Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

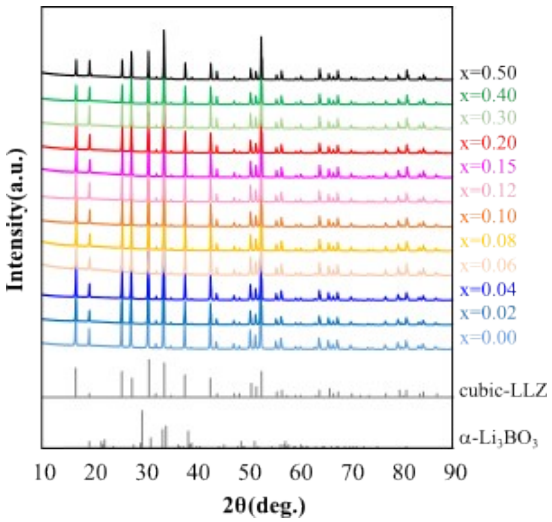


Figure S1 XRD patterns of the synthesized LLZ-CaBi powder.

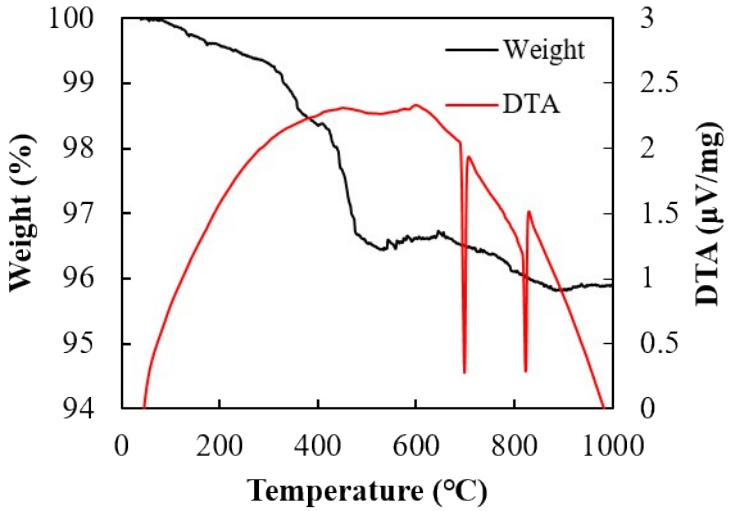


Figure S2 TG-DTA curves of the synthesized Li_3BO_3 powder in a 20% O_2-Ar atmosphere.

