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$\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$: Na^+ conduction in a novel Na-rich double perovskite

Bridging of contiguous Na ions in the novel $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ Na-rich double perovskite ionic conductor material is enabled by the presence of Na ions in both A- and B-sites, resulting in a lower energy barrier for Na-ion diffusion.

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Na_{1.5}La_{1.5}TeO₆: Na⁺ conduction in a novel Na-rich double perovskite†

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Increasing demand for lithium batteries for automotive applications, coupled with the necessity to move to large-scale energy storage systems, is driving a push towards new technologies and has seen Na-ion batteries emerge as a leading alternative to Li-ion. Amongst these, all solid-state configurations represent a promising route to achieving higher energy densities and increased safety. Remaining challenges include the need for Na⁺ solid electrolytes with the requisite ionic conductivities crucial for use in a solid-state cell. Here, we present the novel Na-rich double perovskite, Na_{1.5}La_{1.5}TeO₆. The transport properties, explored at the macroscopic and local level, reveal a low activation energy barrier for Na⁺ diffusion and great promise for use as an electrolyte for all solid-state Na-batteries.

The lower cost and greater availability of sodium compared to lithium, together with its similar redox couple potential of *ca.* 0.3 V lower for Na/Na⁺ compared to Li/Li⁺, has led to enormous interest in the development of Na batteries by the energy storage community over the last decade.¹ The larger cation size and heavier mass of sodium had made it a suitable candidate for medium to large-scale stationary energy storage applications, where gravimetric energy density is not a priority. As with Li-ion batteries, organic liquid Na-electrolytes present concerns in terms of safety and the operating voltage window available. The use of solid-state electrolytes in Na batteries could increase the energy density and safety of the battery, enable longer cyclability and permit the use of versatile cell geometries.^{2,3} Current Na⁺ solid-state electrolytes display Na⁺ conductivities at room temperature from 10^{−10} S cm^{−1}, in the case of the Na(B/Al)H₄ complex hydrides, to benchmark values close to the mS cm^{−1} for the recently reported Na-containing chalcogenides.^{2–4} Other systems include the NASICON phosphate

materials, the classic β''-Al₂O₃ and the more recent layered P2-type Na₂M₂TeO₆ materials.^{2,5} The electrolyte choice should fit the specific battery application, operating temperature and electrode in order to avoid malfunction. For example, β''-Al₂O₃ degrades with moisture content⁶ and the room temperature super-ionic Na-containing sulfide materials suffer from poor electrochemical stability and reaction with Na metal electrodes.⁷ Therefore, research on new Na⁺ solid-state electrolyte systems that could meet requirements lacking in present systems is critical. Here, we present a new sodium-rich solid-state electrolyte Na_{1.5}La_{1.5}TeO₆, where the robust perovskite framework and redox stability of the Te⁶⁺ ions^{8–12} could enable its use in combination with high voltage electrodes.

A₂BB'O₆ double perovskite structure allows for a wide range of potential compositions with multiple combinations of elements on the A, B and B' sites, where B and B' cation positions are ordered in the crystal structure.¹³ The novel Na-rich Na_{1.5}La_{1.5}TeO₆ double perovskite presented here crystallises in the monoclinic *P*₂₁/*n* space group, with 1 mol of Na⁺ and 1 mol of Te⁶⁺ cations occupying the octahedral B and B' sites in a rock-salt type ordered fashion (Fig. 1). From the 2 mols of 8-fold coordinate A-sites, 1.5 mol is occupied by La³⁺ cations and 0.5 mols are occupied by additional Na⁺, producing a “Na-rich” double perovskite with an expanded formula unit of Na_{0.5}La_{1.5}NaTeO₆. A similar alkali-metal rich double perovskite was reported by Rosseinsky and co-workers for the Li_{1.5}La_{1.5}WO₆ composition.¹⁴ The discrepancy between the charges and sizes of the cations sitting in the A and BB' sites produces the distortion of the symmetry from the ideal cubic structure to a monoclinic symmetry through an a[−]a⁺b⁺ tilting system, as expected for a tolerance factor of 0.83 calculated for the Na_{1.5}La_{1.5}TeO₆ composition. The synthesis of Na_{1.5}La_{1.5}TeO₆ was achieved through an energy-efficient microwave-assisted solid-state synthesis. Such routes have been developed by our group in recent years for Li⁺ solid electrolytes,^{15–18} where the presence of hydroxide and oxide precursors increase the reaction kinetics by coupling effectively to microwave irradiation.¹⁹

