

# *Supporting Information*

## **Synergetic Effect of Li-Ion Concentration and Triple Doping on Ionic Conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte**

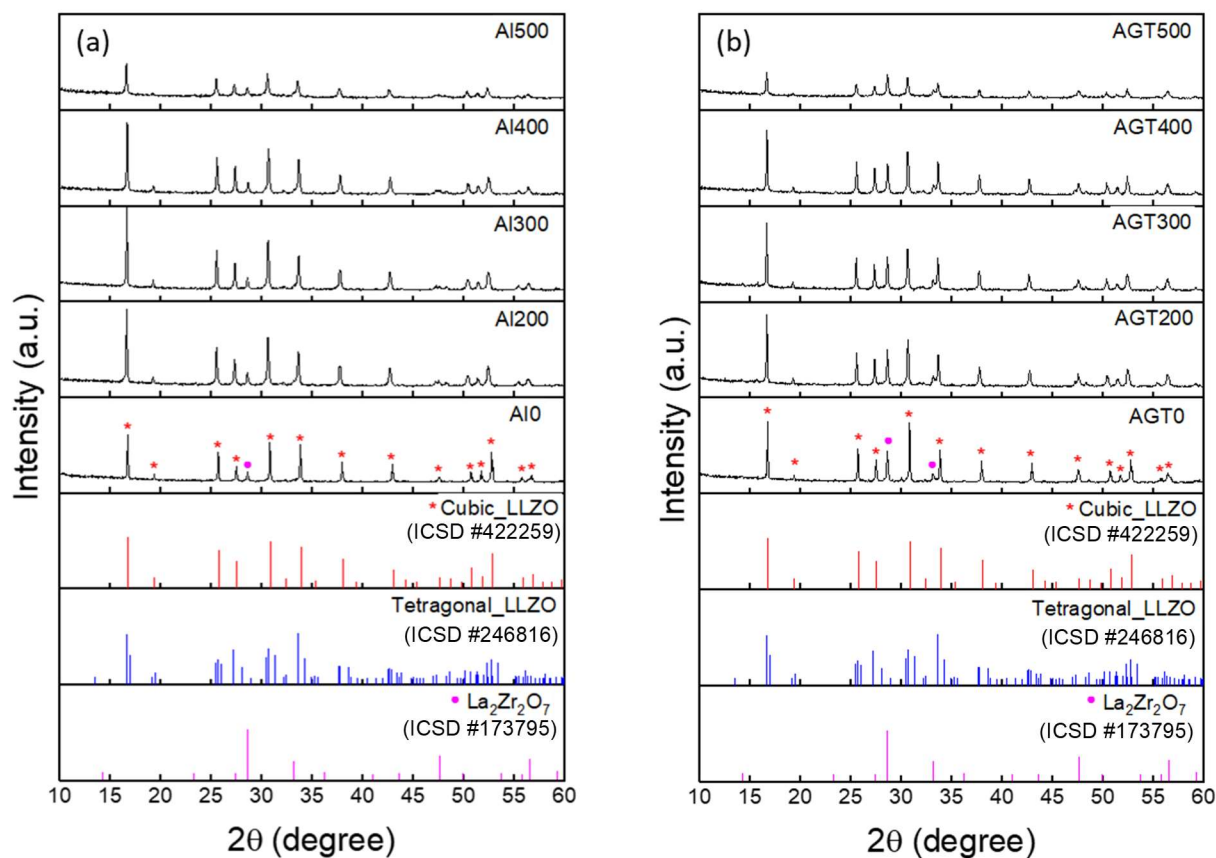
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