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$\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ :  $\text{Na}^+$  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<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub>: Na<sup>+</sup> conduction in a novel Na-rich double perovskite†

Marco Amores,<sup>id</sup><sup>ab</sup> Peter J. Baker,<sup>id</sup><sup>c</sup> Edmund J. Cussen<sup>id</sup><sup>b</sup> and Serena A. Corr<sup>id</sup><sup>\*a</sup>

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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<sup>+</sup> 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<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub>. The transport properties, explored at the macroscopic and local level, reveal a low activation energy barrier for Na<sup>+</sup> 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<sup>+</sup> compared to Li/Li<sup>+</sup>, has led to enormous interest in the development of Na batteries by the energy storage community over the last decade.<sup>1</sup> 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.<sup>2,3</sup> Current Na<sup>+</sup> solid-state electrolytes display Na<sup>+</sup> conductivities at room temperature from 10<sup>-10</sup> S cm<sup>-1</sup>, in the case of the Na(B/Al)H<sub>4</sub> complex hydrides, to benchmark values close to the mS cm<sup>-1</sup> for the recently reported Na-containing chalcogenides.<sup>2-4</sup> Other systems include the NASICON phosphate

materials, the classic β''-Al<sub>2</sub>O<sub>3</sub> and the more recent layered P2-type Na<sub>2</sub>M<sub>2</sub>TeO<sub>6</sub> materials.<sup>2,5</sup> The electrolyte choice should fit the specific battery application, operating temperature and electrode in order to avoid malfunction. For example, β''-Al<sub>2</sub>O<sub>3</sub> degrades with moisture content<sup>6</sup> and the room temperature super-ionic Na-containing sulfide materials suffer from poor electrochemical stability and reaction with Na metal electrodes.<sup>7</sup> Therefore, research on new Na<sup>+</sup> 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<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub>, where the robust perovskite framework and redox stability of the Te<sup>6+</sup> ions<sup>8-12</sup> could enable its use in combination with high voltage electrodes.

A<sub>2</sub>BB'O<sub>6</sub> 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.<sup>13</sup> The novel Na-rich Na<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub> double perovskite presented here crystallises in the monoclinic *P*<sub>2</sub><sub>1</sub>/*n* space group, with 1 mol of Na<sup>+</sup> and 1 mol of Te<sup>6+</sup> 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 La<sup>3+</sup> cations and 0.5 mols are occupied by additional Na<sup>+</sup>, producing a "Na-rich" double perovskite with an expanded formula unit of Na<sub>0.5</sub>La<sub>1.5</sub>NaTeO<sub>6</sub>. A similar alkali-metal rich double perovskite was reported by Rosseinsky and co-workers for the Li<sub>1.5</sub>La<sub>1.5</sub>WO<sub>6</sub> composition.<sup>14</sup> 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<sup>-</sup>a<sup>+</sup>b<sup>+</sup> tilting system, as expected for a tolerance factor of 0.83 calculated for the Na<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub> composition. The synthesis of Na<sub>1.5</sub>La<sub>1.5</sub>TeO<sub>6</sub> was achieved through an energy-efficient microwave-assisted solid-state synthesis. Such routes have been developed by our group in recent years for Li<sup>+</sup> solid electrolytes,<sup>15-18</sup> where the presence of hydroxide and oxide precursors increase the reaction kinetics by coupling effectively to microwave irradiation.<sup>19</sup>

<sup>a</sup> School of Chemistry, University of Glasgow, Glasgow G12 8QQ, UK.  
E-mail: Serena.Corr@glasgow.ac.uk

<sup>b</sup> Department of Pure and Applied Chemistry, The University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow, G1 1XL, UK

<sup>c</sup> ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0QX, UK

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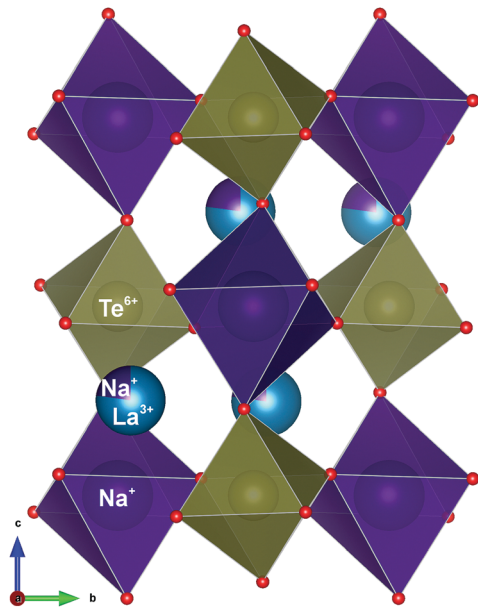


