

Electronic Supporting Information

Elucidating the Influence of Molten Salt Chemistries on the Synthesis and Stability of Perovskites Oxides

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Experimental Section

Molten Salt Synthesis

LiNO₃ was purchased from Sigma Aldrich. All other reagents were purchased from Alfa Aesar. Stoichiometric amounts of La₂O₃ (99.9%), SrCO₃ (99%), and Mn₂O₃ (98%) for a target end stoichiometry of (La_{0.8}Sr_{0.2})MnO₃ were milled together for 2 hours in ethanol at 1500 rpm and then dried overnight at 80°C. The dried powders were then mixed with 8 g of different molten salts. These salts included LiCl (99%) -KCl (99%) in a eutectic mole ratio, 59.2 mol % LiCl, Li₂CO₃(99.0%)-K₂CO₃(99.0%) in a eutectic mole ratio of 60 mol% Li₂CO₃, LiNO₃(ReagentPlus)-KNO₃(99%) in a eutectic mole ratio of 58 mol% LiNO₃, LiNO₃, or KNO₃ in an alumina crucible

and heated to various temperatures in a Carbolite box furnace. The eutectic mole ratios were kept consistent around 60 mol% Li, and the salts were heated well above their respective melting points. Various mass ratios of powder to salt were used, but the mass of powder was kept consistent at 1g. The mixtures were first heated to 150°C for 1 hr to remove any moisture in the salts and then ramped to the final dwell temperature for 2 or 8 hrs. Upon completion of the dwell period, the mixture was cooled back to room temperature. All ramp rates were 5°C/min. In a third experiment, the feed synthesis of LSM was conducted in KNO₃. Upon heating 8 g of KNO₃ to the dwell temperature, the LSM precursors were fed directly into the melt through an external ceramic tube, and the crucible was removed from the heat source after 1 hour. The crucibles were washed several times with hot deionized water and filtered to collect the products. After all the salt was removed, the powders were dried overnight at 80°C, and characterized via X-ray Diffraction (XRD, Bruker D2 Phaser, Cu K α radiation, $\lambda = 1.5406\text{\AA}$). XRD patterns were obtained over a 2-theta range of 10-80° with a step size of 0.03° and a scan rate of 1.5 seconds per step. Electron microscopy was performed on a Zeiss Supra 55 Variable Pressure Scanning Electron Microscope and elemental compositions were analyzed using Energy Dispersive X-ray Spectroscopy (EDX, Oxford Instruments). Stoichiometries of successfully formed products were determined via Inductively Coupled Plasma with Mass Spectrometry (ICP-MS).

Solubility Measurements

Equilibrium concentrations of La, Sr, and Mn were mapped over the course of the LSM molten salt synthesis in LiCl-KCl and KNO₃. Sample preparation was the same as in the outline above and the mixture within the alumina crucible was placed on a HP66YH Wenesco hot plate (See Figure S1) with an insulated stainless-steel hood. The mixture was heated to 150°C for 1 hr,

and then ramped to the dwell temperature for 8 hr. Once at the dwell temperature, the hood of the hot plate was opened and a clean alumina combustion boat was dipped into the melt at specific time increments to collect solubilized precursors. The time intervals for sample collection were 30 min, 1, 2, 4, and 8 hr. The collected samples were dissolved in 5 mL of 3% HNO₃ and subsequent dilutions were performed. The concentrations, in μmol g⁻¹ of salt, of La, Mn, and Sr ions in solution were measured throughout the course of the reaction using ICP-MS. Upon completion of the dwell period, the eutectic mixture was cooled back to room temperature. All ramp rates were 5°C/min. The products were extracted as outlined above. For the actual concentrations, La₂O₃, Mn₂O₃, or SrCO₃ were mixed in the molten salt and collected in the same fashion.

