Mechanochemical Synthesis and Structure of Lithium Tetrahaloaluminates, LiAlX₄ (X = Cl, Br, I): A Family of Li-Ion Conducting Ternary Halides

Nicolás Flores-González, Nicolò Minafra, Georg Dewald, Hazel Reardon, Ronald I. Smith, Stefan Adams, Wolfgang G. Zeier, and Duncan H. Gregory*

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ABSTRACT: State-of-the-art oxides and sulfides with high Li-ion conductivity and good electrochemical stability are among the most promising candidates for solid-state electrolytes in secondary batteries. Yet emerging halides offer promising alternatives because of their intrinsic low Li⁺ migration energy barriers, high electrochemical oxidative stability, and beneficial mechanical properties. Mechanochemical synthesis has enabled the characterization of LiAlX₄ compounds to be extended and the iodide, LiAlI₄, to be synthesized for the first time (monoclinic P2₁/c; Z = 4; a = 8.0846(1) Å; b = 7.4369(1) Å; c = 14.8890(2) Å; β = 93.0457(8)°). Of the tetrahaloaluminates, LiAlBr₄ exhibited the highest ionic conductivity at room temperature (0.033 mS cm⁻¹), while LiAlCl₄ showed a conductivity of 0.17 mS cm⁻¹ at 333 K, coupled with the highest thermal and oxidative stability. Modeling of the diffusion pathways suggests that the Li-ion transport mechanism in each tetrahaloaluminate is closely related and mediated by both halide polarizability and concerted complex anion motions.

Replacing flammable liquid electrolytes in conventional Li-ion batteries (LIBs) with solid-state alternatives could lead to a breakthrough in battery safety and longevity. Moreover, otherwise inaccessible high energy density cells (using Li-metal anodes and high-voltage cathodes) could become a reality by employing thermodynamically stable solid-state electrolytes (SSEs) in all-solid-state batteries (SSBs). Inorganic SSEs with sufficiently high ionic conductivity and chemical/electrochemical stability are almost within reach. Among them, oxide- and sulfide-based materials have been the main focus of research because of the remarkable ionic conductivity that can be achieved at room temperature. However, oxides lack mechanical strength and require high processing temperatures, whereas both the narrow electrochemical windows and limited stability of sulfides have proved challenging to their adoption as SSEs.⁴ Among alternatives, the complex halides, Li₃M³⁺X₆ (M³⁺ = Sc, Y, In, La, Ho, Er; X = halogen) and Li₁₋ₓM₁₋ₓZrₓCl₆ (M³⁺ = Y, Er), are raising interest with appreciable ionic conductivity at room temperature, low activation energies for Li⁺ migration and wide electrochemical windows.⁵⁻¹¹ As originally discovered in the 1990s, the synthesis of Li₃M³⁺X₆ requires several steps including high temperature annealing.¹² By comparison, ternary lithium-light element halides, including LiAlCl₄, have become well-known over the past four decades on account of remarkable ionic conductivity in the solution and molten states. With liquid LiAlCl₄·6SO₄ showing Li⁺ ionic conductivity of >0.10 S cm⁻¹ at room temperature,¹³ such halides have attracted renewed scrutiny recently,¹⁴,¹⁵ while in solution, LiAlX₄ (X = Cl, Br) can surpass the Li-ion conductivity of the ubiquitous electrolyte, LiPF₆.¹⁶ By contrast, the structure and conductivity of lithium tetrahaloaluminates in the solid state have scarcely been studied and only very recently has solid LiAlCl₄ been identified as one of several promising halides for...
electrolytes in SSBs.\(^\text{17}\) In fact, the ionic conductivity of monoclinic LiAlCl\(_4\) was first reported by Weppner and Huggins using DC polarization measurements in 1977.\(^\text{18}\) At 298 K, single crystals of LiAlCl\(_4\) were reported with a conductivity of \(1.2 \times 10^{-6}\) S cm\(^{-1}\), increasing to \(1.4 \times 10^{-4}\) S cm\(^{-1}\) at 413 K (just below the melting temperature). The feasibility of using LiAlCl\(_4\) as a SSE was first demonstrated 15 years later by deploying it in a Li\(_2\)TiS\(_2\)/LiAlCl\(_4\)/Li\(_4-x\)CoO\(_2\) solid-state cell (\(0 \leq x \leq 0.45\)) at 373 K.\(^\text{19}\) The cell exhibited an open-circuit potential of 2.1 V in the charged state. Moreover, it showed excellent discharge characteristics at current densities up to 0.1 mA cm\(^{-2}\) with minimal capacity loss over 100 charge–discharge cycles. Despite this promising result, there has been a lack of studies since. The corresponding bromide is uncharacterized, while the iodide has never been isolated. Consequently, the conductivity of either is unknown in the solid state.