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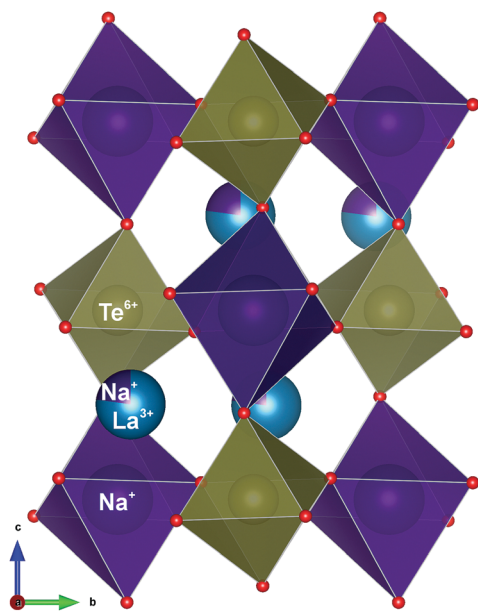


Fig. 1 Crystallographic representation of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ structure with monoclinic symmetry $P2_1/n$, where brown spheres represent octahedrally coordinated Te^{6+} ions, blue spheres represent 8-fold coordinated La^{3+} ions, purple spheres are the Na^+ ions and the oxygen anions are represented in red.

The structure of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite with monoclinic $P2_1/n$ symmetry was established by Rietveld refinements of powder XRD data (Fig. 2). As expected, Na^+ and Te^{6+} cations occupy the rock salt ordered B and B' sites and refinement of site occupancies (Table S1, ESI†) indicated the presence of $\sim 25\%$ vacancies on the La^{3+} occupying the A-site, reminiscent of the related $\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$ double perovskite.¹⁴ Na^+ was refined into these vacant A-sites unoccupied by the La^{3+} , giving an A-site occupancy for this additional Na^+ of 0.239(2) which fills the available A-site vacancies. The calculated angle for the $\text{Na}_B\text{--O--Te}$ was $152.1(4)^\circ$, resulting in a Glazer tilt of 13.9° , in good agreement with the related $\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$ material ($\sim 13.6^\circ$).¹⁴ The precision in the atomic parameters of Na^+ and O^{2-} is necessarily lower than for the stronger X-ray scatterers La^{3+} and Te^{6+} , but the high atomic displacement parameters of the Na^+ ions may be indicative of mobility. The stoichiometry from Rietveld refinement was found to be $\text{Na}_{1.48(1)}\text{La}_{1.534(4)}\text{TeO}_6$, which was further confirmed by EDX analyses, where an atomic ratio of $\text{Na}_{1.52(8)}\text{La}_{1.48(4)}\text{Te}_{1.00(4)}$ was found (Fig. S2, ESI†), in excellent agreement with XRD and the target stoichiometry. Raman analysis (Fig. S1, ESI†) also confirmed the presence of vibrational bands corresponding to the monoclinic $P2_1/n$ group and the absence of carbonate or hydroxide moieties that could arise from secondary phases, typically invisible to laboratory XRD. The material microstructure was studied by SEM (Fig. 2 inset). The $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ particles had sizes ranging from 1 to 5 μm , with irregular, faceted morphologies.