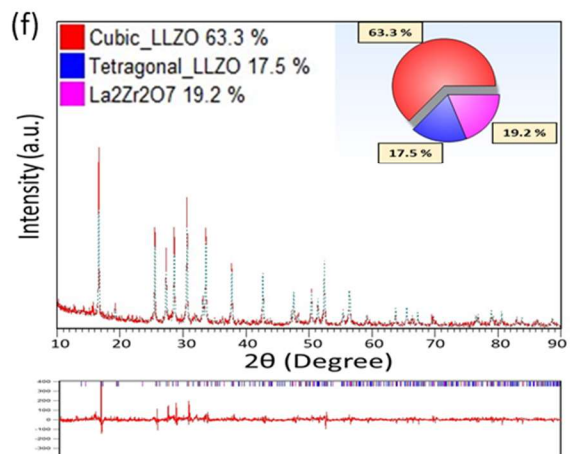
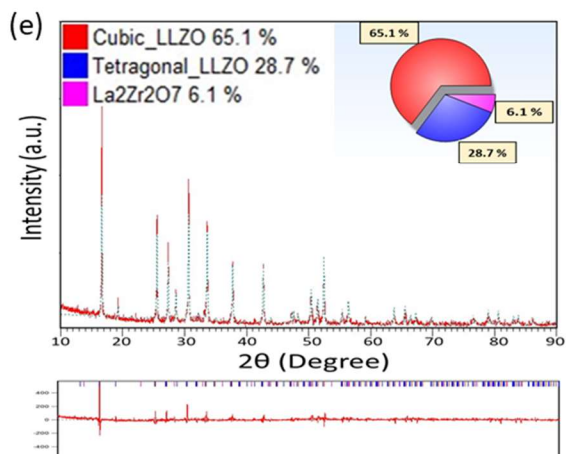
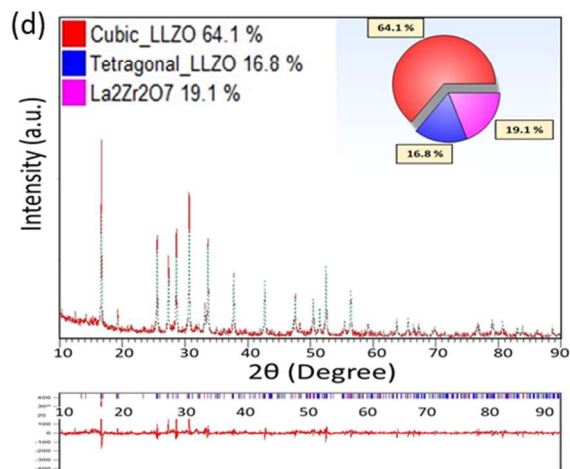
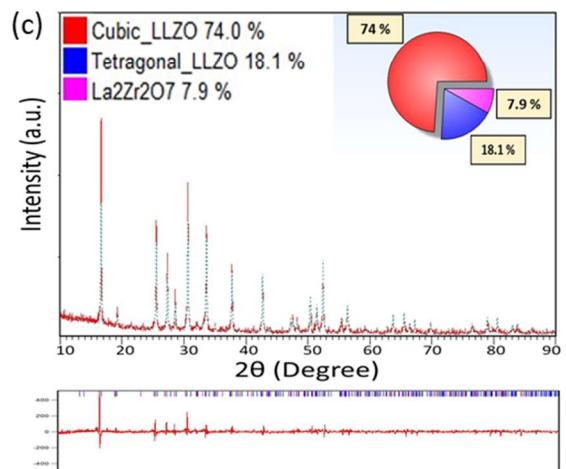
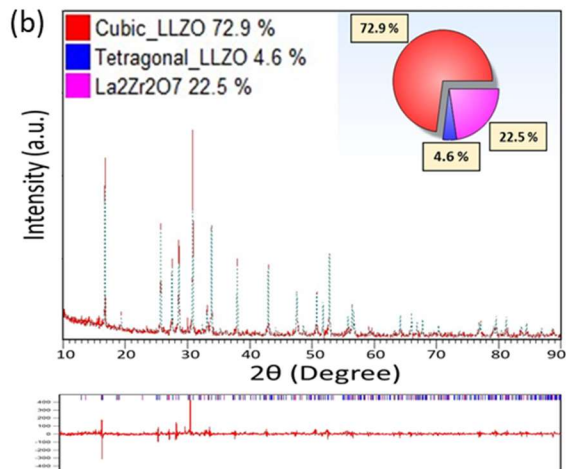
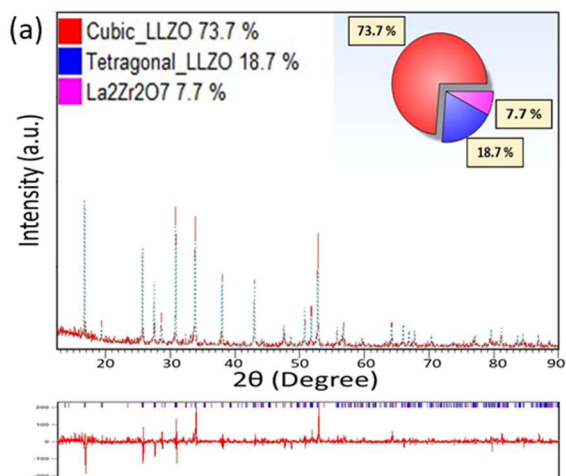