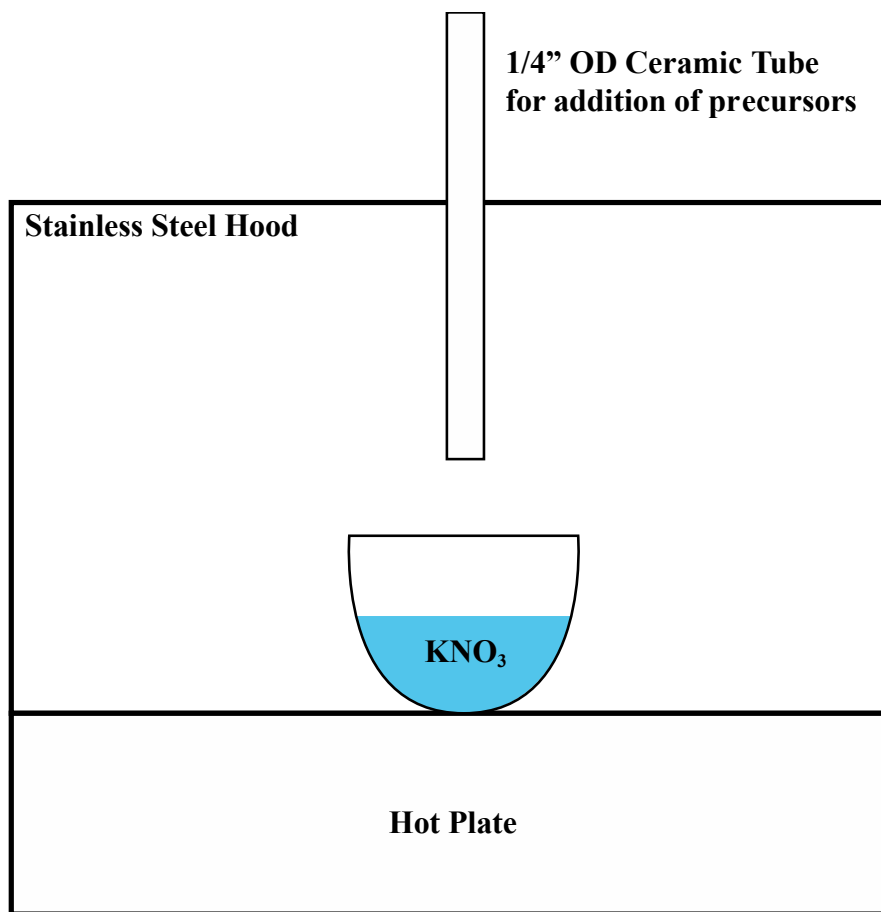


Figure S1. Schematic of Wenesco HP66YH hot plate with an insulated stainless-steel hood used for feeding oxide precursors into KNO_3 melt.

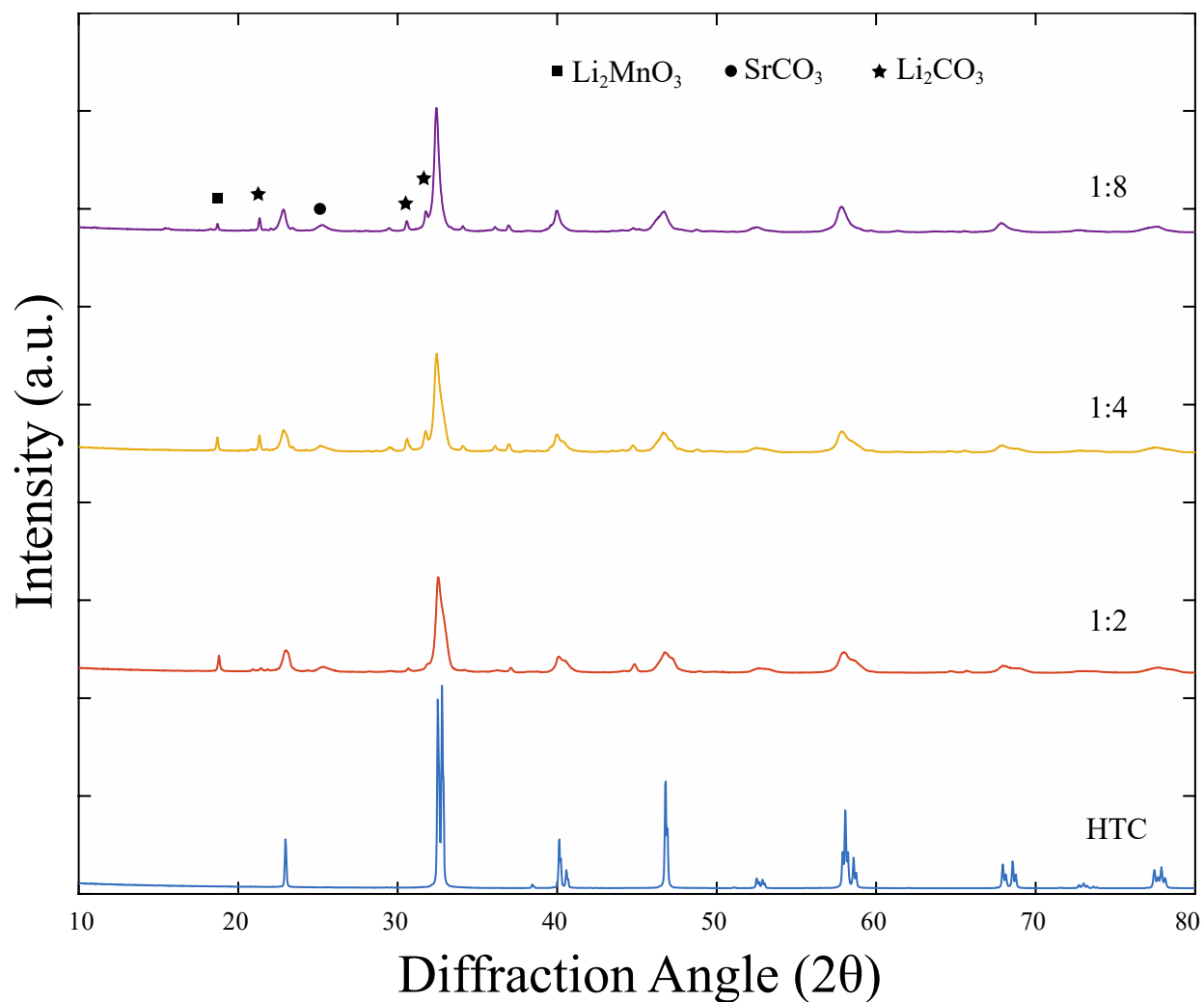


Figure S2. XRD patterns of attempted LSM MSS in $\text{Li}_2\text{CO}_3\text{-K}_2\text{CO}_3$ with varying amounts of LSM precursors relative to salt. The mass ratios are denoted as mass of powder: mass of salt. The XRD of HTC LSM is included for reference. HTC LSM was synthesized in air at 1200°C for 10 hours. All molten salt syntheses were done at 600°C for 2 hours. Peaks matched to secondary phases are labeled accordingly, but only for the major peaks for each phase identified.