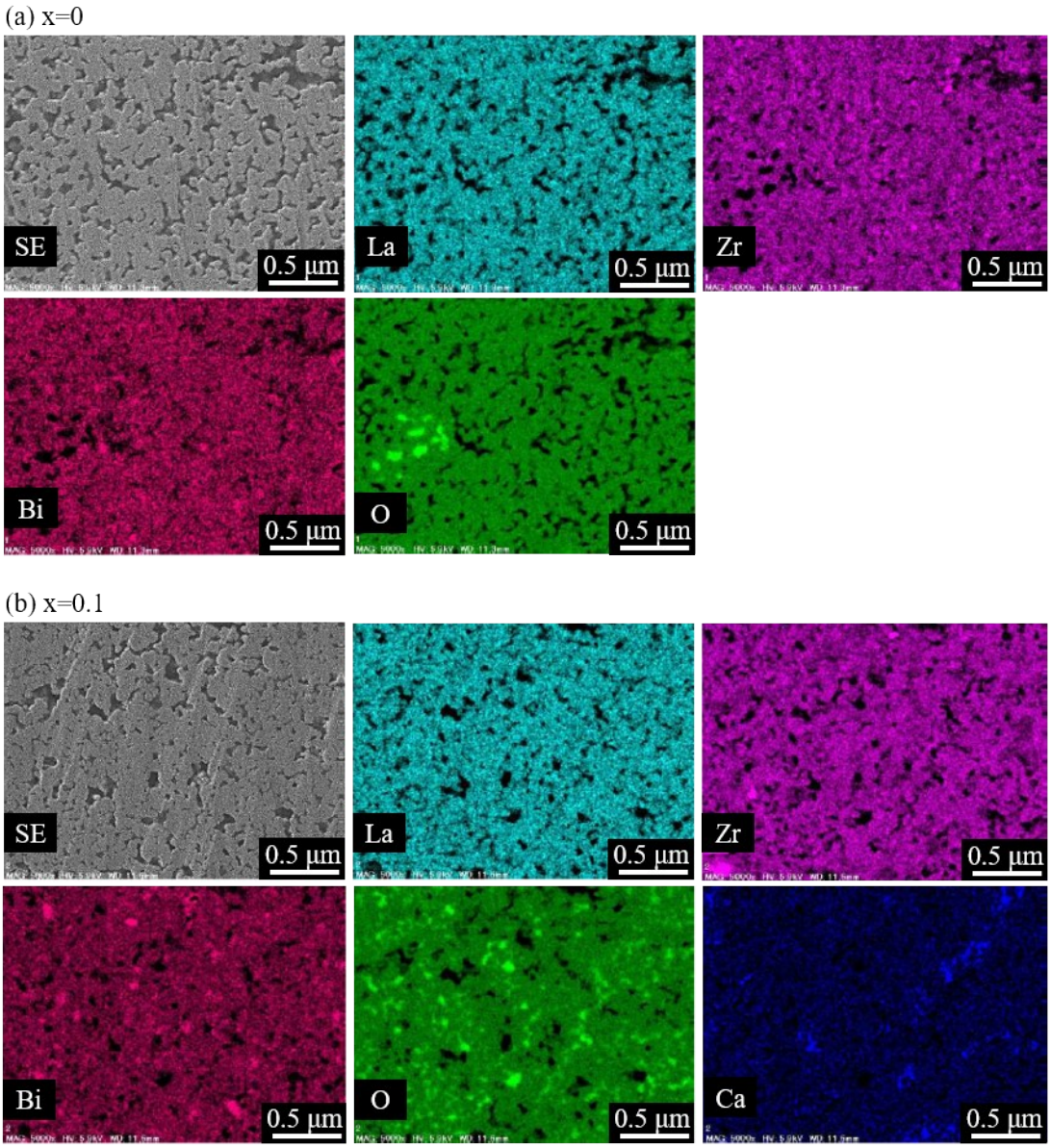


Figure S3 SEM images and elemental mapping of (a) LLZ-Bi an (b) LLZ-CaBi0.1 (x=0.1) and Li_3BO_3 composite electrolytes sintered at 750 °C.

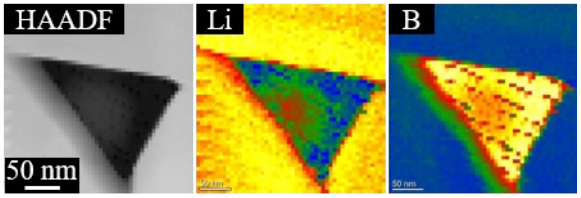


Figure S4 HAADF image and EELS mapping of LLZ-CaBi0.1 (x=0.1) and Li_3BO_3 composite electrolyte sintered at 750 °C.