Fig. 1 Crystallographic representation of the  $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$  structure with monoclinic symmetry  $P2_1/n$ , where brown spheres represent octahedrally coordinated  $\text{Te}^{6+}$  ions, blue spheres represent 8-fold coordinated  $\text{La}^{3+}$  ions, purple spheres are the  $\text{Na}^+$  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,  $\text{Na}^+$  and  $\text{Te}^{6+}$  cations occupy the rock salt ordered B and B' sites and refinement of site occupancies (Table S1, ESI<sup>†</sup>) indicated the presence of  $\sim 25\%$  vacancies on the  $\text{La}^{3+}$  occupying the A-site, reminiscent of the related  $\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$  double perovskite.<sup>14</sup>  $\text{Na}^+$  was refined into these vacant A-sites unoccupied by the  $\text{La}^{3+}$ , giving an A-site occupancy for this additional  $\text{Na}^+$  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  $13.9^\circ$ , in good agreement with the related  $\text{Li}_{1.5}\text{La}_{1.5}\text{WO}_6$  material ( $\sim 13.6^\circ$ ).<sup>14</sup> The precision in the atomic parameters of  $\text{Na}^+$  and  $\text{O}^{2-}$  is necessarily lower than for the stronger X-ray scatterers  $\text{La}^{3+}$  and  $\text{Te}^{6+}$ , but the high atomic displacement parameters of the  $\text{Na}^+$  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<sup>†</sup>), in excellent agreement with XRD and the target stoichiometry. Raman analysis (Fig. S1, ESI<sup>†</sup>) 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  $\mu\text{m}$ , 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 ( $\mu^+\text{SR}$ )

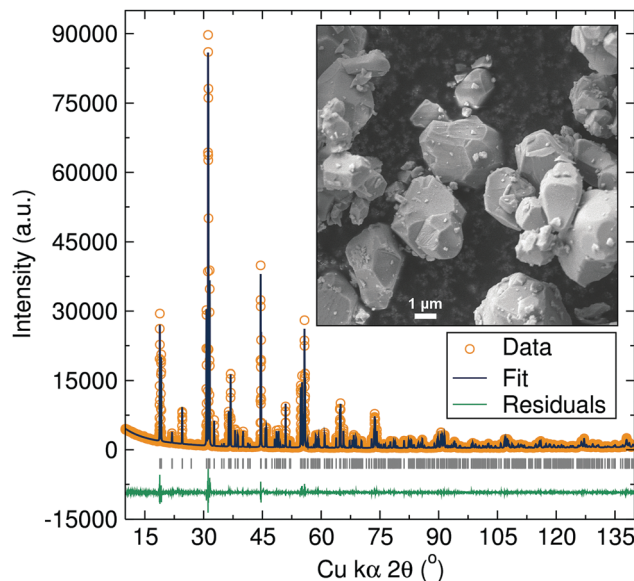


Fig. 2 Rietveld refinements of XRD data for the  $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$  double perovskite to the  $P2_1/n$  monoclinic space group. Bragg peaks positions for the monoclinic  $P2_1/n$  structure are indicated by vertical grey tick marks. Fit in excellent agreement to monoclinic 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.<sup>20</sup> 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.<sup>21–25</sup> 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.<sup>26,27</sup> 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  $\text{mS cm}^{-1}$  range.<sup>5,12</sup> 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





