Supplementary Information

Enhancement of the lithium ion conductivity of Ta-doped $Li_7La_3Zr_2O_{12}$ by incorporation of calcium

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Experimental section

Synthesis. Lithium acetate (99.95%, Aldrich), lanthanum oxide (≥99.9%, Aldrich), zirconium oxynitrate hydrate (99%, Aldrich), Tantalum ethoxide (99.98%, Aldrich) and Calcium carbonate (99.0%, Alfa Aesar) were used as starting materials. The water content of zirconium oxynitrate hydrate was determined thermogravimetrically, and lanthanum oxide was dried at 900°C for 12 h prior to use. For the $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ sample, stoichiometric amounts of the starting materials with 10 mol% excess of Li were used. The Ca-containing phase was prepared using a La/Ca/Zr/Ta molar ratio of 2.9:0.2:1.4:0.6. In the case of the Ca-containing sample, the small La deficiency was required to obtain impurity-free phases. The reagents were dissolved in dilute nitric acid (2 wt%) at ~80°C. Equivalent amount of EDTA (metal ions to EDTA molar ratio is $^{1:2}$) was dissolved in an ammonium hydroxide solution (28.0-30.0% NH_3, Aldrich) and added to the metal ion solution (solution A). A stoichiometric amount of tantalum ethoxide was dissolved in an NH_3/H_2O_2 (1:1, vol/vol) solution at ~80°C (solution B). Solutions A and B were carefully mixed and the resulting clear solution was evaporated at 80°C. The brown gel obtained is then burnt out at 550-600°C, until a white solid precursor is obtained. This white precursor is calcined at 900°C for 2h using a microwave hybrid furnace (CEM Phoenix). For impedance measurements, the powders were uniaxially pressed into pellets and calcined at 1000 °C for 1h

using a thick platinum sheet as a sample holder to avoid any Al contamination which may occur if alumina crucibles are used. To prepare more dense pellets, the powders were hot-pressed into 13 mm diameter cylindrical ingots for 20 min at 1000 °C and 40 MPa. The density of the sintered pellets was calculated using the bulk geometry and the mass, and compared to the theoretical density deduced from Rietveld refinement of the diffraction data.

Characterization methods. XRD studies were performed using a PANalytical X'Pert PRO diffractometer in reflection mode using Cu-Kα radiation. ICP-MS analysis was performed using an Agilent 7700 ICP-MS instrument. NPD data were collected using the Polaris instrument at the ISIS facility, Rutherford Appleton Laboratory, UK. A multi-histogram Rietveld fit to Polaris detector banks 4 and 5 was done using the GSAS and EXPGUI suite of programmes.[1] SEM studies were performed using Carl Zeiss Sigma variable pressure analytical electron microscope. AC impedance measurements were recorded using a Solartron 1260 impedance analyzer in the frequency range of $3\ MHz$ to $1\ Hz$ (an electrical perturbation of $50\ mV$) using gold electrodes. Gold electrodes were gas-phase deposited on the circular sides of the pellets by thermal evaporation and platinum wires were used to collect the current. Variable temperature conductivity measurements were carried out in the temperature range 25-130°C. Prior to each impedance measurement, the samples were equilibrated for $30\ min$ at constant temperature.

Bond Valence Sums. These were calculated to assess the suitability of two candidate sites for the Ca^{2+} cation in the Ca doped sample using published valence parameters.[2,3] The two sites in question are the 24*c* site occupied by lanthanum and the 16a site occupied by a mixture of Zr/Ta.

The 24*c* site has a total of eight bond lengths to oxide anions: four at a distance of 2.510 and four at 2.590 Å. This gives a bond valence sum of 0.230 × 4 + 1.856 × 4 = 1.66 valence units.

The 16*a* site has six identical bonds at a length of 2.079 Å giving a bond valence of 0.74 × 6 = 4.43

1. A.C. Larson, R.B. Von Dreele, General Structural Analysis System, Los Alamos National Laboratory, Los Alamos, NM, **1994**.

