

Probing Structure-Property Relations in Garnet-Type Solid Electrolytes for Next-Generation Electrical Energy Storage with Multimode Analytical Scanning and Transmission Electron Microscopy

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Solid-state batteries (SSBs) based on Li metal, Li-S, Li-O₂ (air), and Li-CO₂ chemistries have been recognized as an emerging electrical energy storage technology to replace organic liquid electrolyte-dominated Li-ion batteries due to the potential ability to provide high-energy-density, wide temperature tolerance, and fewer safety concerns [1]. Solid-state electrolytes represent the most critical component in SSBs which primarily governs future battery development. Among different types of solid-state electrolytes, solid solutions of mixed lithium-transition metal oxide garnets of the lanthanide series, Li₅La₃M₂O₁₂ (M = Zr, Nb, Ta, Bi, Sb), are attracting a rapidly gaining interest due to extremely high Li-ion conductivity (10⁻³ to 10⁻⁴ S/cm), good chemical stability against metallic Li, a large electrochemical window above 6 V vs. Li/Li⁺, and relatively easy ambient environment handling [1, 2]. In this work, ceramic garnet-type compounds based on the nominal composition Li₅La₃(Nb_xTa_{1-x})₂O₁₂ (x = 0.1-0.9), were synthesized using a solid-state reaction with Li₂CO₃, La₂O₃, Nb₂O₅, and Ta₂O₅ precursors mixed in the required ratios, followed by milling, drying, initial sintering at 700° C, grinding, and final sintering at 750° C [3]. For structural analyses and impedance measurements, powders of the selected Li₅La₃NbTaO₁₂ compounds were pressed into pellets and sintered for 5 hours at temperatures ranging from 750° C to 1000° C. Following Rietveld refinement of the X-ray powder diffraction (XRD) data on the occupancy of Li, Nb, and Ta sites, the obtained garnet phases were found to be cubic, with the space group Ia-3d (230). Li-ion conductivity was measured by impedance spectrometry in the 1 MHz to 1 mHz frequency range at temperatures from 25° C to 85° C. Field-emission scanning electron microscopy (FESEM) using secondary (SE₁, SE₂) and backscattered (BSE) electrons was performed on as-received uncoated powders in low- and variable-voltage modes applying a 50 V deceleration bias to reduce severe beam-induced sample charging. The multisignal FESEM observations combined with energy-dispersive X-ray (EDX) chemical imaging using a high-speed silicon-drift detector (SDD) revealed fine details of rough surface morphologies and phase compositions of coalesced grain agglomerates with sizes ranging from 4 μm to 15 μm (Fig. 1). The grain shapes improved with sintering temperature, displaying pronounced facets and gradual size growth. The results of XRD phase analysis pointing to the high crystallinity of the garnet powders were directly corroborated at various structural levels by spatially-resolved low-dose transmission EM (TEM), selected-area electron diffraction (SAED), and high-resolution TEM (HRTEM) (Fig. 2c). Probe-corrected analytical scanning TEM (STEM) in bright-field (BF) and high-angle annular dark-field (HAADF) modes using windowless SDD EDX and electron energy-loss (EEL) spectroscopic imaging indicated meso-to-nanoscale inhomogeneities at the level of individual grains caused by adding a Li₂CO₃ excess to compensate lithium losses during sintering (Figs. 2a, 2b, 2d, 2e) that could essentially influence surface structures, intergrain contacts, local electronic structure, and transport properties. The garnet sample with the nominal composition Li_{3.43(2)}La₃Nb_{1.07(2)}Ta_{0.93(2)}O₁₂ sintered at 1000° C, had the highest ionic conductivity mostly due to better

crystallinity and overall compositional uniformity as confirmed by multimode FESEM and S/TEM-EELS-EDXS analyses.

