Supplementary information

The activation entropy for ionic conduction and critical current density for Li charge transfer in novel garnet-type $Li_{6.5}La_{2.9}A_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (A = Ca, Sr, Ba) solid electrolytes

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1. Derivation of friction coefficient of Li ion and relation with conductivity

The total Coulombic potential experienced by the Li ion within such a cylindrical element of the pathway is given by:

$$U(\rho,z) = \Psi_0 K_0(\frac{2\pi}{l}\rho)\cos\left(\frac{2\pi z}{l}\right) \quad (1)$$

Here, Ψ_0 is a constant, which depends on the charges of the Li ion and the counterions (in the present case oxygen ions). The distribution of the negatively charged oxygen ions in the form of periodic octahedral and tetrahedral arrangements are assumed to result in periodic negatively charged rings on the cylinder wall. In, addition, since we are dealing with charge-charge interactions, Ψ_0 also includes a dependence on the dielectric constant. The precise mathematical form of Ψ_0 appears in the geometrical considerations that are used in the Coulombic summation (used in the derivation of Eq.(1)) procedure developed by Gronbech-Jensen, Hummer and Beardmore.[1] However, in this paper we treat Ψ_0 as a parameter that is determined from experiment hence it is not necessary to write down its detailed mathematical form. K_0 is the modified Bessel's

functions of the second kind while ρ and z are the radial and axial cylindrical coordinates with the limits $0 \le z \le l$ and $\sigma_H \le \rho \le R$ (where σ_H is the hard sphere radius of the Li ion).

The frictional force, in the present context, is the reactive force exerted by the lattice on the Li ion due to the motion of the latter. The Hamiltonian and the corresponding Liouville operator (McQuarrie)[2] are given by:

$$H\left(p_z, p_\rho, z, \rho\right) = \frac{p_z^2}{2m} + \frac{p_\rho^2}{2m} + \Psi_0 K_0\left(\frac{2\pi}{l}\rho\right)\cos\left(\frac{2\pi z}{l}\right) \tag{2}$$

$$L\left(z, \rho, p_z, p_\rho\right) = -i\left[\frac{p_z}{m}\frac{\partial}{\partial z} + \frac{p_\rho}{m}\frac{\partial}{\partial \rho} + \frac{2\pi\Psi_0}{l}\sin\left(\frac{2\pi z}{l}\right)K_0\left(\frac{2\pi}{l}\rho\right)\frac{\partial}{\partial p_z} + \frac{2\pi\Psi_0}{l}\cos\left(\frac{2\pi z}{l}\right)K_1\left(\frac{2\pi}{l}\rho\right)\frac{\partial}{\partial p_\rho}\right] \tag{3}$$

Here, p_z and p_ρ are the components of **p** along the z and ρ axes of a cylindrical frame respectively.

Using the standard techniques, the force component experienced by the lattice due to the Li ion in the z direction will be given by $F_z = iLp_z$. If the external field acts along the z axis we consider F_z only:

$$F_z\left(z, \rho\right) = iLp_z = \frac{2\pi\Psi_0}{l}K_0\left(\frac{2\pi\rho}{l}\right)\sin\left(\frac{2\pi z}{l}\right) \tag{4}$$

Here, $F_z\left(z, \rho\right)$ is the force at an initial point in time, which we take to be $t = 0$ and the value of this force at a later point in time t will be given by: $F_z\left(z, \rho, t\right) = e^{iLt}F_z\left(z, \rho\right)$. This leads to the force-force correlation function:

$$G\left(t\right) = \left\langle F_z e^{iLt} F_z \right\rangle \tag{5}$$

Invoking the principles of non-equilibrium statistical mechanics, the friction coefficient of the Li ion will be given by a time integral of the correlation function (commonly referred to as the Kubo-Green formula):

$$\zeta = \frac{1}{kT}\int_0^\infty dtG(t) \tag{6}$$

Here, the pointed brackets in Eq. (6) are the equilibrium statistical mechanical averages involving the equilibrium distribution function f_{eq} which, in the present case can be written as a product of the momentum distribution and the three spatial coordinates:

$$f_{eq}\left(z,\rho,p_z,p_\rho\right) \equiv \psi\left(p_z\right)\psi\left(p_\rho\right)\phi\left(z,\rho\right) \tag{7}$$

$G\left(t\right)$ can be written as a power series:

$$G\left(t\right) = \sum_{n=0}^{\infty}\frac{\left(-t\right)^{n+1}}{n!}c_{n+2} \tag{8}$$

Where, c_v is the v^{th} *moment* defined as follows:

$$c_v = \left\langle p_z \left(iL\right)^v p_z \right\rangle \tag{9}$$

Using a well-known mathematical method known as the Pade' approximant method just the moments c_2 and c_4 are sufficient for the calculation.