To investigate the ionic macro- and microtransport properties of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ materials, electrochemical impedance spectroscopy and muon spin relaxation measurements ($\mu^+\text{SR}$)

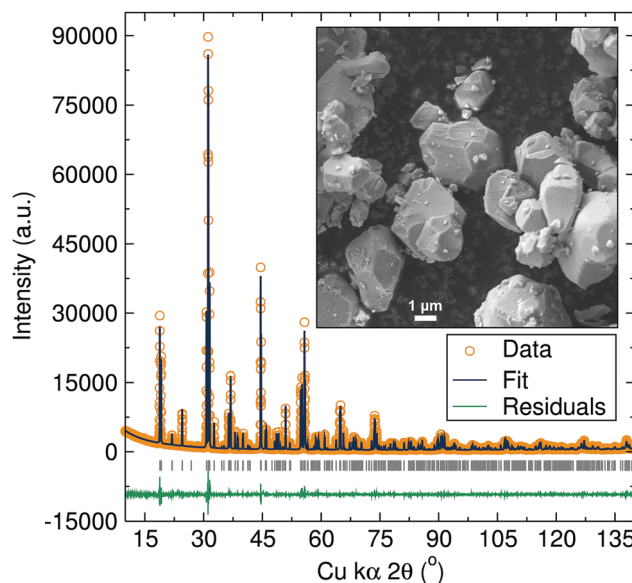


Fig. 2 Rietveld refinements of XRD data for the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite to the $P2_1/n$ monoclinic space group. Bragg peaks positions for the monoclinic $P2_1/n$ structure are indicated by vertical grey tick marks. Fit in excellent agreement to monoclinic space group $P2_1/n$, with cell parameters $a = 5.69186(2) \text{ \AA}$, $b = 5.83933(2) \text{ \AA}$, $c = 8.13119(3) \text{ \AA}$, $\beta = 90.186(1)^\circ$ and $V = 270.253(1) \text{ \AA}^3$. $R_{\text{wp}} = 0.0743$, $R_{\text{exp}} = 0.0530$ and $\chi^2 = 7.051$. Inset: SEM image of $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite.

were carried out. Fig. 3a shows the Nyquist plots of the impedance measurements, where two main components are observed. A semicircle component is noted at high frequencies, due to the resistance of the material towards ionic diffusion, and a second component in form of a linear tail can be seen at low frequencies resulting from the sodium-blocking gold electrodes employed in these measurements, indicating the predominantly ionic character of the observed impedance.²⁰ These data were fitted using equivalent electrical circuit composed of a resistor in parallel with a constant phase element, in series with a Warburg resistance. This gave a value for the ionic conductivity of $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ at room temperature of $5.4 \times 10^{-8} \text{ S cm}^{-1}$. This is on the order of that first reported for phosphate NASICON materials, which has since seen improvements up to $10^{-3} \text{ S cm}^{-1}$ through stoichiometric and structure-tailoring strategies.^{21–25} These structure-tailoring strategies include element substitutions in the NASICON framework to increase the carrier concentrations or to increase the conduction channel size and hence the ionic conductivity of these materials.^{26,27} In the case of the P2-type $\text{Na}_2\text{M}_2\text{TeO}_6$ tellurates oxides materials, the original work reported conductivities of $10^{-6} \text{ S cm}^{-1}$ which have been now optimized to reach the mS cm^{-1} range.^{5,12} It is reasonable to expect therefore that similar improvements are possible for the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite presented here through, for example, aliovalent doping or morphological control.

