

Supplemental Information

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

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Chemicals

All reagent-grade chemical employed were purchased from the following suppliers and used without further purification unless otherwise noted: NaOH (98%) and La₂O₃ (99%) from Sigma-Aldrich, and TeO₂ (99.99%) was purchased from Alfa Aesar.

Synthesis of the Na_{1.5}La_{1.5}TeO₆ double perovskite

For the microwave-assisted synthesis of the Na_{1.5}La_{1.5}TeO₆ double perovskite, stoichiometric amounts of La₂O₃ (previously dried at 900 °C for 24h), TeO₂ and NaOH were ball milled for 30 min at a vibrational frequency of 20 Hz in a stainless steel jar. Subsequently, the fine powder was pelleted at 3 tonnes under uniaxial pressure. The pelleted material was heated at 700 °C for 6 hours in a 2.45 GHz CEM Phoenix hybrid microwave furnace for the decomposition of the precursor materials. Subsequently, the material was reground and pelletized for a second heat treatment carried out in air at 900 °C for 6 hr in the same microwave furnace. The last treatment consisted in 1 hour at 1000 °C of the repelletised material in the same hybrid microwave furnace. In every calcination the heating rate was held at 2 °C/min.

Powder X-Ray Diffraction experiments and Rietveld Refinements

Powder X-Ray Diffraction (PXRD) has being the main tool employed for the assessment of the purity and study of the crystal parameters for the Na_{1.5}La_{1.5}TeO₆ material. A PANalytical X'Pert PRO Diffractometer was used for this purpose using Cu-K α radiation in the 2 θ range 10-140° with a nominal scan rate of 800 seconds per step and a step size of 0.0167° in reflection geometry at room temperature.

Rietveld refinements of PXRD patterns were performed with the Generalized Structure Analysis System (GSAS) along with the graphical user interface EXPGUI by means of a least square approach.

Scanning Electron Microscopy and Energy-Dispersive X-Ray spectroscopy

In order to analyse the size and morphology of the particles synthesised, Scanning Electron Microscopy (SEM) images were acquired with a Phillips XL30 ESEM microscope. The sample was ground and a tiny amount of the fine powder was deposited over a carbon-taped sample holder.

Energy-Dispersive X-Ray (EDX) spectra were recorded using an Oxford Instruments Energy 250 energy dispersive spectrometer system attached to the SEM device. Copper tape was employed as a standard for calibration and the voltage of the incident beam was 25 KeV.

Electrochemical Impedance Spectroscopy

Impedance measurements were performed on a Biologic VSP-3 multichannel potentiostat in the frequency range of 1-10⁶ Hz with a voltage perturbation of 500 mV and a temperature range between 20 and 70 °C. Na_{1.5}La_{1.5}TeO₆ powders were cold-pressed under uniaxial pressure at 5 tons and the resultant pellets were heated for 1 hour at 1000 °C. In order to enhance the connection between the pellet and the electrodes, a thin layer of gold was deposited on the pellet surface by physical vapor deposition.

μ^+ SR studies

μ^+ SR studies were performed using the EMU instrument at the ISIS pulsed muon facility. The sample, *c.a.* 1.5 g, was packed into a disk of 30 mm diameter and 1.5 mm thickness and sealed in a titanium sample holder where the front window was made of 25 μm thickness titanium foil. 3.2 MeV spin-polarised positive muons were implanted into the sample and the outgoing positrons were detected by 96 scintillator segments grouped in two circular arrays. The temperature was controlled up to 500 K by a hot stage attached to a closed cycle refrigerator and the measurements were acquired at three different applied longitudinal magnetic fields (0, 5 and 10 G). A 20 G transverse magnetic field was also applied for the initial asymmetry calibration.

Table S1: Refined parameters of the PXRD data of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite to the $\text{P2}_1/\text{n}$ monoclinic space group and selected metal-oxygen distances.