2. N. E. Brese, M. O'Keeffe, Bond-valence parameters for solids, *Acta Cryst.* **1991**, *B47*, 192-197.

3. M. W. Lufaso, P. W. Barnes, P. M. Woodward, Structure prediction of ordered and disordered multiple octahedral cation perovskites using SPuDS, *Acta Cryst.* **2006**, B62, 397-410.

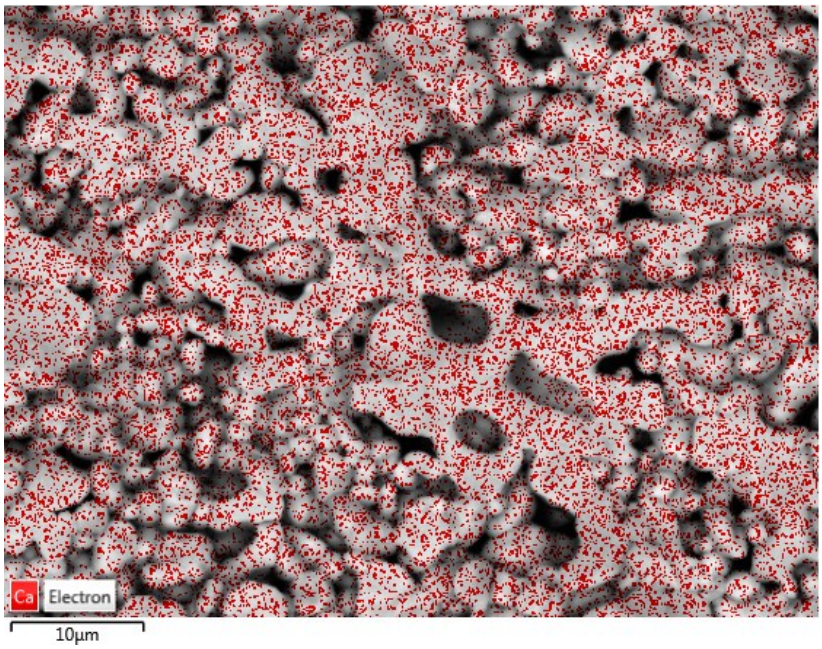

Figure S1. EDX elemental map of Ca-containing $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, showing the distribution of Ca (red).