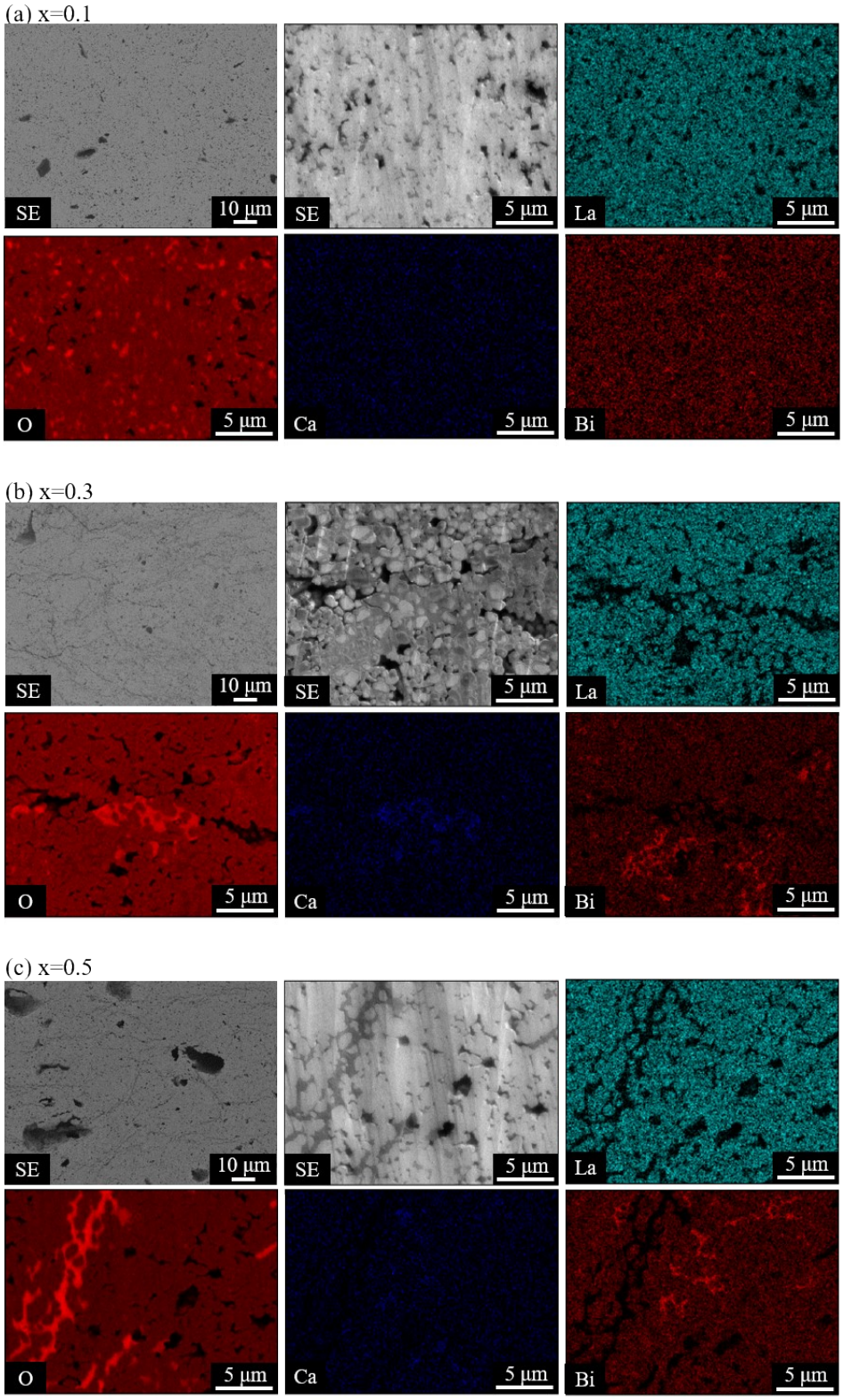


Figure S5 SEM images and elemental mappings of (a) LLZ-CaBi0.1 (x=0.1), (b) LLZ-CaBi0.3 (x=0.3), and (c) LLZ-CaBi0.5 (x=0.5) and Li_3BO_3 composite electrolytes sintered at 750 °C.

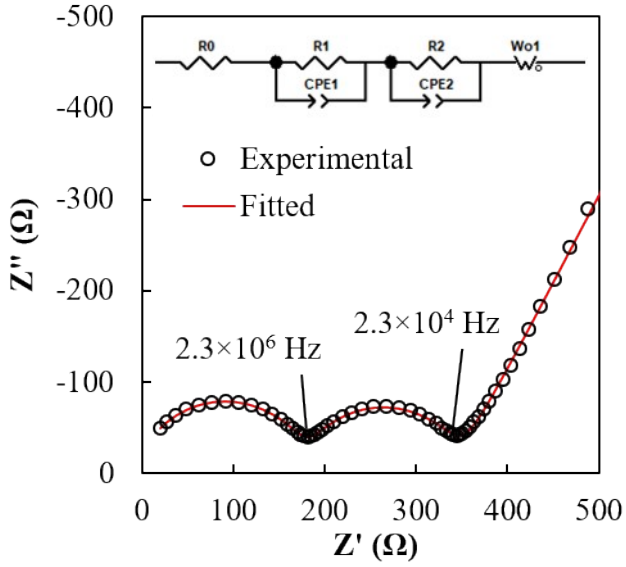


Figure S6 Typical impedance plots at 298 K for LLZ-CaBi0.1 (x=0.1) and Li_3BO_3 composite electrolytes sintered at 750 °C.