Atom	Site	Frac.	x	y	z	Uiso ($100/\text{\AA}^2$)
La1	4e	0.767(2)	0.0118(2)	0.9552(1)	0.7486(1)	0.91(2)
Na1	2d	1.00(1)	$1/2$	0	0	2.4(2)
Na2	4e	0.239(2)	0.0118(2)	0.9552(1)	0.7486(1)	2.4(2)
O1	4e	1	0.279(1)	0.692(1)	0.9559(9)	1.5(2)
O2	4e	1	0.168(1)	0.216(1)	0.9441(9)	1.4(2)
O3	4e	1	0.910(1)	0.534(1)	0.7719(8)	1.3(2)
Te1	2c	1	$1/2$	0	$1/2$	0.16(2)

$$a = 5.69186(2) \text{ \AA}, b = 5.83933(2) \text{ \AA}, c = 8.13119(3) \text{ \AA}, \beta = 90.186(1)^\circ, V = 270.253(1) \text{ \AA}^3$$

$$R_{\text{wp}} = 0.0743, R_p = 0.0530, \chi^2 = 7.051$$

Bond	Distance (\AA)	Bond	Distance (\AA)
B-site cations			
Te-O1 (2x)	1.976(7)	Na1-O1 (2x)	2.225(7)
Te-O2 (2x)	1.967(7)	Na1-O2 (2x)	2.315(6)
Te-O3 (2x)	1.932(6)	Na1-O3 (2x)	2.280(6)
A-site cations			
Na2/La-O1	2.726(7)		
Na2/La -O1	2.482(7)		
Na2/La -O1	2.849(7)		
Na2/La -O2	2.387(7)		
Na2/La -O2	2.771(7)		
Na2/La -O2	2.878(7)		
Na2/La -O3	2.514(6)		
Na2/La -O3	2.456(6)		

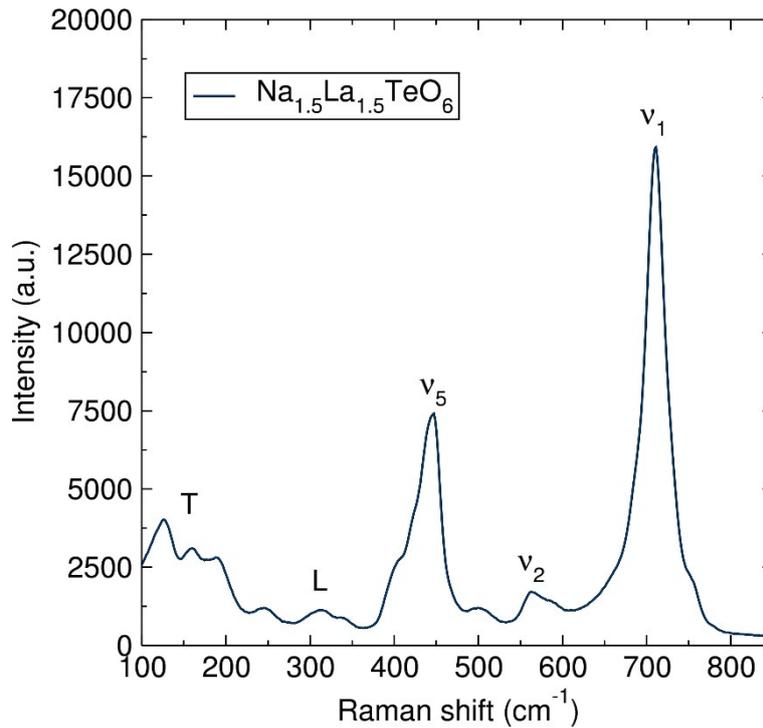
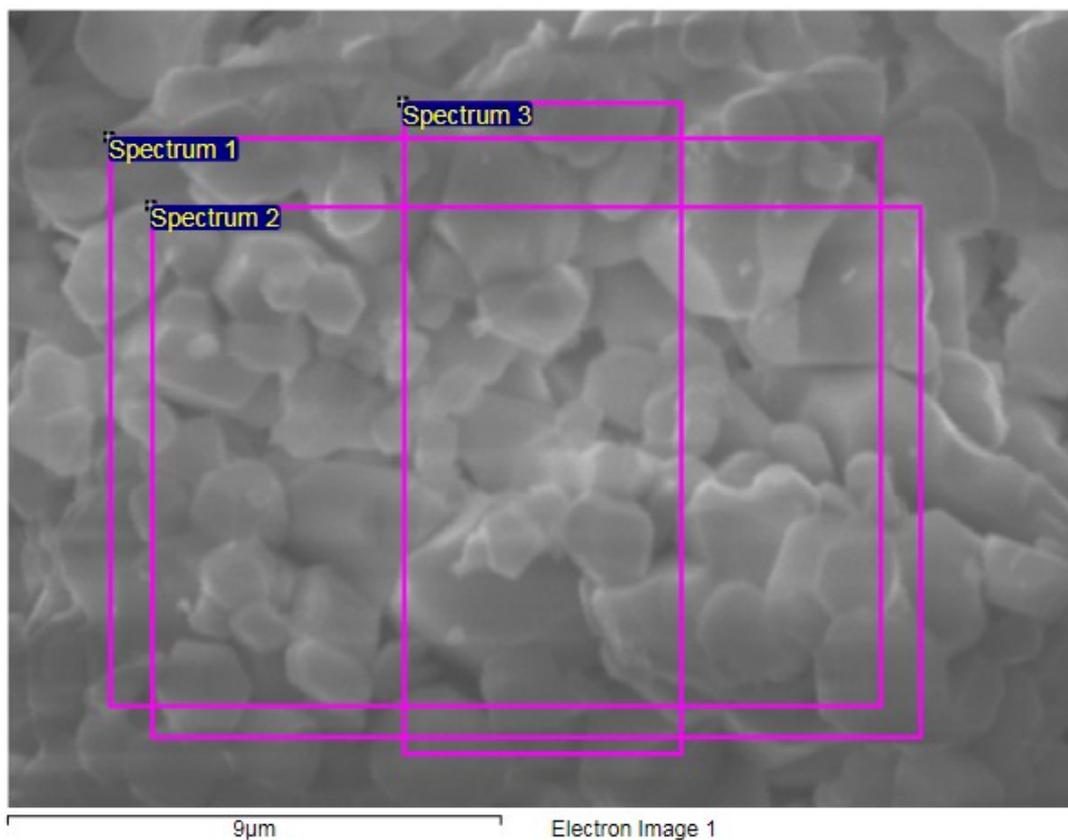