Inspired by the recent performance of halides in the solid state and by the historically promising properties of halide salts, we were motivated to investigate the structures, stabilities and electrochemical properties of the solid lithium tetrahaloaluminates, LiAlX\(_4\), (X = Cl, Br, I) systematically. Here, we present the results of PXD and time-of-flight (ToF) powder neutron diffraction (PND) experiments to locate the Li positions accurately and to determine anisotropic thermal displacement parameters, allowing full characterization of the underlying structural chemistry of the LiAlX\(_4\) materials. Figure 1 shows the profile fits for LiAlI\(_4\) from structure refinement against PND and SPXD data, respectively. The respective plots for the chloride and bromide analogues can be found in the Supporting Information (Figures S12, S13, and S15).

Crystallographic data from these refinements are collated in Tables S3–S18. Our room temperature diffraction data confirmed that LiAlBr\(_4\) and LiAlI\(_4\) are isostructural to the chloride analogue (monoclinic, space group P2\(_1\)/c). The structural models for the bromide and iodide were further assessed by means of the Global Instability Index (GII),\(^\text{20,21}\) which corroborated their plausibility with low values of 0.10 and 0.07, respectively. The crystal structure of the haloluminates can be described as a slightly distorted \(hcp\) X\(^-\) sublattice within which Li\(^+\) and Al\(^3+\) occupy octahedral and tetrahedral interstices, respectively. The extended structure can be considered to be constructed from distorted LiX\(_4\) octahedra and AlX\(_4\) tetrahedra. Two LiX\(_4\) octahedra link across a common edge to form “Li\(_2\)X\(_{10}\) dimers”. Each Li–X dimer is connected to four others by 2 axial and 2 equatorial vertices in a “trans” confirmation that creates stepped or buckled layers that propagate in all three dimensions. Meanwhile, each AlX\(_4\) tetrahedron is connected to one Li–X dimer via two edges and two other dimers by one vertex each (Figure 2a and b).

![Figure 2. Crystal structure of mechanochemically synthesized LiAlI\(_4\) (P2\(_1\)/c) projected along the b-axis as visualized with VESTA\(^\text{26}\) (a) showing a polyhedral representation of the extended structure and the linking of Li–X “dimers”, (b) showing the linkage between an LiX\(_4\) octahedron and neighboring AlX\(_4\) tetrahedra, and (c) highlighting the positions of the Li\(^+\) cations with respect to the isolated haloaluminate anions: Li (4e, green spheres), Al (4e, light blue spheres), and I (4e, purple).

Alternatively, considering only complex [AlX\(_4\)]\(^-\) anions and Li\(^+\) cations, then the latter can be seen to occupy space within “pseudo-layers” between the isolated haloaluminates tetrahedra (Figure 2c).