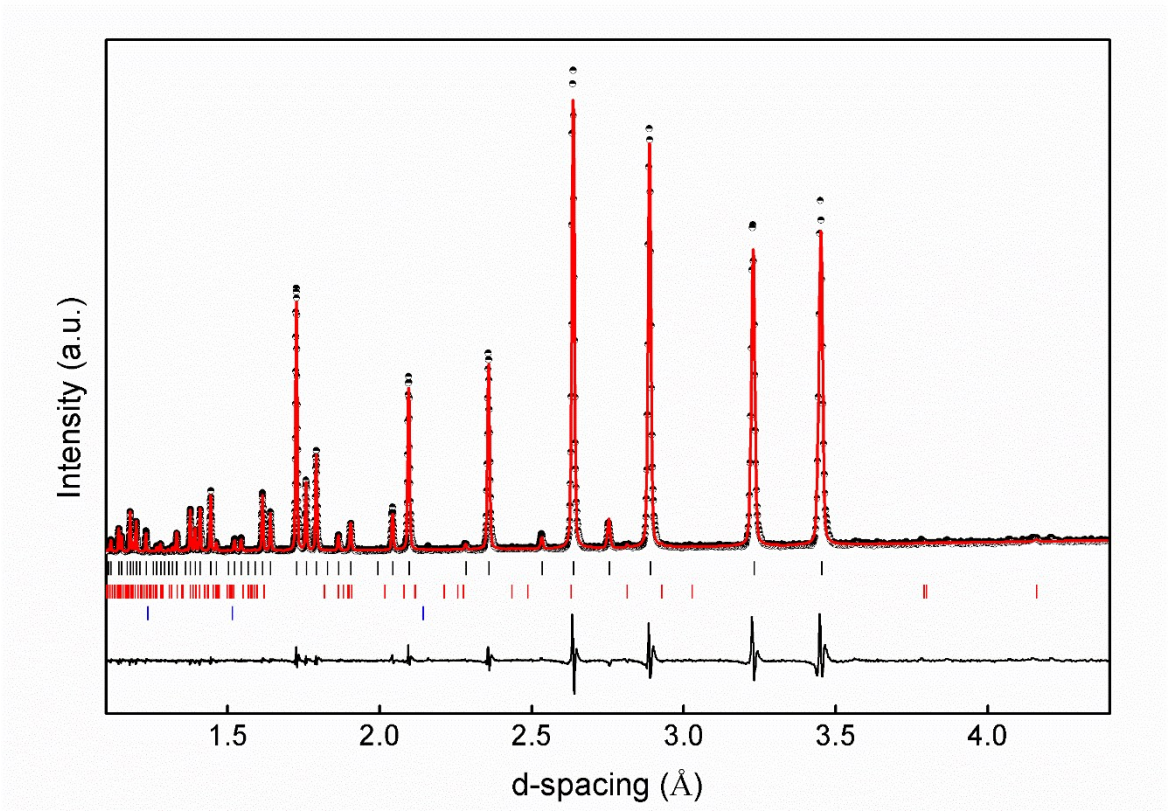

Figure S2. Rietveld fit to XRD data for Ca-doped $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ calcined at 900 °C. The top markers (black) are for the garnet phase; the middle markers (red) are for Li_2CO_3; the bottom markers (blue) are for V. The fit is a part of the simultaneous refinement of both XRD and neutron diffraction data.

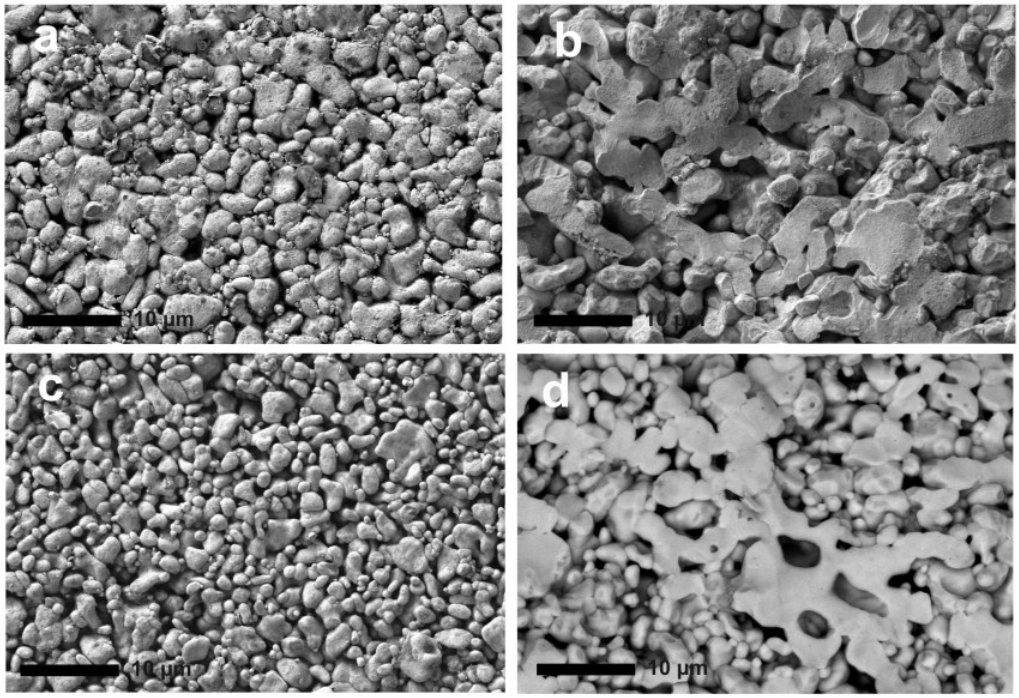

Figure S3. SEM images of a) cold-pressed $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, b) hot-pressed $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, c) cold-pressed Ca-doped $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$, and d) hot-pressed Ca-doped $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$.