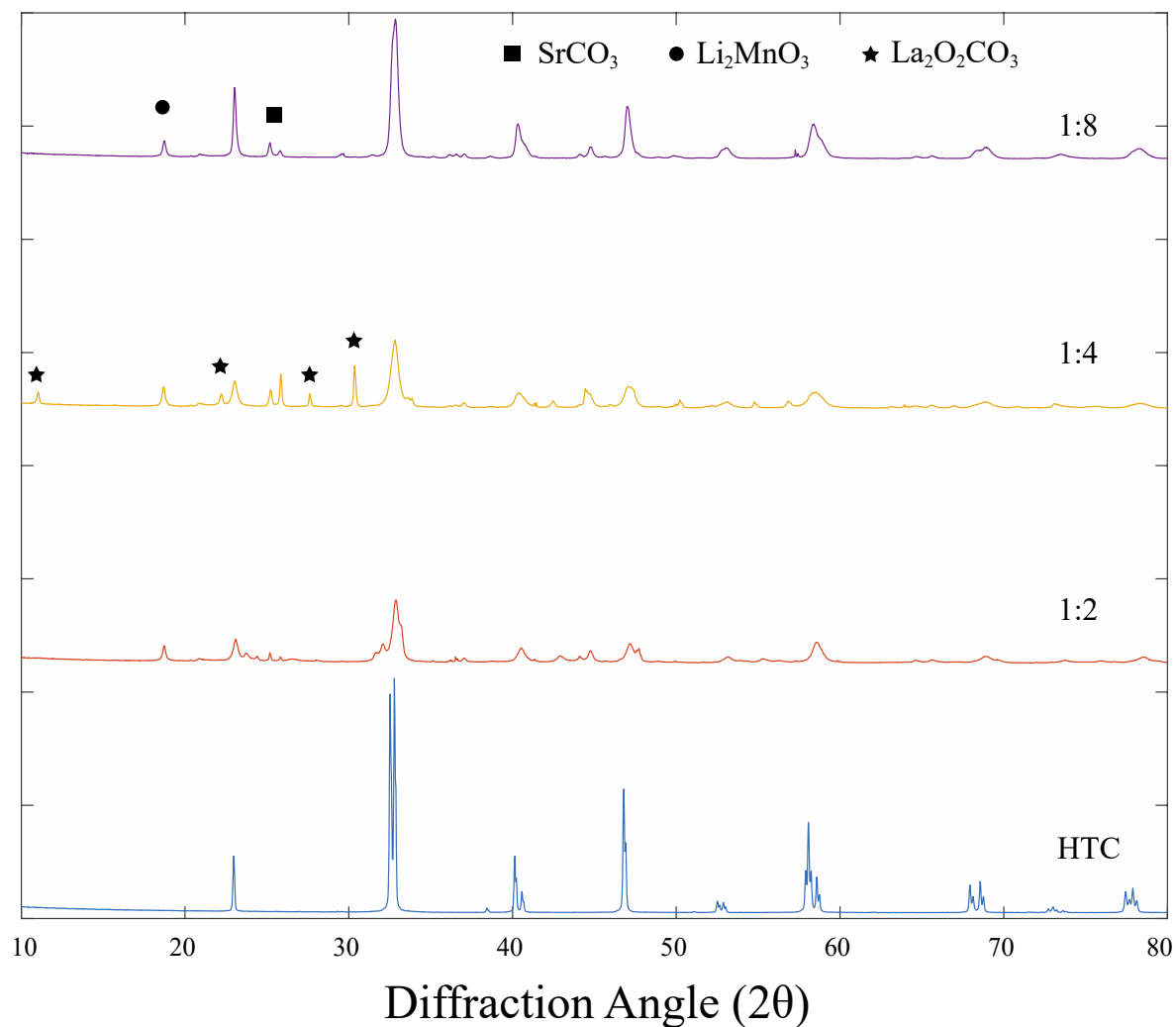


Figure S3. XRD pattern of attempted LSM MSS in LiNO₃-KNO₃ eutectic. The mass ratio between LSM precursor powder and salt was varied from 1:2 to 1:8 (mass powder: mass salt). The XRD of HTC LSM is included for reference. All syntheses were done at 600°C for 2 hours. Peaks matched to secondary phases are labeled accordingly, but only for the major peaks for each phase identified.