The computation of the moments is straightforward but tedious hence only the final results will be given:

$$c_2 = 4\pi^2 kT\frac{\Psi_0}{l^2}I_1 \tag{10}$$

$$c_4 = \frac{8\pi^4 kT}{l^4 m_c}\Psi_0\left[3kT\left(I_2 - I_1\right) + 2\Psi_0\left\{I_3 - 3\left(I_4 + I_5\right) + I_6\right\}\right] \tag{11}$$

The quantities I_j are defined as follows:

$$I_1 = \left\langle \cos\left(\frac{2\pi z}{l}\right) K_0\left(\frac{2\pi\rho}{l}\right) \right\rangle_\phi , I_2 = \left\langle \cos\left(\frac{2\pi z}{l}\right) K_2\left(\frac{2\pi\rho}{l}\right) \right\rangle_\phi ,$$
$$I_3 = \left\langle \cos^2\left(\frac{2\pi z}{l}\right) K_0\left(\frac{2\pi\rho}{l}\right)^2 \right\rangle_\phi , I_4 = \left\langle \cos^2\left(\frac{2\pi z}{l}\right) K_1\left(\frac{2\pi\rho}{l}\right)^2 \right\rangle_\phi , \quad \backslash^*$$
$$I_5 = \left\langle \sin^2\left(\frac{2\pi z}{l}\right) K_0\left(\frac{2\pi\rho}{l}\right)^2 \right\rangle_\phi , I_6 = \left\langle \sin^2\left(\frac{2\pi z}{l}\right) K_1\left(\frac{2\pi\rho}{l}\right)^2 \right\rangle_\phi$$

MERGEFORMAT (12)

Here, the subscript ϕ implies that only the spatial part of the distribution function as defined in Eq. * MERGEFORMAT (8) is involved. Before leaving Eq. * MERGEFORMAT (12) it is useful to comment on the physical meaning of the quantities designated by the symbol I_j. From Eq. * MERGEFORMAT (9) the repeated application of the Liouville operator will result in the force given by the negative gradient of the potential $U(\rho,z)$, as shown in Eq. * MERGEFORMAT (4), which will then be followed by higher order derivatives and then thermally averaged. Ideally, we should calculate all infinite derivatives of the force which is, clearly impossible and we truncate the expansion * MERGEFORMAT (8) at $n=4$ thus the seven quantities averaged in Eq. * MERGEFORMAT (12) are:

$$-U^{(0,4)}(\rho,z); U_a^{(2,2)}(\rho,z); U_b^{(2,2)}(\rho,z); U^{(0,2)}(\rho,z)^2; U^{(1,0)}(\rho,z)U^{(1,2)}(\rho,z);$$
$$U^{(0,1)}(\rho,z)U^{(0,3)}(\rho,z); U^{(1,1)}(\rho,z)^2$$

The superscripts are the orders of the differentiation of $U(\rho,z)$ with respect to ρ and z respectively.

The friction coefficient now becomes:

$$\zeta = \frac{\pi \, |c_2|^{3/2}}{kT\sqrt{2|c_4|}} \tag{13}$$

The conductivity, σ and friction coefficient, ζ are related by the standard Nernst-Einstein formula:

$$\sigma = q_{Li}^2 \rho_{Li} \frac{1}{\zeta} \tag{14}$$

where q_{Li} is the charge carried by the Li ion, ρ_{Li} is the number density of the Li ion.