The activation energy required for macroscopic ionic conduction, calculated from an Arrhenius plot of EIS data, showed a promising value of 0.27(2) eV (Fig. 3c). This value is significantly lower compared to that obtained for the analogous



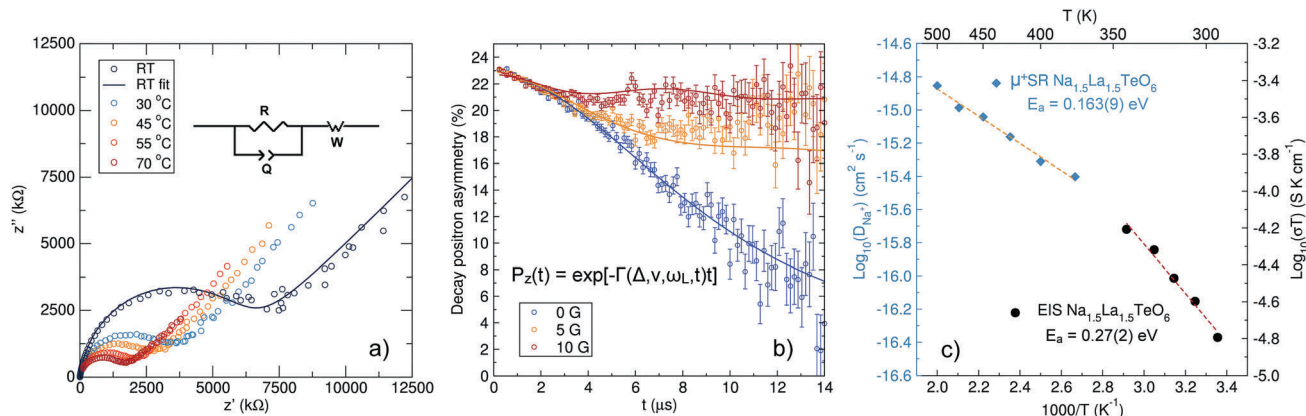


Fig. 3 (a) Nyquist plot of EIS data for $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ at different temperatures and a representative fit to the equivalent electrical circuit. (b) Room temperature $\mu^+\text{SR}$ data collected for $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ at zero field and applied longitudinal fields of 5 G and 10 G, fitted (solid lines) using the Keren function. (c) Arrhenius plots of the ionic conductivity and diffusion coefficient of $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ from $\mu^+\text{SR}$ and EIS.

$\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$ double perovskite material of 0.50(5) eV.¹⁴ This lower energetic requirement for ionic diffusion found for $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ could be related to the high relative density of the sintered material, nearly 96%, which results in a lower inter-grain energy requirement for Na^+ diffusion between sintered particles. The macroscopic activation energy found for this Na-rich double perovskite is similar to current benchmark systems with low activation energy values from EIS measurements,^{2,3,28} for example Na_3PSe_4 which displays an activation energy of 0.21 eV.²⁹ Preliminary EIS analysis of a Na-metal electrode-sandwiched $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ cell at 80 °C revealed the lack of a Warburg element, confirming Na^+ as the conducting species (Fig. S3, ESI†). An increase in impedance over time is observed, which may point to a reaction with the sodium metal electrode at this temperature. Further examination of this, together with the use of similar protection approaches used for Li-metal anodes, could overcome these compatibility issues at high temperatures.^{30,31}

The local Na^+ diffusion properties were also investigated by $\mu^+\text{SR}$ measurements performed on the EMU instrument at the ISIS Neutron and Muon source. The use of $\mu^+\text{SR}$ as a local probe to study Li^+ and Na^+ diffusion in battery materials has grown in recent years.^{15,32–34} The natural abundance of the spin 1/2 ^{23}Na isotope is 100%, making Na^+ an ideal candidate to be studied by $\mu^+\text{SR}$. The temporal evolution of the decay positron asymmetry for $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ at three different longitudinal magnetic fields is shown in Fig. 3b. At short times, the decay positron asymmetry followed a moderate decay, while at longer times the asymmetry decrease followed a slower trend, as expected for this Na-rich double perovskite with no paramagnetic ions in its structure and which also contains active nuclear spins (^{23}Na , ^{139}La and ^{125}Te) which can interact with the muon spin. To obtain the fluctuation rate of the muons due to sodium-ion diffusion (Fig. S4, ESI†), the muon decay asymmetry data were fitted using Keren's analytic generalization of the Abragam function (Fig. 3b).³⁵ The Na^+ diffusion coefficients from the muon fluctuation rate at different temperatures were then calculated applying eqn (1),³⁶ where N_i is the number

of accessible Na sites in the i -th path, $Z_{v,i}$ is the vacancy fraction of the destination sites, s_i the jump distance between Na^+ sites, and ν the calculated muon fluctuation rate at each temperature.