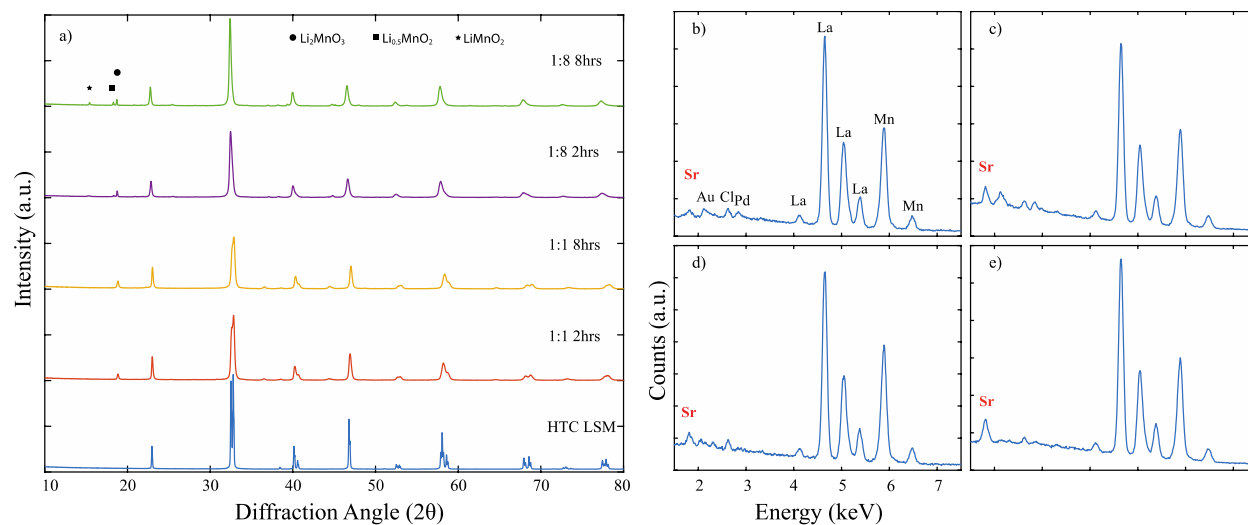


Figure S4. a) XRD patterns of attempted LSM MSS in LiCl-KCl in varying mass ratio of powder precursors to salt (mass powder: mass salt) and varying times. The major peaks for the secondary phases are labeled. EDX spectra for each attempted synthesis is shown in b-e) where the Sr L-line is low in intensity compared to the background. The spectra are labeled as b) 1:1, 2hrs, c) 1:1, 8hrs, d) 1:8, 2hrs, and e) 1:8, 8hrs. The temperature for each was 600°C.