Figure S1: Raman spectra of the Na_{1.5}La_{1.5}TeO₆ double perovskite under excitation of a wavelength $\lambda = 532$ nm Argon-ion laser.

The Raman spectrum of the Na_{1.5}La_{1.5}TeO₆ double perovskite presents bands that could be assigned to a monoclinic P2₁/n group with an irreducible representation $\Gamma = v_1(A_g + B_g) + v_2(2A_g + 2B_g) + v_5(3A_g + 3B_g) + T(3A_g + 3B_g) + L(3A_g + 3B_g)$ for the Raman active modes. Vibrational modes (v) are related to internal M-O stretching and bending modes, the translational modes (T) arise from translations of the A cations and the librational modes (L) are due to the asymmetric MO₆ octahedral rotation. Translational modes appear at low Raman shift, around 100 to 200 cm⁻¹ close to the elastic peak and the librational modes appear at higher Raman shift between 200 and 400 cm⁻¹. The symmetric stretch v_1 presents the most intense peak of the spectra at *ca.* 710 cm⁻¹ and the asymmetric stretch v_2 is observed at *ca.* 565 cm⁻¹. The internal oxygen bending mode v_5 appears at *ca.* 440 cm⁻¹.



Processing option : All elements analysed (Normalised)

Spectrum	In st...	Na	Te	La
Spectrum 1	Yes	39.7	24.2	36.1
Spectrum 2	Yes	38.9	24.3	36.8
Spectrum 3	Yes	35.5	25.7	38.8
Mean		38.0	24.8	37.2
Std. deviation		2.3	0.9	1.4
Max.		39.7	25.7	38.8
Min.		35.5	24.2	36.1

All results in atomic%

Material	Na (atomic %)	La (atomic %)	Te (atomic %)	Na:La:Te ratio
$\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$	38(2)	37(1)	25(1)	1.52(8):1.48(4):1.00(4)

Figure S2: EDX analyses of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ material exposed to an electron beam of 25 kV for 2 min per spectrum. Value of atomic % for Te has been used as reference for the metal ratio calculation.

Table S2: Ionic conductivity values obtained from AC EIS measurements at different temperatures for the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ double perovskite material. The conductivity values have been calculated by applying Pouillet's law, $\sigma = l / (A \times R)$, where l is the sample thickness, A the area of the pellet and R the resistance calculated from the Nyquist plots.