$$D_{\text{Na}^+} = \sum_{i=1}^n \frac{1}{N_i} Z_{v,i} s_i^2 \nu \quad (1)$$

Since a detailed model of the Na^+ diffusion pathways for this novel Na-rich double perovskite is still not available, a simplified model based on the calculations reported by Rosseinsky and co-workers for the $\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$ perovskite was employed.¹⁴ The model is shown in Fig. S5 (ESI†) where Na^+ diffuses from the A sites to the two neighbouring B sites and from the B sites to the four neighbouring A sites, creating a 3D network for Na^+ diffusion. Additionally, a conservative 0.01 vacancy fraction in the Na^+ positions was introduced in both A and B sites to allow diffusion. From this preliminary model, and introducing the two different Na_A – Na_B distances of 3.33 and 3.46 Å, a Na^+ diffusion coefficient at room temperature of $4.2 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ was obtained. This diffusion coefficient is similar to that reported for the $\text{Na}_x(\text{Mn/Co})\text{O}_2$ layered cathode materials (10^{-11} – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$), indicating excellent compatibility of these components in terms of Na^+ diffusion.^{34,37,38} The microscopic diffusion of $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ is also in line with other Na^+ ionic conductors such as the $\text{Na}_x\text{WO}_2\text{Cl}_2$ tungsten bronze with a Na^+ diffusion coefficient of $10^{-13} \text{ cm}^2 \text{ s}^{-1}$,³⁹ and Na_3PS_4 with a value in the range of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$.⁴⁰ The $\mu^+\text{SR}$ measurements indicate that the activation energy required for local Na^+ diffusion is 0.163(9) eV. This low activation energy is similar to related oxide materials, such as the Ga-doped $\text{Na}_2\text{Zn}_2\text{TeO}_6$ with an activation energy of 0.12 eV as observed from NMR measurements,¹² or β' -alumina single crystals with activation energies in the 0.12–0.16 eV range.⁴¹

The higher activation energy values obtained from the macroscopic EIS measurements which probes long range Na^+ conduction through multiple intra-grain crystalline sites and grain boundaries, compared to microscopic $\mu^+\text{SR}$ measurements which are more sensitive to individual Na^+ hops within



the crystalline grain, could have its origin in the contribution to the resistance from grain boundaries to ionic conduction which is virtually invisible to μ^+ SR. Lower conductivity values and higher energy barriers to diffusion could also result from the presence of La^{3+} ions in the A-sites, which could hinder long-range Na^+ conductivity. Nevertheless, the excellent microscopic Na^+ transport properties displayed by this novel $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ Na-rich double perovskite indicates that, upon further optimization, this material could be a promising candidate as a solid electrolyte for Na batteries.

In conclusion, we have demonstrated the synthesis of a novel Na-rich double perovskite, $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ through microwave methods, which crystallises with monoclinic $P2_1/n$ space group with Na^+ on both the A- and B-sites. The material displays a macroscopic ionic conductivity on the order of $10^{-8} \text{ S cm}^{-1}$ at room temperature with a low activation energy of 0.27(2) eV. μ^+ SR measurements reveal a microscopic diffusion coefficient for Na^+ at room temperature in the order of $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ and a very low activation energy of 0.163(9) eV. These findings reveal the promising transport properties for this $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ material and further developments are forthcoming to optimize the macroscopic transport to its maximum microscopic potential.

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Conflicts of interest

There are no conflicts to declare.

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