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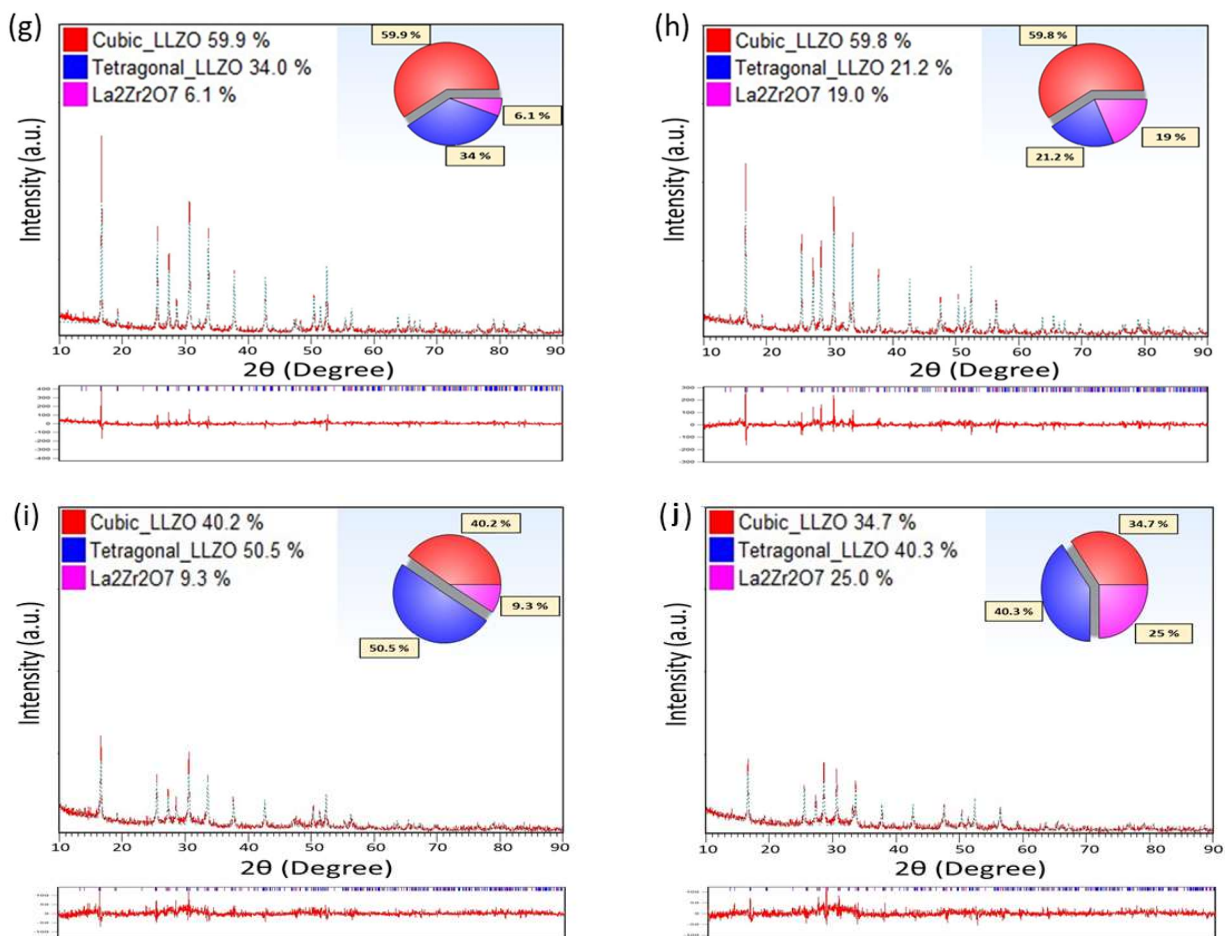
**Table S1.** Average particle size of Al/Ga/Ta-doped LLZO powders prepared with different ball milling parameters through PSA measurement.