Temperature (K)	Total conductivity (S cm^{-1})
298	5.4×10^{-8}
308	8.2×10^{-8}
318	1.1×10^{-7}
328	1.5×10^{-7}
343	1.8×10^{-7}

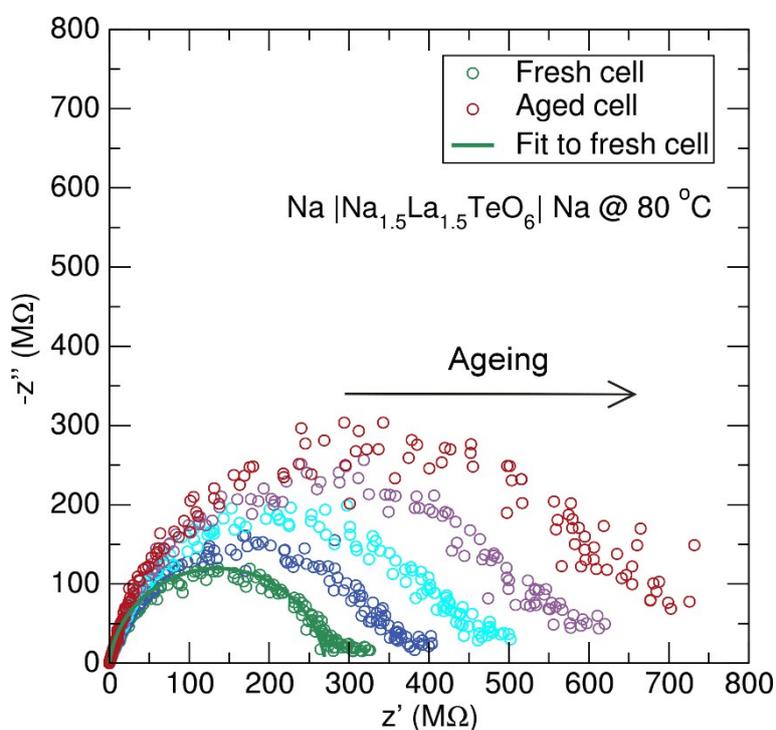


Figure S3: Nyquist plots of the EIS data for the symmetric $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ cell at $80\text{ }^\circ\text{C}$ over time. Experimental data is represented in open circle and the fit to an R/Q equivalent electrical circuit is represented by the solid line.

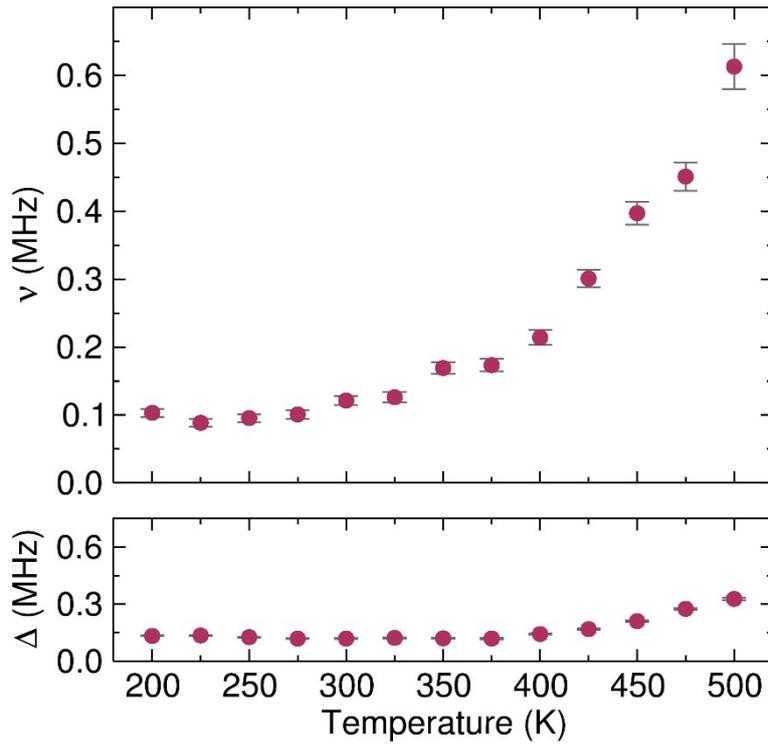


Figure S4: Temperature dependence of ν and Δ values obtained for the fits to the Keren function for the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ material measured from 200 K to 500 K.

