable information (see Figure S3). The thermal displacement on the Wyckoff $6g$ position appears to be slightly higher in both differently prepared samples, indicating larger mobility for lithium in this layer ((001) -plane).

To obtain a better understanding of the behavior of the lithium ions in their lattice sites, Figure 5 shows the anisotropic thermal displacement ellipsoids of Li^+ based on the different syntheses. Whereas a quantitative estimation of anisotropic thermal displacement parameters may not be obtainable from powder diffraction data, qualitative differences can be quite helpful in understanding influences on the diffusion behavior of the mobile species.²⁴ While the room-temperature thermal displacement ellipsoids of the ampoule synthesized compound in Figure 5a suggests a rather dominant diffusion along the ab -plane, the ellipsoids in the mechanochemically synthesized compound (Figure 5b) are rotated and suggest a stronger diffusion along the c -axis for lithium on the Wyckoff $6h$ position (dark red), possibly making the diffusion more three-dimensional.

Figure 5: Anisotropic thermal displacement ellipsoids (90 % probability, at room temperature) for the ampoule (a) and mechanochemically synthesized (b) compound. A change in the direction of the thermal displacement amplitude seems to occur when considering Li^+ on Wyckoff $6h$, possibly indicating increased three-dimensional diffusion.

The lithium substructure of Li_3YBr_6 . The structure of Li_3YBr_6 is significantly different from Li_3YCl_6 . The space-group of Li_3YBr_6 structure is C2/m , describing a monoclinic unit cell as initially found by Bohnsack *et al.*²⁵ Yttrium mostly occupies the Wyckoff $2a$ position, representing the corners of the unit cell and the center position within the (001)-plane (Figure 6a). Furthermore, we found the yttrium to occupy a lithium position (Wyckoff $4h$) with an occupancy of 12 % for the mechanochemical synthesis and 6 % for the ampoule synthesis (Figure 6b, c, e), resulting in a Li/Y-site disorder.²⁶ Recent reports suggest the existence of octahedrally coordinated lithium within the structure only.^{6,26} In this work, however, we propose an additional tetrahedrally coordinated lithium position (LiBr_4^{3-}), resulting in a total of three different lithium positions (Figure 6b, c). Although the edge sharing arrangement of lithium octahedra results in multiple tetrahedral voids, only one of those was found to be occupied, with the others remaining vacant (Figure 6b, c). Edge-sharing LiBr_6^{5-} octahedra on the Wyckoff $4g$ position construct a honeycomb-like structure along the (001) ab-plane, with the LiBr_6^{5-} octahedra on the Wyckoff $4h$ position ((002)-plane) being shifted by half a unit cell in the b -direction. The LiBr_4^{3-} tetrahedra share an edge (Figure 6b) and connect both LiBr_6^{5-} octahedra via a face (Figure 6c). Furthermore, the LiBr_4^{3-} tetrahedra connect a LiBr_6^{5-} and YBr_6^{3-} octahedra via a face as well along the (001) plane (Figure 6d, f). Similar to Li_3YCl_6 , Li_3YBr_6 can be understood as a layered-like structure, with a (002) mirror plane (Figure 6d-f).

Figure 6: Crystal structure of Li_3YBr_6 . YBr_6^{3-} octahedra occupy the Wyckoff 2a position (a). The lithium sub-structure (b,c) is heavily interconnected, with LiBr_6^{5-} octahedra sharing an edge, two LiBr_4^{3-} tetrahedra sharing one edge and connecting a LiBr_6^{5-} octahedra on the Wyckoff 4g and 4h position via a face. The unit cell can be understood as a layered structure, with a (002) mirror plane (d, e, f).

Figures 7a,b show the evolution and comparison of the lattice parameters of the differently prepared Li_3YBr_6 samples, in which a non-linear behavior can be observed. The angle of the

unit-cell does not appear to change significantly initially and then drops for both samples at 300 K (Figure 7c). The overall lattice volume of the mechanochemically synthesized Li_3YBr_6 sample is slightly larger when compared to the classic ampoule synthesis (Figure 7d). The non-linear change in the lattice volume and the observed changes in the cell angle are possible reasons for the observed deviations from Arrhenius behavior in Figure 1. However, more in-depth work is needed to correlate the transport data and structural changes above room temperature.

Figure 7: Thermal evolution of lattice-related values for the two differently prepared samples of Li_3YBr_6 (mechanochemical synthesis = purple, ampoule synthesis = black). While the lattice parameters constantly increase (a, b) the unit-cell angle decreases abruptly around room temperature (c), suggesting a minor distortion within the structure. The volume of the mechanochemically synthesized sample is large (d); however, the difference to the ampoule synthesis decreases with increasing temperature.