2. ΔS calculation for $Li_{6.5}La_{2.9}Ba_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ at 294 K.

$$\Delta S = k \ln \left[\frac{\pi^2 \sqrt{2m_c |\Psi_0|}}{l q_{Li}^2 \rho_{Li}} \sigma \right] + \frac{E_a}{T}$$

$$= \frac{1.3806 \, x \, 10^{-23} \, m^2 kg S^{-2} K^{-2}}{} \ln \left[\frac{(3.14)^2 \sqrt{2 \, x \, 8.544 \, x \, 10^{-11} \, kg| - 3.21 \, x \, 10^{-19} J|}}{8.544 \, x \, 10^{-11} m \, x \, (1.602 \, x \, 10^{-19} \, C)^2 \, x \, 2.49 \, x \, 10^{28} \, m^{-3}} 4 \, x \, 10^{-2} \frac{S}{m} \right] + \frac{6.25 \, x \, 10^{-20} J}{294 \, K}$$

= 3.63 x 10^{-22} *J/K*

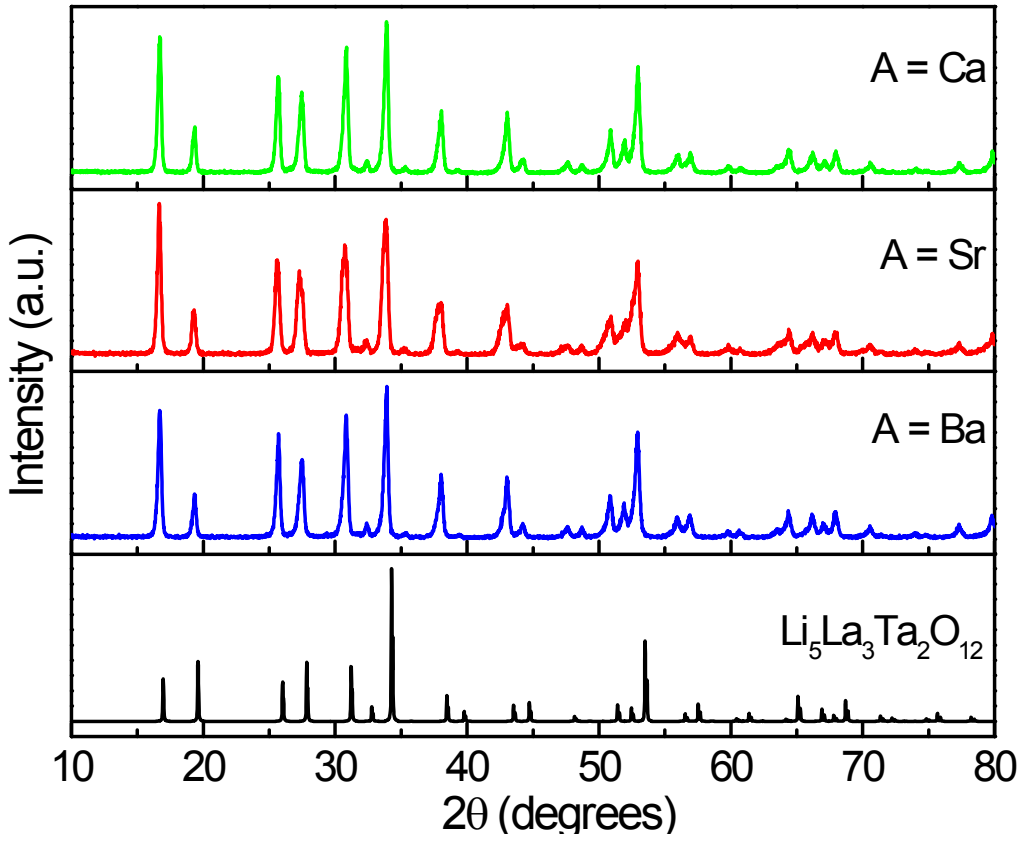

Fig. S1. XRD patterns of garnet-type $Li_{6.5}La_{2.9}A_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (A = Ca, Sr, Ba) pellets prepared by SPS process and the calculated pattern of cubic garnet-type $Li_5La_3Ta_2O_{12}$ (space group: $Ia\bar{3}d$; a = 12.80 Å) using the PowderCell program.[3]