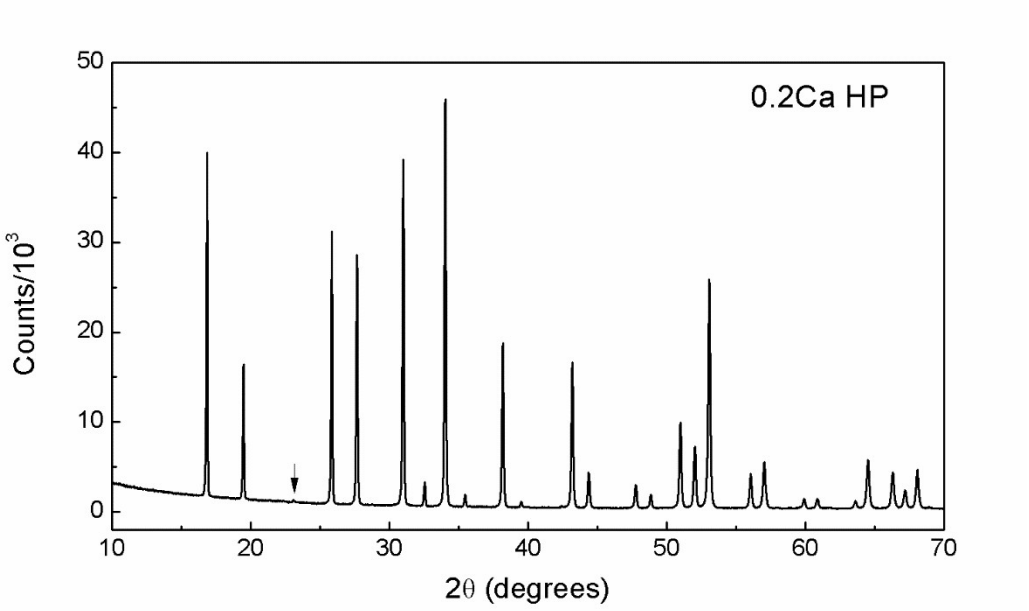

Figure S4. XRD pattern of Ca-doped $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ after hot-pressing (1000 °C). A minor impurity of a lithium zirconium oxide phase ($Li_4Zr_3O_8$: PDF-01-073-4098) appeared (see arrow).