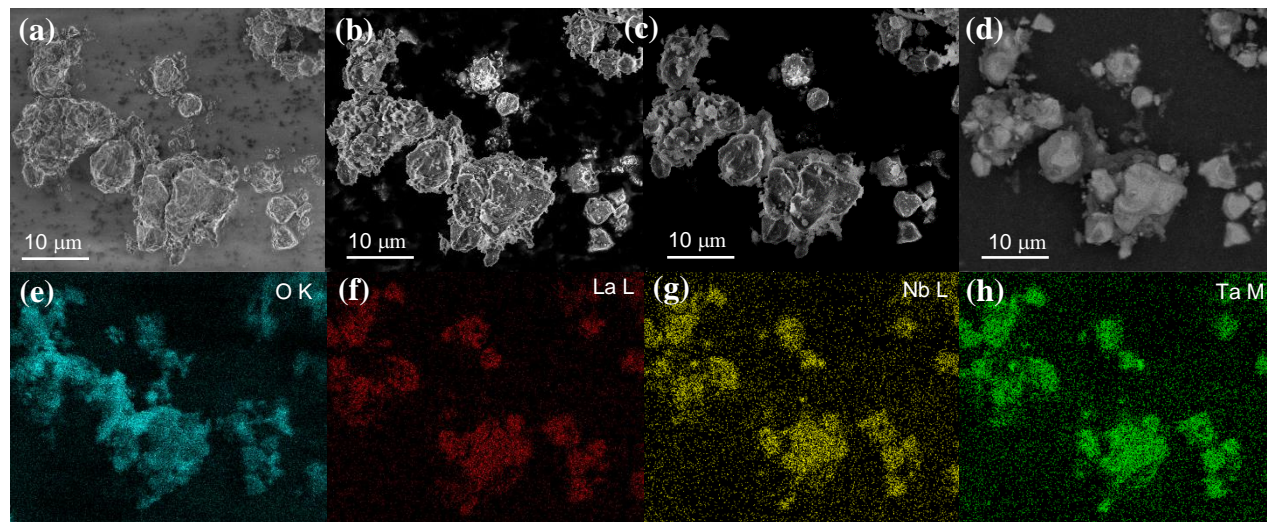


Figure 1. Multiple signal FESEM-EDX of a $\text{Li}_{3.43(2)}\text{La}_3\text{Nb}_{1.07(2)}\text{Ta}_{0.93(2)}\text{O}_{12}$ garnet powder: (a) 1 kV, SE_1 . (b) 5 kV, SE_1+SE_2 . (c) 10 kV, SE_1+SE_2 . (d) 10 kV, BSE, compo. X-ray maps corrected for background and peak overlaps: (e) oxygen (cyan), (f) lanthanum (red), (g) niobium (yellow), and (h) tantalum (green).

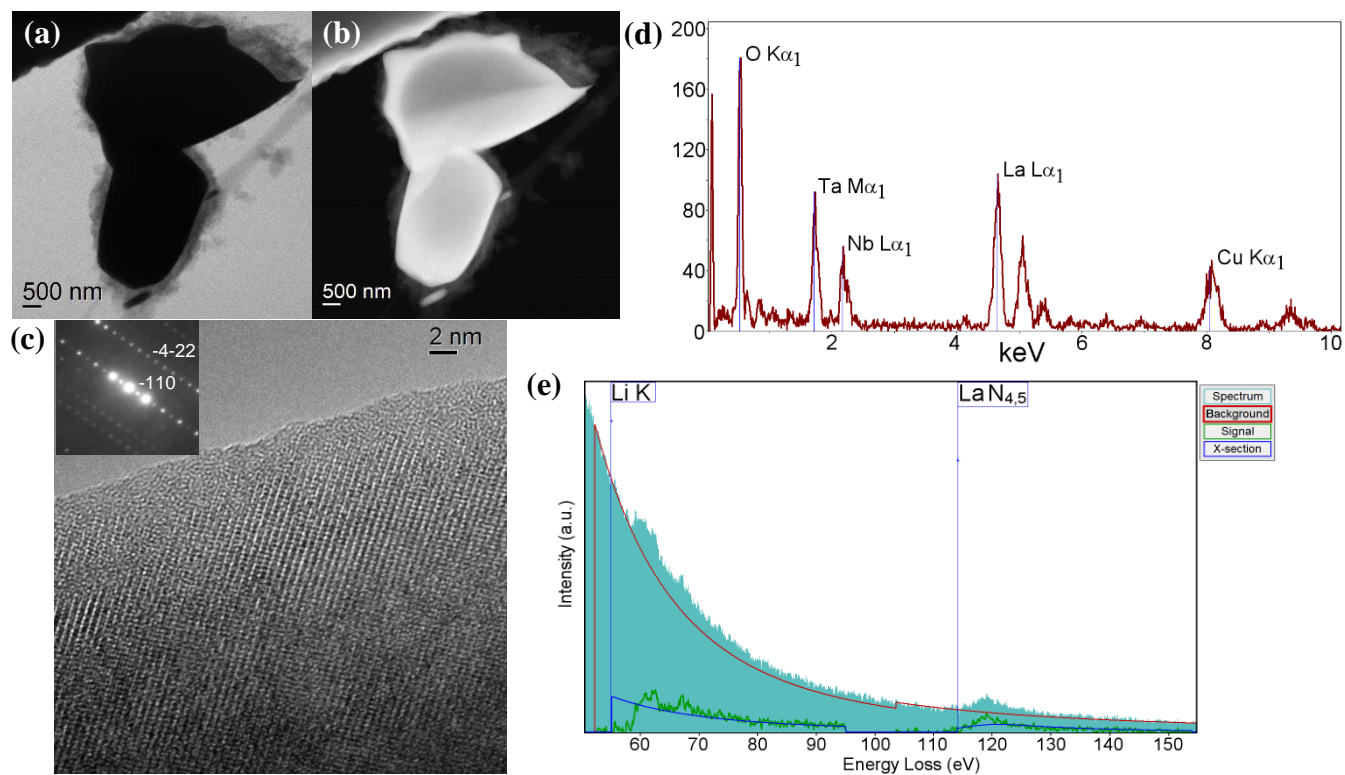


Figure 2. (a) BF-STEM and (b) HAADF-STEM images of the garnet powder grains with Li_2O shells. (c) HRTEM image displays 0.52 nm (211), 0.31 nm (400), and 0.26 nm (422) lattice fringes at the edge of a cubic garnet grain. The point SAED pattern (inset) of the single crystal grain near the [113] zone

axis. (d) X-ray spectrum reveals the presence of oxygen, tantalum, niobium, and lanthanum. (e) EEL spectrum shows the Li K-edge at 55 eV and the delayed La N_{4,5}-edge at about 115 eV, the atomic ratio La/Li = 0.62.

References:

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