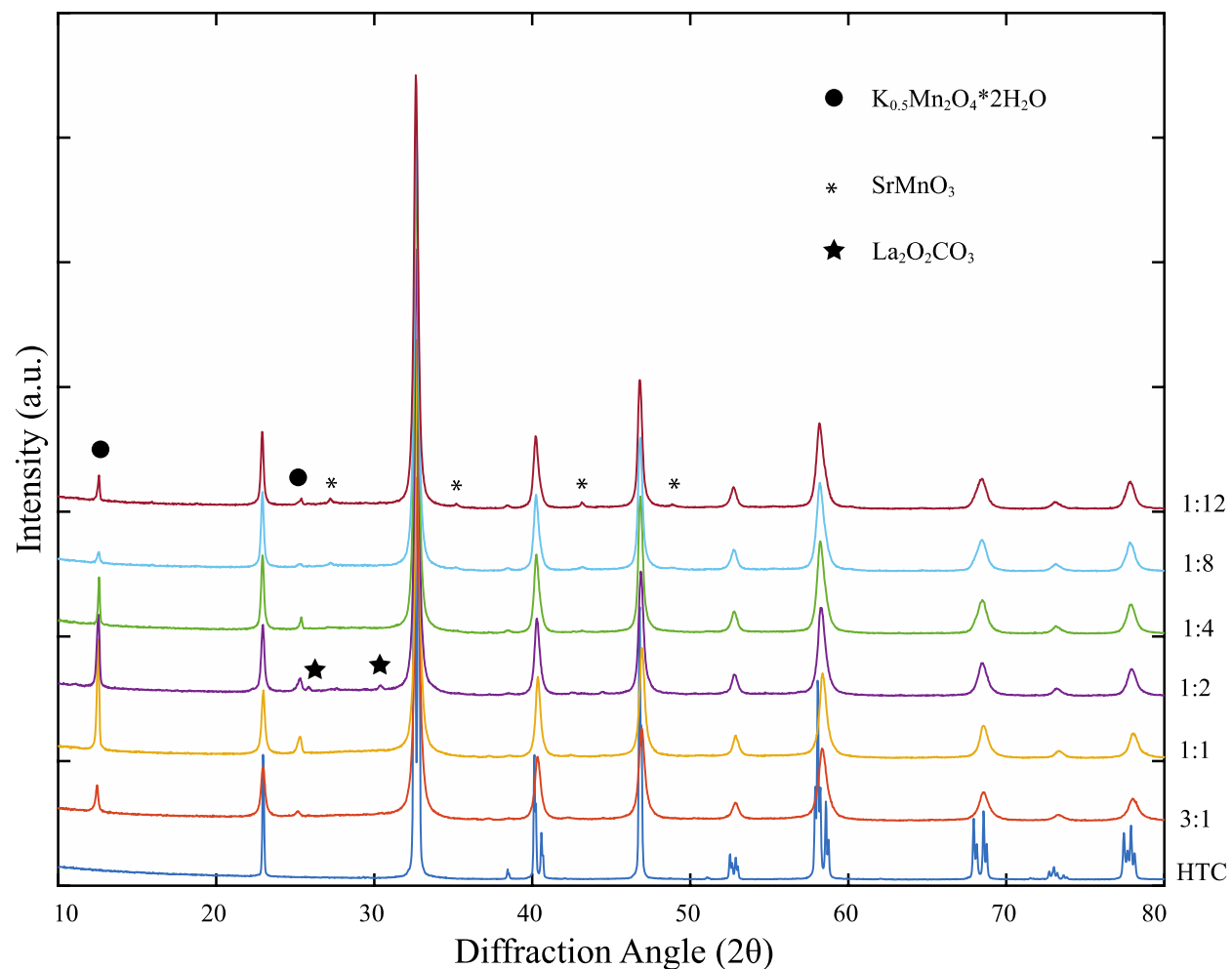


Figure S5. XRD patterns of LSM MSS in KNO_3 in varying the mass ratio of LSM precursor to KNO_3 . The $\text{K}_{0.5}\text{Mn}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ phase is present in all MSS patterns, SrMnO_3 is present in the higher mass ratio samples, and $\text{La}_2\text{O}_2\text{CO}_3$ is present in the 1:2 sample potentially as a result of inadequate mixing of the precursors in the salt before heating. Synthesis conditions were 600°C for 2 hours. The pattern for HTC LSM is included for reference.