To obtain the fluctuation rate of the muons due to sodium-ion diffusion, the muon decay asymmetry data were fitted using Keren's analytic generalization of the Abragam function appropriate for μSR $P_z(t) = \exp[\Gamma(\Delta, \nu, \omega_L, t)t]$ where the $\Gamma(\Delta, \nu, \omega_L, t)$ term refers to the muon polarization after subtracting a fixed background component. The Δ parameter corresponds to the static width of the local field distribution at the implanted sites in the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ material, ν is the muon's spin fluctuation rate and ω_L is the Larmor precession frequency in the applied magnetic field. The temperature evolution of the muon's spin fluctuation rate (ν) follows a plateau from 200 K to 300 K, experiencing an exponential increase above this latter temperature. This is indicative of thermally activate diffusion of the Na^+ ions in the double perovskite structure above this temperature (*ca.* 300 K). In the case of the field width distribution (Δ), the parameter tends to a constant value of 0.15 MHz at low to medium temperatures, with a small increase towards 0.3 MHz at high temperatures. This slightly increase of the Δ parameter near 500 K could be related to possible small structural rearrangements, such as oxygen displacements near the muon implanting positions. The most important fact to note is the absence of a drastic decrease in Δ , which would have indicated muon self-diffusion in the material.

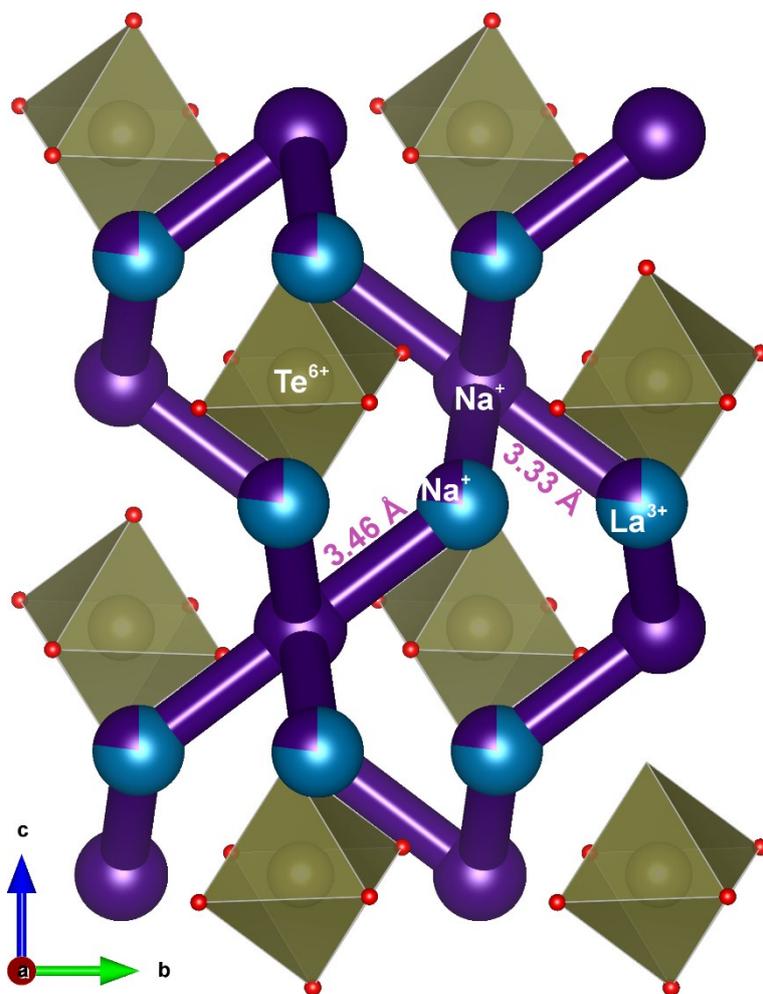


Figure S5: Representation of the $\text{Na}_{1.5}\text{La}_{1.5}\text{TeO}_6$ crystal structure where the proposed Na_A - Na_B hopping pathways are explicitly displayed in purple. Na^+ ions are represented in purple, La^{3+} in blue and Te^{6+} in brown with their coordination octahedron displayed also in brown with oxygen anions represented in red.