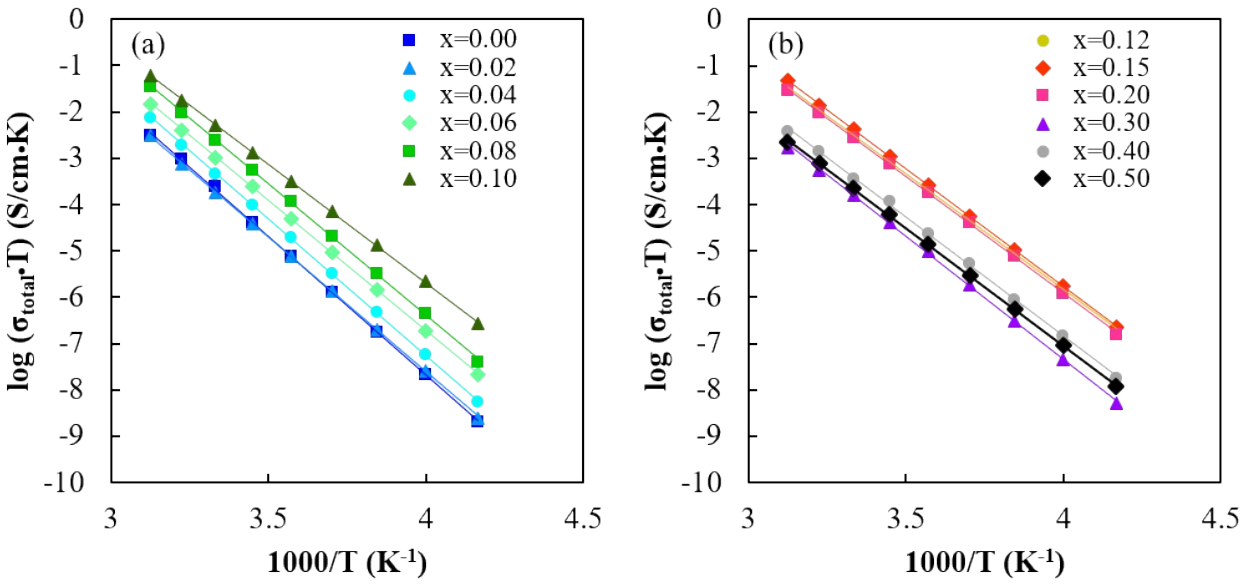


Figure S7 Arrhenius plots of LLZ-CaBi with (a) x=0–0.1 and (b) x=0.12–0.5 and Li_3BO_3 composite electrolytes sintered at 750 °C over the temperature range of 240–320 K.

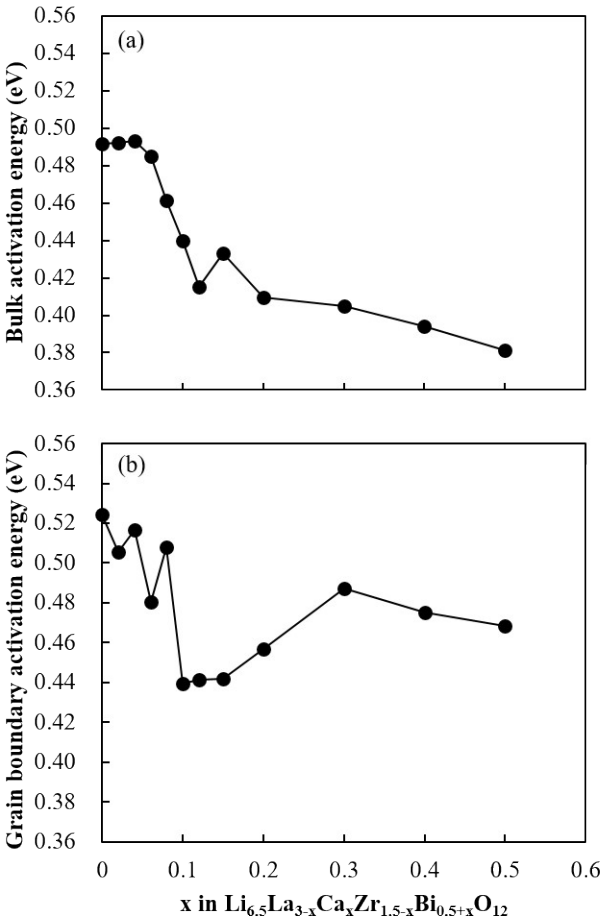


Figure S8 Dependence of (a) bulk and (b) grain boundary activation energy on LLZ-CaBi and Li_3BO_3 composite electrolytes sintered at 750 °C.