The unit cell expands linearly in all three dimensions as Cl\(^-\) (167 pm) is replaced by Br\(^-\) (182 pm) and I\(^-\) (206 pm),\(^\text{23}\) and there is a concomitant increase in both the average Li–X and Al–X bond lengths. The monoclinic distortion of the cell decreases very slightly with increasing halide radius (Figure S16). Other than these expected differences in cell volume, our refinements hinted at differences between the structural
models of the mecha-nochemically synthesized lithium tetrahaloaluminates and the previously reported structures of (thermally synthesized) LiAlCl₄ and LiAlBr₄ (although the latter structure was previously determined only from single crystal data at 100 K). From attempts were made to refine the occupancy of the Li site in each halide, and although for X = Br, this did not vary from 100%, for X = Cl and I, respectively, values of 91(4)% and 94(2)% were obtained with slight reductions in R-factors. More interestingly, if the Li occupancy of the normally vacant t₂ interstitial position (0.236, 0.014, 0.792) identified by SoftBV in the conduction mechanism (see Table S20) was simultaneously refined, then occupancies of 0.84(3) and 0.16(3) were obtained for the normal and interstitial Li sites in LiAlCl₄ when the respective thermal parameters were fixed. By contrast, no evidence for antisite mixing (Li–Al disorder) was obtained for any of the halides. Although these results are not conclusive, they do tend to support observations from solid-state NMR spectroscopy of a partially occupied interstitial site in LiAlCl₄∀ and provide a rationale for the Li⁺ diffusion mechanism elucidated by BVSE and MD analyses for the haloaluminates (see below). It will be interesting to see whether local structural approaches, such as pair distribution function (PDF) analysis can provide further information regarding the links between defect structure and Li-ion motion.

The thermal stabilities of LiAlX₄ were studied by simultaneous thermogravimetric-differential thermal analysis (TG-DTA). For all samples, the TG profiles are typical of thermal decomposition with volatile decomposition products (Figures S17–19). The decomposition is preceded by melting in each case (the melting points, as determined by the respective DTA peak onsets, are summarized in Table 1). The melting points of the tetrahaloaluminates increase from X = Cl through Br to I, with the new iodide, LiAlI₄, melting at 593 K. The comprehensive structural models obtained from neutron and synchrotron diffraction allowed the probable Li⁺ diffusion pathways in the haloaluminates to be established via bond-valence site energy (BVSE) analysis. In this class of materials, the Li⁺ transport properties play a key role in determining the overall ionic conductivity. This is because the Li⁺ ions act as mobile charge carriers in these materials, and their movement is facilitated by the presence of defects such as interstitial Li sites and vacancy-type defects. The Li⁺ diffusion coefficients and activation energies are critical parameters that determine the ionic conductivity of these materials. The theoretical predictions of BVSE can be compared with experimental measurements to validate the structural models and to gain insights into the defect chemistry.

Table 1. Thermal Properties and Transport Data of Mechanochemically Synthesized Lithium Tetrahaloaluminates

| Material | Melting point (K) | Decomposition onset temperature (K) | σₓ × 10⁻⁸ (S cm⁻¹) | σᵧ × 10⁻⁸ (S cm⁻¹) | Eₓ (eV) |
|----------|------------------|-------------------------------------|---------------------|---------------------|--------|
| LiAlCl₄  | 420.0 [419, 422, 425] | ~643                               | 2.9(2) [2.1, 2.5]  | 8.6(7)              | 0.473(2) [0.47, 0.50] |
| LiAlBr₄  | 464.9 [466, 469]   | ~593                               | 3.3(2)              | 2.5(4)              | 0.437(4) |
| LiAlI₄   | 509.0             | ~593                               | 1.2(1)              | 0.61(7)             | 0.429(3) |