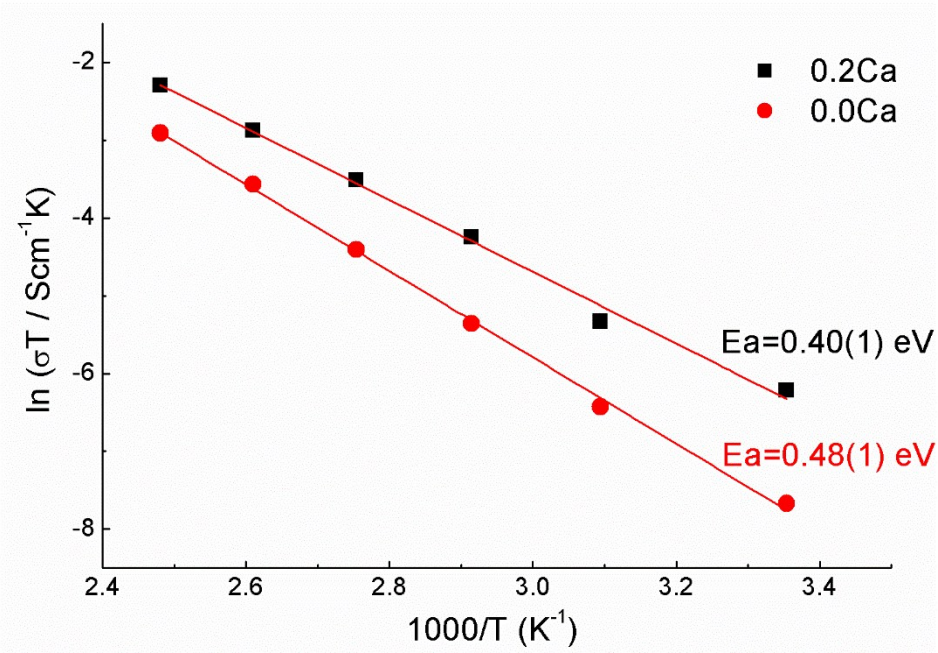

Figure S5. Arrhenius plots for the total conductivity of cold-pressed samples calcined at 1000 °C.

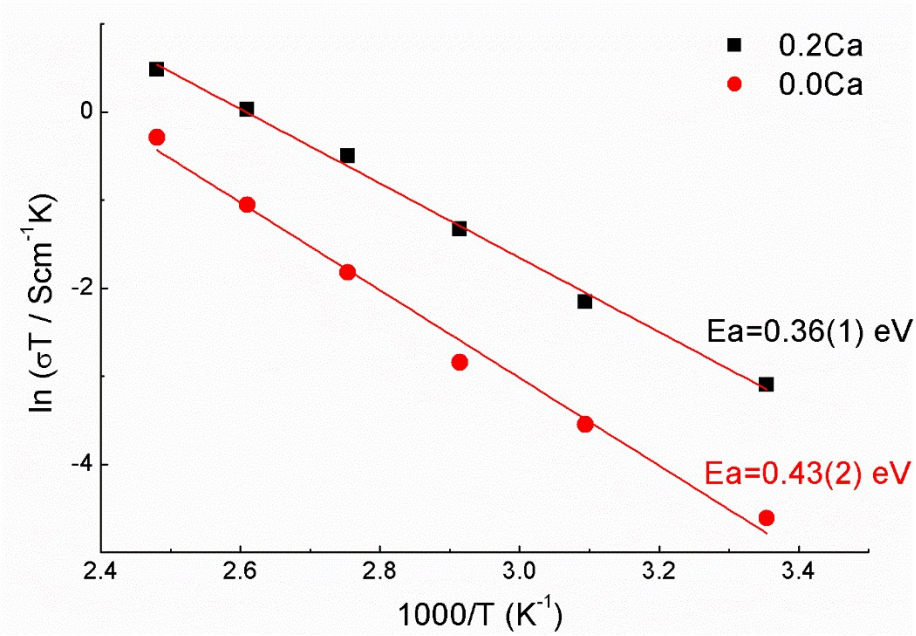

Figure S6. Arrhenius plots for the total conductivity of hot-pressed samples at 1000 °C.

Table S1. Refined structural parameters for Ca-doped $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ calcined at 900 °C, from Rietveld fits against XRD and Polaris neutron powder diffraction data[a]

atom	site	occupation	x	y	Z	U_{iso} (Å^2)
Li1	24d	0.605(25)	0.375	0	0.25	0.046(4)
Li2	48g	0.201(21)	0.125	0.680(1)	0.570(1)	0.014(2)
Li3	96h	0.272(12)	0.094(1)	0.1901(8)	0.4219(7)	0.014(2)
La	24c	0.96	0.125	0	0.25	0.0112(2)
Ca	24c	0.074(8)	0.125	0	0.25	0.0112(2)
Zr	16a	0.7	0	0	0	0.0084(2)
Ta	16a	0.3	0	0	0	0.0084(2)
O	96h	1	0.10169(5)	0.19653(6)	0.28155(5)	0.0141(2)

[a]Space group $Ia\bar{3}d$, a = 12.92204(8) Å; final fit statistics: χ^2= 4.578; bank 5 (Polaris): wRp = 0.0178, Rp = 0.0278; bank 4 (Polaris): wRp = 0.0234, Rp = 0.0316; bank 1 (XRD): wRp = 0.1206, Rp = 0.0921. The sample contains Li_2CO_3 (2.0(1) wt%) as a secondary phase.