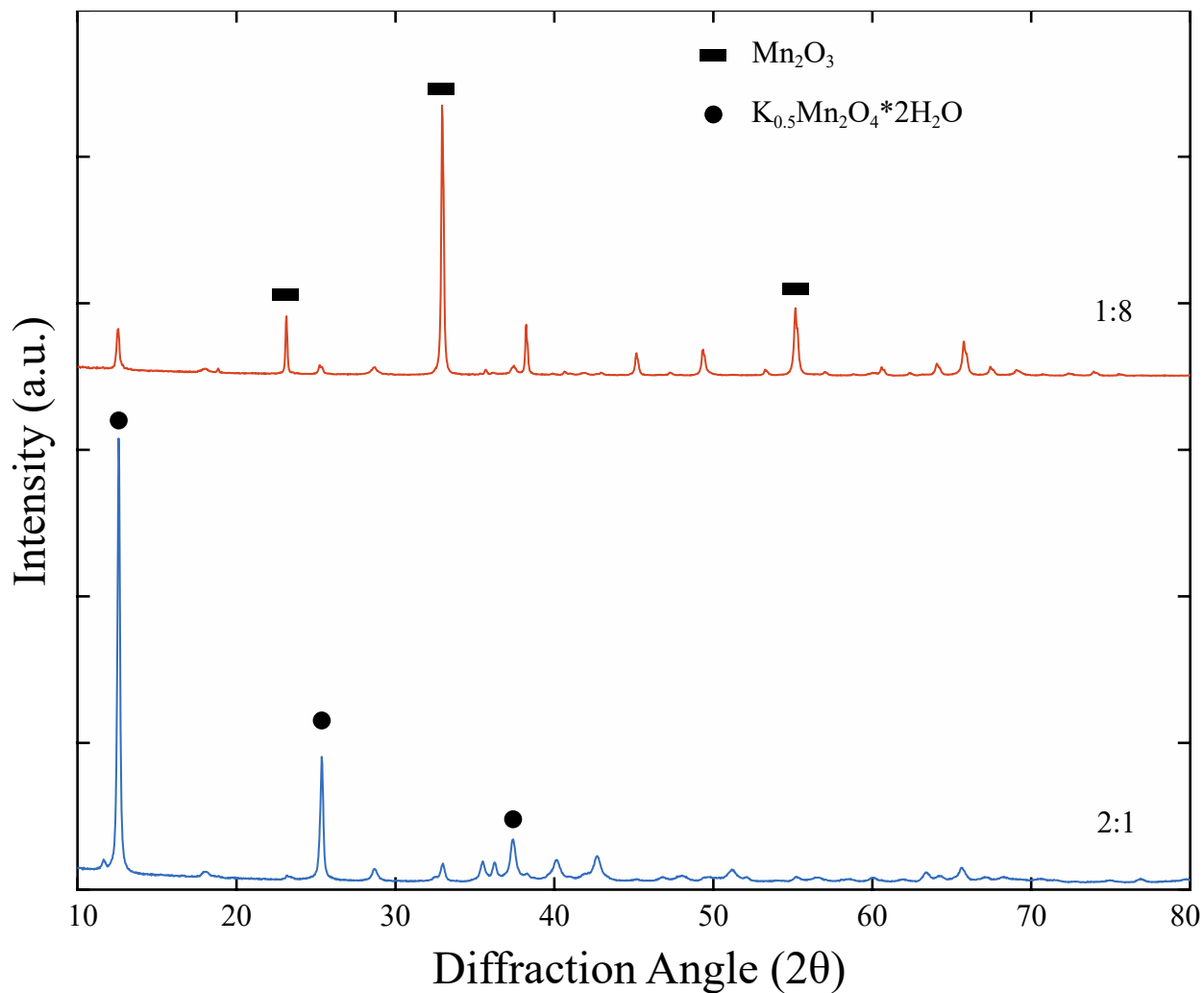


Figure S6. XRD patterns of Mn₂O₃ dwelt in KNO₃ at 600°C for 2 hours. The mass ratios of powder to KNO₃ investigated were 2:1 and 1:8, respectively. The three most intense peaks for each phase are labeled.

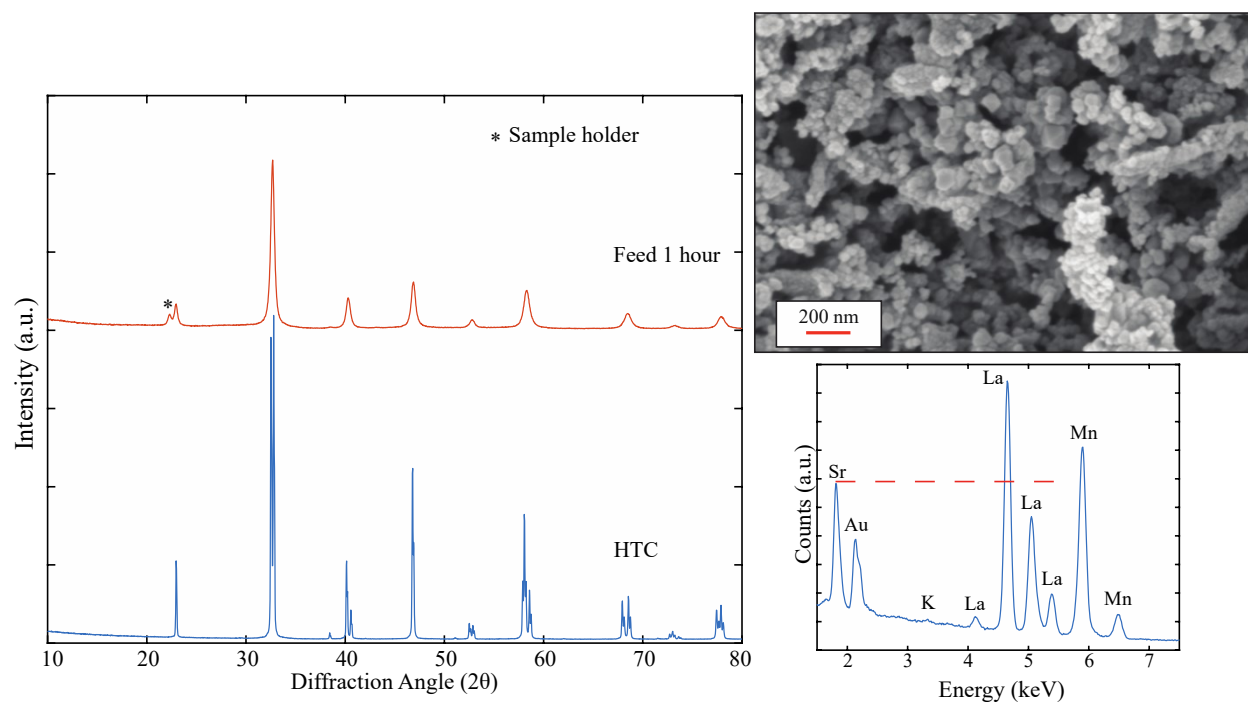


Figure S7. XRD patterns of HTC LSM compared to LSM Fed into equilibrated KNO_3 at 600°C for 1 hour before quenching. The small secondary peak identified is the sample holder since a small amount of powder was scanned. The SEM image shows uniform nanoparticles and the EDX spectrum indicates comparable Sr L-line intensity for the LSM KNO_3 Feed to that of the HTC LSM spectrum shown prior.