At lower frequencies, impedance contributions are observed with capacitances of 2.5 × 10⁻⁹ (X = Br) and 8.1 × 10⁻⁷ F cm⁻² (X = I). This can be attributed to a surface layer, which may be formed on thermal decomposition during gold coating, for example.6,28 Arrhenius behavior was noted for all samples in the LiAlX₄ series across a temperature range of 233–333 K (Figure 3b). Room-temperature total ionic conductivities (σₓ) and the parameters extracted from linear fits of the Arrhenius plots (σᵧ, Eₓ) are summarized in Table 1. We found that the room temperature Li⁺ conductivity first increases but then subsequently decreases when switching from X = Cl through Br to I. The results corroborate the premise that both the exponential prefactor, σᵧ, and the activation energy for Li⁺ diffusion decrease with increasing anion polarizability, although the differences in the Eₓ values for LiAlBr₄ and LiAlI₄ are not statistically significant.9,30 In this regard, it should be noted that a reduction in Eₓ does not always lead to improved ionic conductivity, since Eₓ and σᵧ are correlated in line with the Meyer–Neldel rule.31,32 By considering both parameters in Table 1, it can be appreciated why LiAlI₄ might have the lowest ionic conductivity within the haloaluminate series. It should be noted that the ionic conductivity for LiAlCl₄ measured here is 1 order of magnitude higher than that reported by Weppner and Huggins.18 Although our mecha-nochemical syntheses are quicker and less energy-intensive to that recently reported for LiAlCl₄ by Tanibata et al., the EIS data do further support the premise that ball milling positively influences the ionic conductivity in the lithium halides (likely facilitating defect formation compared to thermal synthesis methods, which are evidently not viable for X = I).23 Indeed, EIS measurements performed on a pellet of the LiAlCl₄ sample that was subsequently annealed at 373 K for 14 h yielded a lower room temperature conductivity (of 1.2(2) × 10⁻⁵ S cm⁻¹) than that of the cold-pressed mecha-nochemically synthesized chloride.
materials, our analysis shows that the ionic conductivity is governed by the presence of intrinsic tetrahedral and octahedral interstitial sites. The BVSE map of LiAlI₄ is presented as an example in Figure 4a, and shows that a bottleneck for 2D conduction involves Li⁺ hopping from its normal octahedral 4e site (“i7” in the BVSE map notation in Figure 4b). Alternatively, 3D conduction requires hops from/to interstitial octahedral 4e lattice sites (“i3” → “i2”). Qualitatively, the BVSE models of the migration barriers in the LiAlX₄ series depict very similar energy landscapes (while noting that the overall activation energies for LiAlCl₄ and LiAlI₄ are higher than the experimental values due to the level of accuracy of SoftBV, Figures 4b, S20, and S21). These energy profiles indicate that the conduction pathways do not change significantly with the halide and that the observed differences in ionic conductivity cannot be rationalized only via a static, crystal chemistry treatment.

Empirical molecular dynamics simulations for a 768 atom 4 × 4 × 2 supercell of LiAlCl₄ over the temperature range 250–400 K over 1500–18000 ps harmonize to the experimentally observed conductivity (Figure S22). A more detailed analysis shows that the 2D Li⁺ motion in the y–z plane is coupled to dynamic anion disorder (librations) that in the experimental data encourages further investigations of the role of defects and dynamic anion effects in LiAlX₄ materials and how such effects might be tuned.

In view of the promising ionic transport behavior, preliminary linear sweep voltammetry (LSV) experiments were conducted to determine the oxidative stability of LiAlX₄. InLi and a carbon + SSE composite were employed as the counter and working electrodes, respectively. The oxidative stability limits were defined by the onset potentials (E_{onset}) and calculated via linear fitting of the nonfaradaic and faradaic region. The room temperature voltammograms are shown in Figure 5.

![Figure 4](image1.png)

**Figure 4.** (a) BVSE map showing Li⁺ migration pathways in a (100) projection of the LiAlI₄ structure, as visualized with VESTA. The highest isosurface level of 0.64 eV over the global minimum is shown in yellow. Red dots indicate octahedral Li⁺ lattice sites and yellow spheres indicate tetrahedral/octahedral interstitial sites. (b) BVSE model of migration barriers for LiAlI₄ derived from Rietveld refinements against SPXD and PND data. The relative site energy is zero for Li⁺ lattice sites.

![Figure 5](image2.png)

**Figure 5.** Room temperature linear sweep voltammogram (0.1 mV s⁻¹) of InLi|LiAlX₄|LiAlX₄ + C cells. Dashed lines indicate linear fits of the faradaic region. The bottom x-axis shows the values of the voltage versus In/Li, the top x-axis shows the corresponding values of voltage versus Li⁺/Li.