Similar to Li_3YCl_6 , for an understanding of the substructure, the polyhedra of the different cations are of interest. Figure 8 shows the volumes of the different polyhedra. Due to the non-linear lattice-expansion (Figure 7a,b,d), a non-linear evolution of the polyhedral sizes, as observed in Figure 8a-d, is not surprising. The yttrium-octahedra (Figure 8a) initially decrease in size. Such a trend, reversed to the overall lattice evolution, has been previously discussed for $\text{Na}_{3-x}\text{Er}_{1-x}\text{Zr}_x\text{Cl}_6$ and seems to be due to the low symmetry space group and a thereby possible reorientation of the halide anions, resulting in a slight polyhedral rotational distortion (see SI Figure S4). The observation of the changing distortion coincides directly with the angle change of the unit cell (Figure 7c), indicating a direct correlation.

As mentioned above, lithium can also be found in a tetrahedral environment in Li_3YBr_6 (Figure 8b) with significant occupancies of up to 15 % at 300 K. While the tetrahedra size does not increase initially, the two lithium octahedra expand with increasing temperature. Again, the different trends for all polyhedra suggest a slight rearrangement of the halide anions, resulting in a distortion of the polyhedra.

Figure 8: Polyhedral volumes of (a) the yttrium octahedra, (b) the tetrahedral lithium site, (c, d) the octahedral lithium sites, 4g and 4h respectively. Except for the yttrium-octahedra that initially slightly decreases in size, the polyhedra follow the trend of the expanding unit-cell. The initial decrease is possibly related to a minor distortion.

To gain a more detailed insight into the lithium polyhedra, Figure 9 shows the evolution of their occupancy, with the corresponding thermal displacement parameters shown in the Supporting Information (Figure S5). While the occupancy of the tetrahedral site increases steadily for the ampoule synthesized compound, the mechanochemical synthesis only suggests a tetrahedral occupancy for the room temperature measurement. The occupancies of the lithium octahedra

within the two respective planes do not appear to deviate significantly from each other, suggesting similar stability for lithium in both planes.²⁷ However, the highest thermal displacement can be found for the Wyckoff 4g position in the (001) plane, suggesting slightly higher mobility of lithium in this plane. To understand why the tetrahedral site is less occupied in the mechanochemically synthesized compound, the local coordination environment can be very helpful. In the mechanochemically synthesized compound, more yttrium can be found on this mixed cation-polyhedron with 12 % disorder, compared to 6 % in the ampoule synthesis. Each face of this occupied tetrahedral site is shared with either a lithium, or a mixed lithium-yttrium-octahedron (Figure 9b,c). The shortest distance can be found between the mixed lithium-yttrium-octahedra and the lithium tetrahedra; therefore, those sites can be expected to influence the occupancy on the tetrahedral site most significantly. The resulting stronger electrostatic repulsion by Y^{3+} occupation possibly pushes lithium out of the energetically less favorable tetrahedral coordination. Therefore, no Li^+ can be located in the tetrahedral site at lower temperatures in the mechanochemically synthesized compounds. Overall, the occupancy of the intermediate tetrahedral site suggests more favorable transport due to a wider Li^+ disordering and three-dimensional connection of sites.

Figure 9: Occupancy of lithium on the respective polyhedral sites (a). The significantly higher occupancies on the octahedral sites suggest better stability of lithium in an octahedral environment within this structure. Relevant distances from the center of the tetrahedron to adjacent octahedra (b, c). A closer distance with larger occupancy of the surrounding octahedra has the largest influence on the tetrahedral site.

An additional indication for the differences in the ionic transport in the ampoule synthesized compounds may be obtained by visually assessing the anisotropic thermal displacement parameters (Figure 10). The refinement of anisotropic thermal displacement parameters for lithium on the Wyckoff 4h and 8j positions yielded the same, however less reliable results due to very small values. Therefore, only the anisotropic thermal displacement of lithium on the Wyckoff 4g position is shown. A larger displacement of lithium in the a-direction can be

observed for the ampoule synthesized compound (Figure 10a,c), while the mechanochemically synthesized compounds suggest a larger displacement in b-direction (Figure 10b,d).

As seen in Li_3YCl_6 , this change in the thermal amplitude possibly be related to the surrounding yttrium octahedra. The hypothesis that the larger yttrium occupancy in close vicinity to the lithium 4g site is responsible for the larger tetrahedral occupancy is supported by the reorientation of the anisotropic thermal displacement ellipsoids of lithium on the Wyckoff 4g position. With the already discussed increasing electrostatic repulsion resulting from the large yttrium occupancy, the anisotropic thermal displacement ellipsoids are being rotated away from the yttrium octahedra (Figure 10a,c) and thereby being pushed towards into the tetrahedral position.^{28,29} Contrary to this, the lower occupancy in the mechanochemically synthesized compound allows for lithium to displace to the energetically more stable octahedral sites (Figure 10b,d).