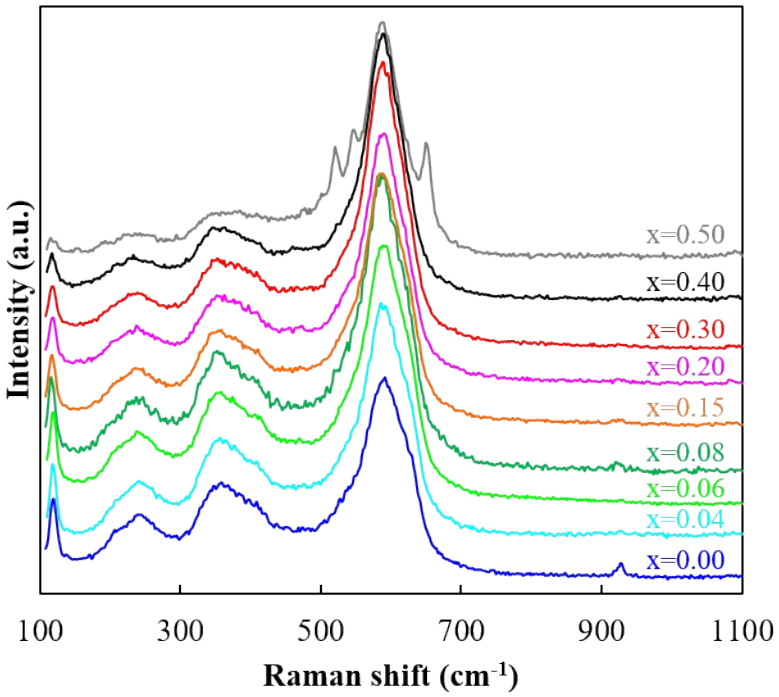
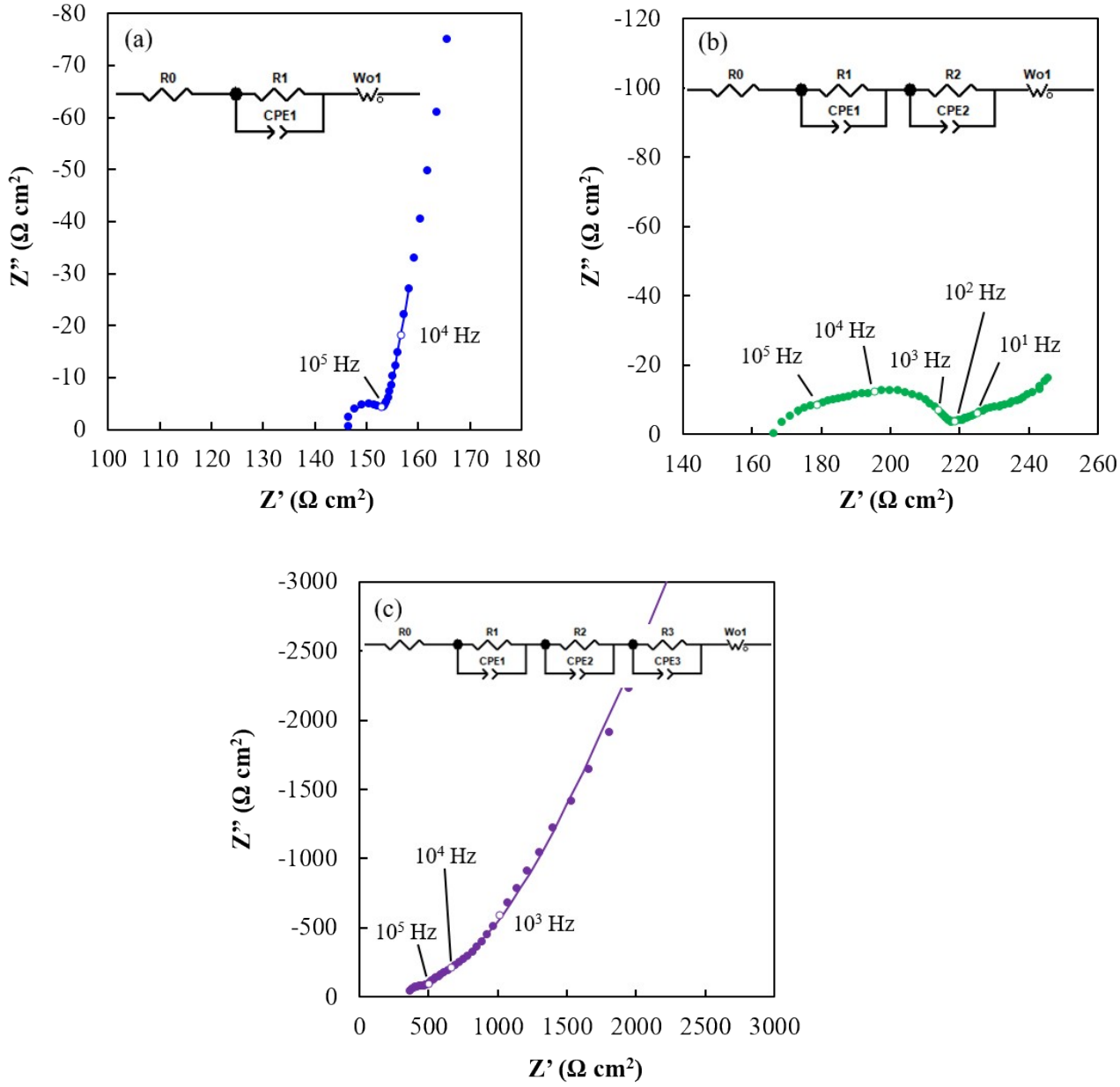