We determined that oxidation of LiAlX₄ materials starts at 3.8 (4.4), 2.8 (3.4), and 2.0 (2.6) V versus In/Li (vs Li⁺/Li) for X = Cl, Br, and I, respectively. Density functional theory (DFT) calculations predicted the electrochemical windows of LiAlX₄ to be either 1.7–4.5 V or 1.54–4.45 V for X = Cl and 1.8–3.9 V for X = Br. Above the oxidation limits, LiAlX₄ are predicted to produce AlX₃ and X₂, while below the reduction limits, LiAlX₄ are predicted to form Al and LiX, indicating that lithium tetrachloro- and tetrabromoaluminates are not stable against Li metal, as is true for the liquid electrolyte, LiAlCl₄·3SO₂. These results indicate the feasibility of combining LiAlCl₄ with high voltage cathode materials, while the bromide and iodide analogues would be better suited to use with lower potential electrodes, such as sulfide-based cathodes, for potential cell applications. Equally, use of LiAlBr₄ and LiAlI₄ with high voltage cathodes might be enabled with an appropriate coating of the positive electrode to prevent SSE decomposition. Further investigations into various half- and full-cell architectures and their performance are currently underway and will be reported elsewhere.

In summary, we have shown that high purity lithium tetrahaloaluminate powders can be easily synthesized by mechanochemical methods. This approach is extremely effective in preparing bulk quantities of LiAlX₄ including the new iodide, LiAlI₄, which could not be synthesized by thermal
methods. Synchrotron and neutron diffraction have shown not only that the bromide and iodide are isstructural to the chloride analogue but that Li vacancies and interstitials are likely prevailing features of mechanically synthesized tetrohaloaluminates. Each material exhibits appreciable Li-ionic conductivity, good thermal stability and reasonable stability to oxidation, such that the chloride, especially, might be employed with high voltage cathodes. Moreover, Li' conductivity and stability can likely be improved still further by tuning the microstructure, composition and defect chemistry of the halooaluminates through doping, substitution and compositing. The LiAlX₄ family suggests these and other polyanion halides offer considerable promise as new classes of cation conductor and as candidates for testing systematically as SSEs.

**ASSOCIATED CONTENT**

* Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00055. Experimental procedures, characterization techniques, crystallographic information, TG-DTA profiles, BVSE analysis, and details of MD simulations (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

Duncan H. Gregory — School of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.; orcid.org/0000-0002-4585-3280; Email: duncan.gregory@glasgow.ac.uk

**Authors**

Nicolas Flores-Gonzalez — School of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

Nicolo Minafra — Institute for Inorganic and Analytical Chemistry, University of Münster, 48149 Münster, Germany

Georg Dewald — Institute of Physical Chemistry, Justus-Liebig-University Giessen, D-35392 Giessen, Germany

Hazel Reardon — School of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

Ronald I. Smith — ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Didcot, Oxfordshire OX11 0QX, U.K.; orcid.org/0000-0002-4990-1307

Stefan Adams — Department of Materials Science and Engineering, National University of Singapore, 117575, Singapore; orcid.org/0000-0003-0710-135X

Wolfgang G. Zeier — Institute for Inorganic and Analytical Chemistry, University of Münster, 48149 Münster, Germany; orcid.org/0000-0001-7749-5089

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00055

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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**REFERENCES**