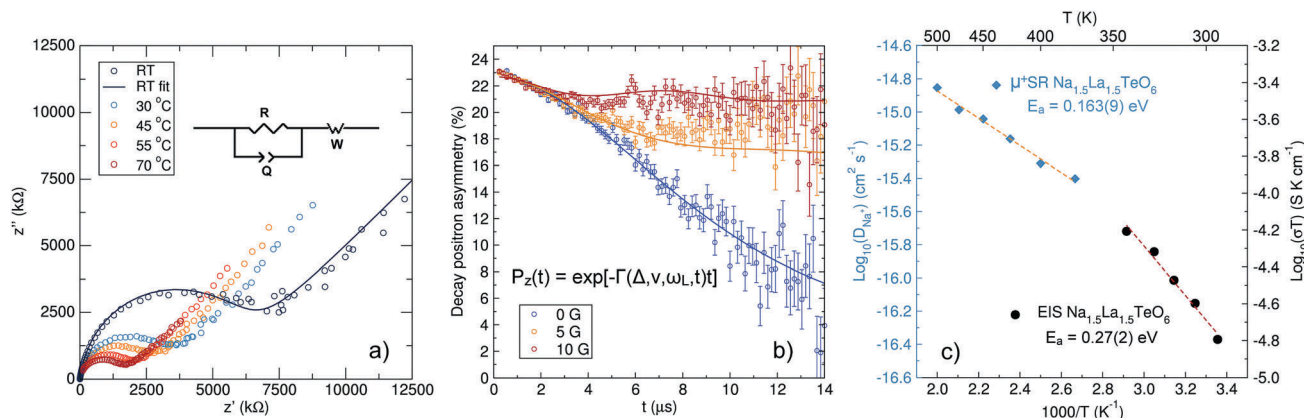


Fig. 3 (a) Nyquist plot of EIS data for  $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$  at different temperatures and a representative fit to the equivalent electrical circuit. (b) Room temperature  $\mu^+\text{SR}$  data collected for  $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$  at zero field and applied 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.<sup>14</sup> 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  $\text{Na}^+$  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,<sup>2,3,28</sup> for example  $\text{Na}_3\text{PSe}_4$  which displays an activation energy of 0.21 eV.<sup>29</sup> 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  $\text{Na}^+$  as the conducting species (Fig. S3, ESI<sup>†</sup>). 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.<sup>30,31</sup>

The local  $\text{Na}^+$  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  $\text{Li}^+$  and  $\text{Na}^+$  diffusion in battery materials has grown in recent years.<sup>15,32–34</sup> The natural abundance of the spin 1/2  $^{23}\text{Na}$  isotope is 100%, making  $\text{Na}^+$  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 ( $^{23}\text{Na}$ ,  $^{139}\text{La}$  and  $^{125}\text{Te}$ ) which can interact with the muon spin. To obtain the fluctuation rate of the muons due to sodium-ion diffusion (Fig. S4, ESI<sup>†</sup>), the muon decay asymmetry data were fitted using Keren's analytic generalization of the Abragam function (Fig. 3b).<sup>35</sup> The  $\text{Na}^+$  diffusion coefficients from the muon fluctuation rate at different temperatures were then calculated applying eqn (1),<sup>36</sup> 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  $\text{Na}^+$  sites, and  $\nu$  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  $\text{Na}^+$  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.<sup>14</sup> The model is shown in Fig. S5 (ESI<sup>†</sup>) where  $\text{Na}^+$  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  $\text{Na}^+$  diffusion. Additionally, a conservative 0.01 vacancy fraction in the  $\text{Na}^+$  positions was introduced in both A and B sites to allow diffusion. From this preliminary model, and introducing the two different  $\text{Na}_A$ – $\text{Na}_B$  distances of 3.33 and 3.46 Å, a  $\text{Na}^+$  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  $\text{Na}^+$  diffusion.<sup>34,37,38</sup> The microscopic diffusion of  $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$  is also in line with other  $\text{Na}^+$  ionic conductors such as the  $\text{Na}_x\text{WO}_2\text{Cl}_2$  tungsten bronze with a  $\text{Na}^+$  diffusion coefficient of  $10^{-13} \text{ cm}^2 \text{ s}^{-1}$ ,<sup>39</sup> and  $\text{Na}_3\text{PS}_4$  with a value in the range of  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ .<sup>40</sup> The  $\mu^+\text{SR}$  measurements indicate that the activation energy required for local  $\text{Na}^+$  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,<sup>12</sup> or  $\beta'$ -alumina single crystals with activation energies in the 0.12–0.16 eV range.<sup>41</sup>

The higher activation energy values obtained from the macroscopic EIS measurements which probes long range  $\text{Na}^+$  conduction through multiple intra-grain crystalline sites and grain boundaries, compared to microscopic  $\mu^+\text{SR}$  measurements which are more sensitive to individual  $\text{Na}^+$  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  $\mu^+$ SR. Lower conductivity values and higher energy barriers to diffusion could also result from the presence of  $\text{La}^{3+}$  ions in the A-sites, which could hinder long-range  $\text{Na}^+$  conductivity. Nevertheless, the excellent microscopic  $\text{Na}^+$  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  $\text{Na}^+$  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.  $\mu^+$ SR measurements reveal a microscopic diffusion coefficient for  $\text{Na}^+$  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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