Figure 10: Anisotropic thermal displacement parameters for the ampoule (a, c) and mechanochemically (b, d) synthesized compounds. The larger yttrium occupancy in the *ab*-plane in the ampoule synthesized compound appears to push lithium towards the tetrahedral sites, possibly trapping it there. In comparison, the lower occupancy in the *ab*-plane in the

mechanochemically synthesized compound allows for lithium to move towards the free octahedral sites in b-direction.

Regarding all structural observations, it is still not clear why the transport properties of Li_3YBr_6 deviate so significantly with different synthesis procedures. Here, likely a combination of a multitude of effects play a role.¹ Most significantly might be the tetrahedral occupancy found for every measured temperature in the ampoule synthesized compound, but only at room temperature for the mechanical synthesis, suggesting a much better three-dimensional transport. Regarding the activation energy in Figure 1b, the high-temperature region appears to have significantly enhanced transport properties, possibly influenced by the increasing occupancy of the tetrahedral site in the ampoule synthesized compound with increasing temperature. However, at this stage and without high temperature neutron diffraction data, this is purely speculative.

Change in the lithium substructure as a function of synthesis conditions. Overall, likely many different factors play a role in why the mechanochemically synthesized Li_3YCl_6 compound has a better electrochemical performance and why this observation is reversed for Li_3YBr_6 . Larger disorders, especially one that results in a frustrated energy landscape has been shown to benefit the ionic transport.^{27,30–32} The mechanochemical synthesis leads to a local distortion of the structure, which has already been reported to benefit the ionic conductivity and activation energy.⁹ The larger yttrium-disorder leads to a directional change of the lithium thermal amplitudes indicating changes to the diffusion behavior. In the case of Li_3YBr_6 , the larger occupancy on a tetrahedral site is the most significant difference, indicating that this may be the main reason for the changing ionic transport. By comparing both structures, the following general observations can be inferred.

1. The low symmetry space groups enable a slight halide-repositioning, resulting in polyhedral distortions (as shown in the Supporting Information Figure S2 and S4).
2. The volumes for the polyhedra in the different layers are differently sized, further suggesting a distortion that is non-equivalent for the different layers. Furthermore, it is highly interesting that the yttrium related octahedra do not appear to change significantly in size with increasing temperature, but the lithium related polyhedra do. It appears as if the lithium polyhedra drive the observed lattice expansion.
3. In both compounds the different yttrium occupancy in the different layers does not appear to influence the surrounding lithium occupancies significantly, as the

octahedral sites are roughly equally occupied for both syntheses routes. However, the thermal displacement of lithium in the (001) plane, which holds the highest yttrium content in both structures, is larger, indicating enhanced mobility of lithium on this site. One may speculate that this increased mobility may be related to the stronger electrostatic repulsion caused by yttrium.

4. Although both compounds show a similar lithium substructure, a tetrahedral coordination of lithium could only be observed in Li_3YBr_6 , which is possibly related to a simple size argument, as the bromine-containing polyhedral are generally larger compared to the chlorine ones. However, this tetrahedral occupancy does indicate a higher probability for three-dimensional diffusion, suggesting the reason why Li_3YBr_6 has the higher ionic conductivity.

In general, all these effects must be strongly interconnected. Mechanochemical syntheses followed by a rapid crystallization and subsequent quenching can trap disorder in materials,²⁸ which here manifests itself in more yttrium-disorder. The higher disorder affects the lithium polyhedral volumes and the thermal displacement amplitudes of Li^+ , indicating an influence on the observed changes in ionic transport. A combination of these convoluted influences is shown in Figure 11.

Figure 11: Convolution of effects that likely influence each other. The lattice expansion is driven by the lithium octahedra, which then influence the yttrium octahedra occupancy. The changing occupancy results in different behavior for the lithium thermal displacement.

Conclusion

In this manuscript, we try to shed light on the influence of the synthesis procedure on the crystal structure, the local lithium sub-structure and the associated ion transport properties of Li_3YCl_6 and Li_3YBr_6 . While in the case of Li_3YCl_6 the mechanochemically synthesized compound shows a significantly higher ionic conductivity, this trend is reversed for Li_3YBr_6 . Although multiple structural features are responsible for this observation, we propose the main effect to be a direct correlation to the yttrium disorder within the structures. We show that the disorder in these materials affects the polyhedral volumes of Li^+ , their directional thermal amplitude as well as the partial occupancies of additional sites in the case of Li_3YBr_6 .

Whereas more work is needed to in-depth understand this class of materials, this work shows how influential the synthesis technique is on the lithium substructure and transport of superionic conductors and especially the class of superionic lithium-halide materials

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Supporting Information

Nyquist impedance spectra of all explored compositions are reported, alongside with the crystallographic information files, additional structural trends and the tables of the crystallographic information obtained by Rietveld refinements.

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