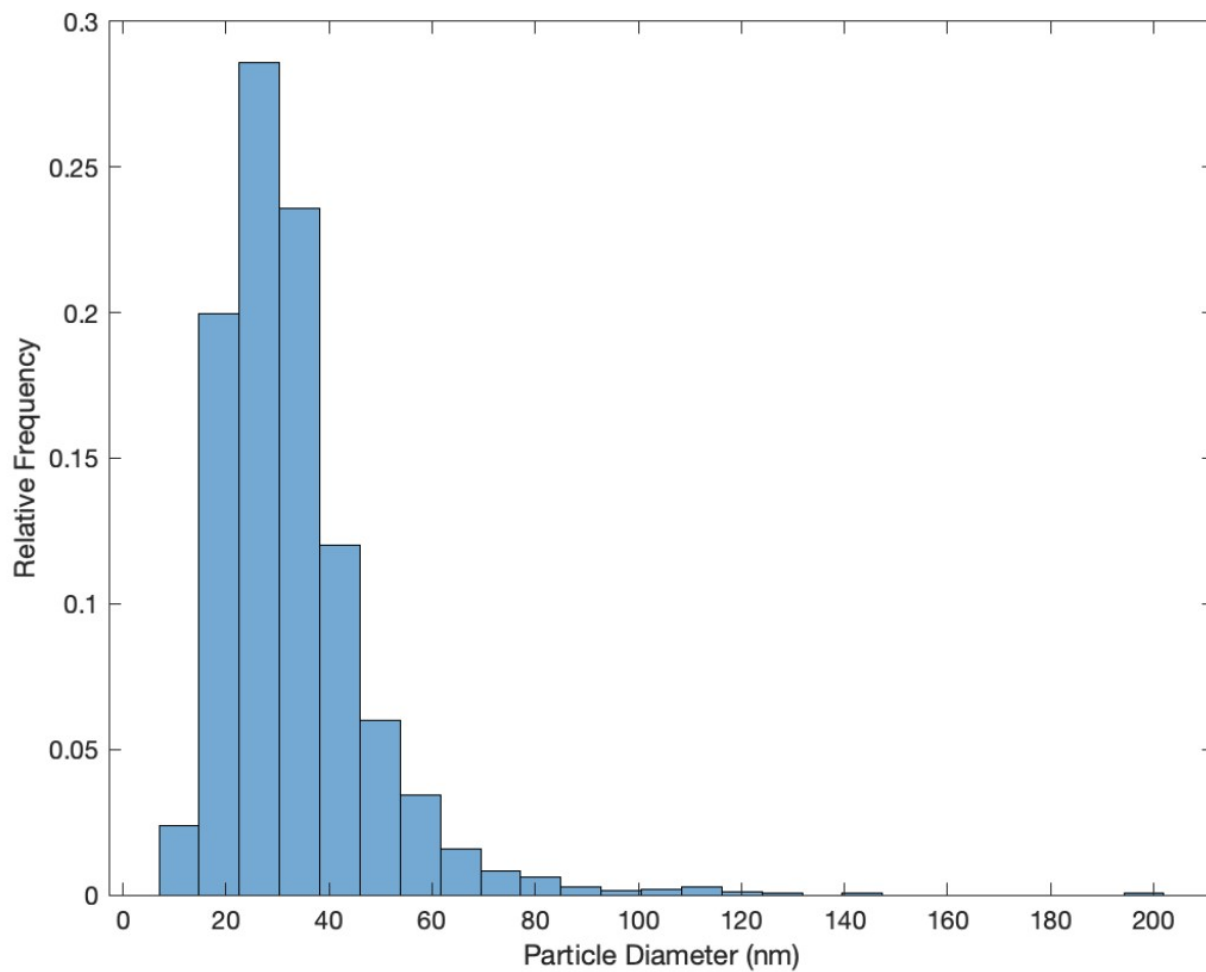


Figure S8. Particle size distributions of the LSM KNO₃ Feed 1 hour. Diameters span from ~10 nm to 200 nm in length, with the majority of particles ranging from 15-45 nm.