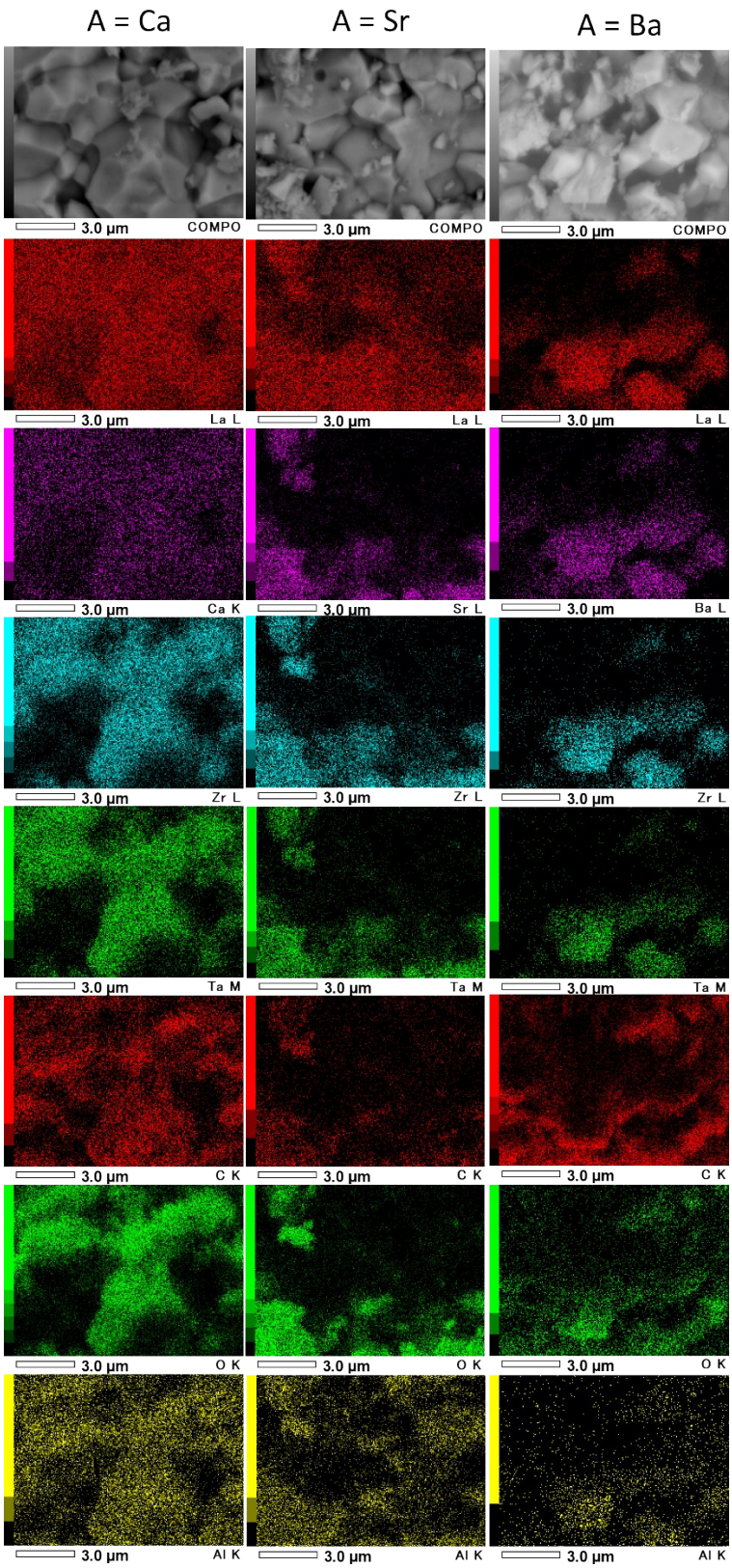

Fig. S2. SEM images and corresponding elemental mapping of $Li_{6.5}La_{2.9}A_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (A = Ca, Sr, Ba) garnet electrolytes prepared by spark plasma sintering technique.