Figure S9 Raman spectra of LLZ-CaBi and Li_3BO_3 composite electrolytes sintered at 750 °C.



F igure S10 Impedance plots at 333K of (a) SUS plate|PEO|SUS plate (b) Li|PEO|Li (c) SUS plate|PEO|LLZ-CaBi0.1+Li_3BO_3|Au. The inset is the equivalent circuit used for fitting.

Table S1 Parameters obtained from fitting impedance data of LLZ-CaBi and Li_3BO_3 composite electrolytes sintered at 750 °C.

x in LLZ-CaBi	R_b (Ω)	CPE_b (F)	ω_b (rad/s)	τ_b (s)	R_{gb} (Ω)	CPE_{gb} (F)	ω_{gb} (rad/s)	τ_{gb} (s)
x = 0	427	1.7×10^{-10}	1.4×10^{7}	7.4×10^{-8}	1047	9.2×10^{-9}	1.0×10^{5}	9.6×10^{-6}
x = 0.02	497.7	1.3×10^{-10}	1.6×10^{7}	6.5×10^{-8}	570.5	1.0×10^{-8}	1.7×10^{5}	5.8×10^{-6}
x = 0.04	315.5	2.1×10^{-10}	1.5×10^{7}	6.6×10^{-8}	336.8	1.4×10^{-8}	2.1×10^{5}	4.8×10^{-6}
x = 0.06	307.7	3.0×10^{-10}	1.1×10^{7}	9.1×10^{-8}	285.3	1.6×10^{-8}	2.2×10^{5}	4.6×10^{-6}
x = 0.08	192.4	3.7×10^{-10}	1.4×10^{7}	7.1×10^{-8}	195.6	2.3×10^{-8}	2.2×10^{5}	4.5×10^{-6}
x = 0.10	187.4	3.5×10^{-10}	1.5×10^{7}	6.6×10^{-8}	159	2.6×10^{-8}	2.5×10^{5}	4.1×10^{-6}
x = 0.12	181.0	2.5×10-10	2.2×10^{7}	4.5×10^{-8}	267.2	1.7×10^{-8}	2.2×10^{5}	4.6×10^{-6}
x = 0.15	185.2	3.3×10^{-10}	1.7×10^{7}	6.1×10^{-8}	241	2.3×10^{-8}	1.8×10^{5}	5.6×10^{-6}
x = 0.20	244.4	3.8×10^{-10}	1.1×10^{7}	9.2×10^{-8}	256.9	4.4×10^{-8}	8.8×10^{4}	1.1×10^{-5}
x = 0.30	316.4	6.1×10^{-10}	5.2×10^{6}	1.9×10^{-7}	947.5	1.1×10^{-8}	9.9×10^{4}	1.0×10^{-5}
x = 0.40	383.9	9.2×10^{-10}	2.8×10^{6}	3.5×10^{-7}	569.2	6.2×10^{-8}	2.8×10^{4}	3.5×10^{-5}
x = 0.50	518.5	8.0×10^{-10}	2.4×10^{6}	4.1×10^{-7}	1021	7.0×10^{-8}	1.4×10^{4}	7.2×10^{-5}