(1) Janek, J.; Zeier, W. G. A solid future for battery development. Nat. Energy 2016, 1, 16141.
(2) Han, F.; Zuo, Y.; He, X.; Mo, Y.; Wang, C. Electrochemical Stability of Li₄GeP₅S₄ and Li₄La₃ZrCl₁₁ Solid Electrolytes. Adv. Energy Mater. 2016, 6, 1501590.
(3) Han, X.; Gong, Y.; Fu, K.; He, X.; Hitz, G. T.; Dai, J.; Pease, A.; Liu, B.; Wang, H.; Rubloff, G.; Mo, Y.; Thangadurai, V.; Wachsmann, E. D.; Hu, L. Negating interfacial impedance in garnet-based solid-state Li metal batteries. Nat. Mater. 2017, 16, 572–579.
(4) Asano, T.; Sakai, A.; Ouchi, S.; Sakaida, M.; Miyazaki, A.; Hasegawa, S. Solid Halide Electrolytes with High Lithium-Ion Conductivity for Application in 4 V Class Bulk-Type All-Solid-State Batteries. Adv. Energy Mater. 2018, 30, 1803075.
(5) Schlem, R.; Muy, S.; Prinz, N.; Banik, A.; Shao-Horn, Y.; Zobel, M.; Zeier, W. G. Mechanochemical Synthesis: A Tool to Tune Cation Site Disorder and Ionic Transport Properties of LiₓMClₓ (M = Y, Er) Superionic Conductors. Adv. Energy Mater. 2020, 10, 1903719.
(6) Schlem, R.; Berges, T.; Li, C.; Kraft, M. A.; Minafra, N.; Zeier, W. G. Lattice Dynamical Approach for Finding the Lithium Superionic Conductor LiₓErₓ. ACS Appl. Energy Mater. 2020, 3, 3684–3691.
(7) Wang, S.; Bai, Q.; Nolan, A. M.; Li, Y.; Gong, S.; Sun, Q.; Mo, Y. Lithium Chlorides and Bromides as Promising Solid-State Chemistries for Fast Ion Conductors with Good Electrochemical Stability. Angew. Chem., Int. Ed. 2019, 58, 8039–8043.
(8) Li, X.; Liang, J.; Chen, N.; Luo, J.; Adair, K. R.; Wang, C.; Banis, M. N.; Sham, T.-K.; Zhang, L.; Zhao, S.; Lu, S.; Huang, H.; Li, R.; Sun, X. Water-Mediated Synthesis of a Superionic Halide Solid Electrolyte. Angew. Chem., Int. Ed. 2019, 58, 16427–16432.
(9) Xu, Z.; Chen, X.; Li, K.; Chen, R.; Zeng, X.; Zhu, H. Influence of Anion Charge on Li Ion Diffusion in a New Solid-State Electrolyte, LiₓLaₓ. Chem. Mater. 2019, 31, 7425–7433.
(10) Liu, Y.; Wang, S.; Nolan, A. M.; Ling, C.; Mo, Y. Tailoring the Cation Lattice for Chloride Lithium-Ion Conductors. Adv. Energy Mater. 2020, 10, 2002356.
(11) Park, K.-H.; Kaup, K.; Assoud, A.; Zhang, Q.; Wu, X.; Nazar, L. F. High-Voltage Superionic Halide Solid Electrolytes for All-Solid-State Li-Ion Batteries. ACS Energy Lett. 2020, 5, 533–539.
(12) Steiner, H.-J.; Lutz, H. D. Neue schnelle Ionenleiter vom Typ MₓMⁿ⁺Clₓ (Mⁿ⁻ = Li, Na; Ag; Mⁿ⁻ = In, Y). Z. Anorg. Allg. Chem. 1992, 613, 26–30.
(13) Foster, D. L.; Kuo, H. C.; Schläfke, C.; Rady, A. N. New Highly Conductive Inorganic Electrolytes: The Liquid Solvates of the Alkali and Alkaline Earth Metal Tetrahaloaluminates. J. Electrochem. Soc. 1988, 135, 2682–2686.
(14) Grundsh, N.; Ames, C.; Goodenough, J. B. Communication—Characterization of LiAlCl₄·SO₃ Inorganic Liquid Li’ Electrolyte. J. Electrochem. Soc. 2018, 165, A1694–A1696.
(15) Ramar, V.; Pazzolla, C.; Rapp, M.; Berck, M.; Zinck, L. Nonflammable Inorganic Liquid Electrolyte Lithium-Ion Batteries. J. Electrochem. Soc. 2020, 167, 070521.
(16) Scholz, F.; Unkzw, W.; Eiden, P.; Schmidt, M. A.; Garso, A.; Krossing, I. Synthesis, Spectroscopic Characterization, Crystal Structures, Energetics, and Thermal Stabilities of Li[XAlₓ] (X = Cl, Br, I, PH₃, BF₃, SO₂, SO₃).