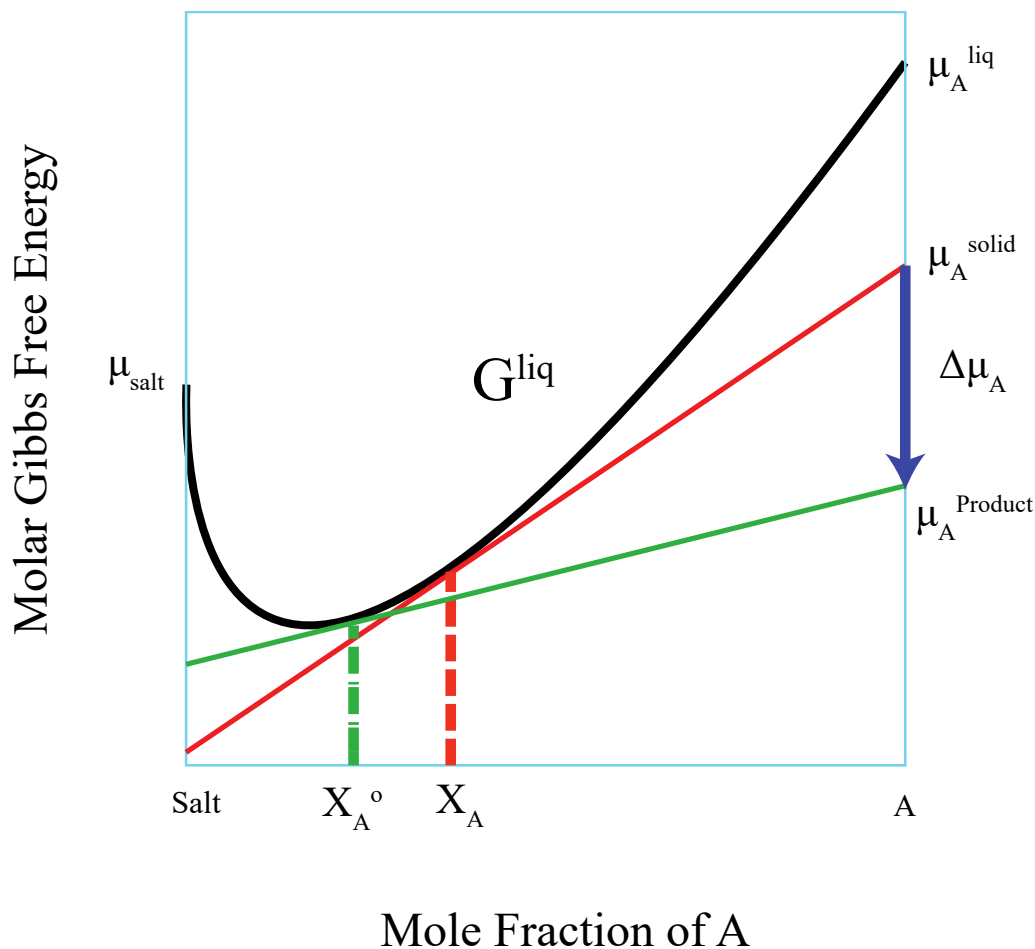


Figure S9. Relation between the molar free energy of liquid molten salt phase and component A. Adapted from Kimura¹. X_A is the solubility of component A when the solid phase A alone is in equilibrium with the molten salt, and X_A^o is the solubility of A in the product perovskite phase in equilibrium with the molten salt and any excess reactants. The contact point between G^{liq} and the tangent line from G^{liq} to μ_A^{solid} yields X_A (red lines). The same is true for X_A^o (green lines).

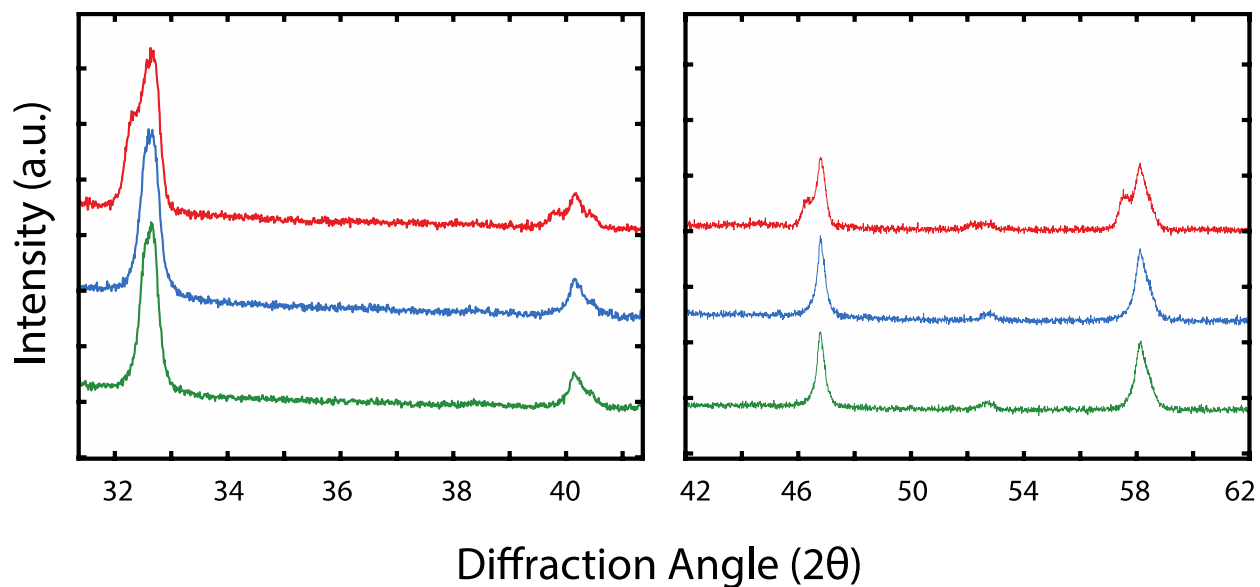


Figure S10. XRD patterns of high temperature calcined $(\text{La}_{0.6}\text{Sr}_{0.4})_{0.95}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$ (LSCF) purchased from Fuel Cell Materials (blue), LSCF dwelt in LiCl-KCl eutectic (red), and LSCF dwelt in KNO_3 (green) at 600 °C for 4 hours.

Table S1. Molar ratios of each element in LSCF powders pre and post dwelt in molten salts. Standard deviation of mole ratios: +/- 0.07.

LSCF	La Mole Ratio	Sr Mole Ratio	Sr/La Ratio	Co Mole Ratio
FCM, pre-dwell	0.61	0.41	1.49	0.21
LiCl-KCl	0.71	0.11	6.45	0.15
KNO_3	0.59	0.40	1.48	0.21

References

1. T. Kimura, In *Molten Salt Synthesis of Ceramic Powders*, ed. Costas Sikalidis, Intech Open, London, United Kingdom 2011, Ch. 4, 75-100