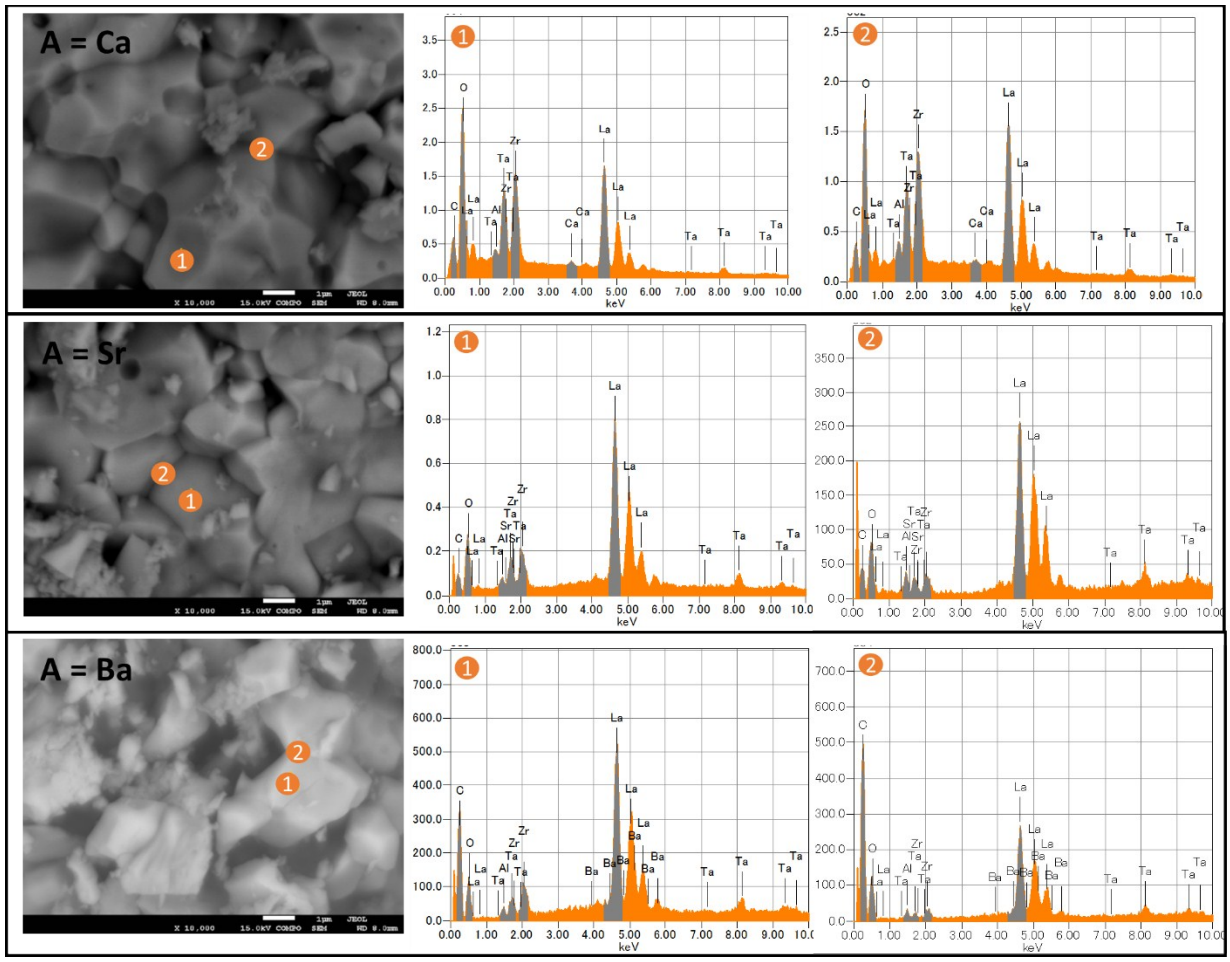

Fig. S3. SEM images and corresponding EDS spectra ((grain (1) and grain-boundary (2)) of $Li_{6.5}La_{2.9}A_{0.1}Zr_{1.4}Ta_{0.6}O_{12}$ (A = Ca, Sr, Ba) garnet electrolytes prepared by spark plasma sintering technique.

References

1 N. Gronbech-jensen, G. Hummer and K. M. Beardmore, *Mol. Phys.*, 1997, **92**, 941–946.

2 D. A. McQuarrie, *Statistical mechanics*, Harper & Row, New York, 1976.

3 E. J. Cussen, *Chem. Commun.*, 2006, 412–413.