Sample	1 <sup>st</sup> ball milling conditions	Calcination	2 <sup>nd</sup> ball milling conditions	Average particle size (μm)
AGT_LLZO	250 rpm / 6 h	-	-	1.03
	250 rpm / 6 h	900 °C / 6 h	-	24.4
	250 rpm / 6 h	900 °C / 6 h	200 rpm / 2 h	1.66
	250 rpm / 6 h	900 °C / 6 h	300 rpm / 2 h	1.05
	250 rpm / 6 h	900 °C / 6 h	400 rpm / 2 h	1.12
	250 rpm / 6 h	900 °C / 6 h	500 rpm / 2 h	0.78

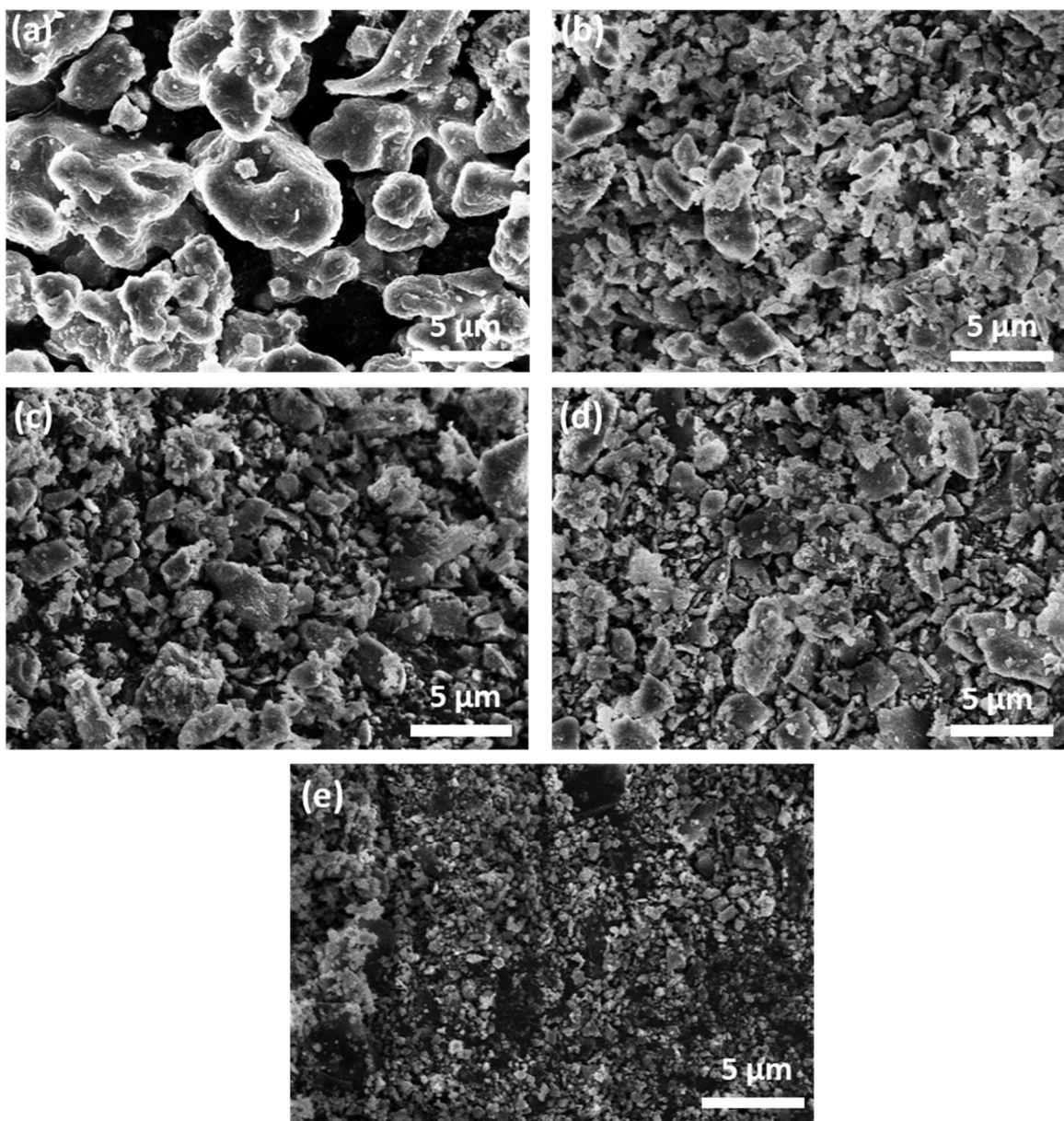


**Figure S1:** XRD patterns of (a) Al-doped LLZO powders and (b) Al/Ga/Ta-doped LLZO powders after the second ball milling process with different rotation speeds (0, 200, 300, 400, and 500 rpm).

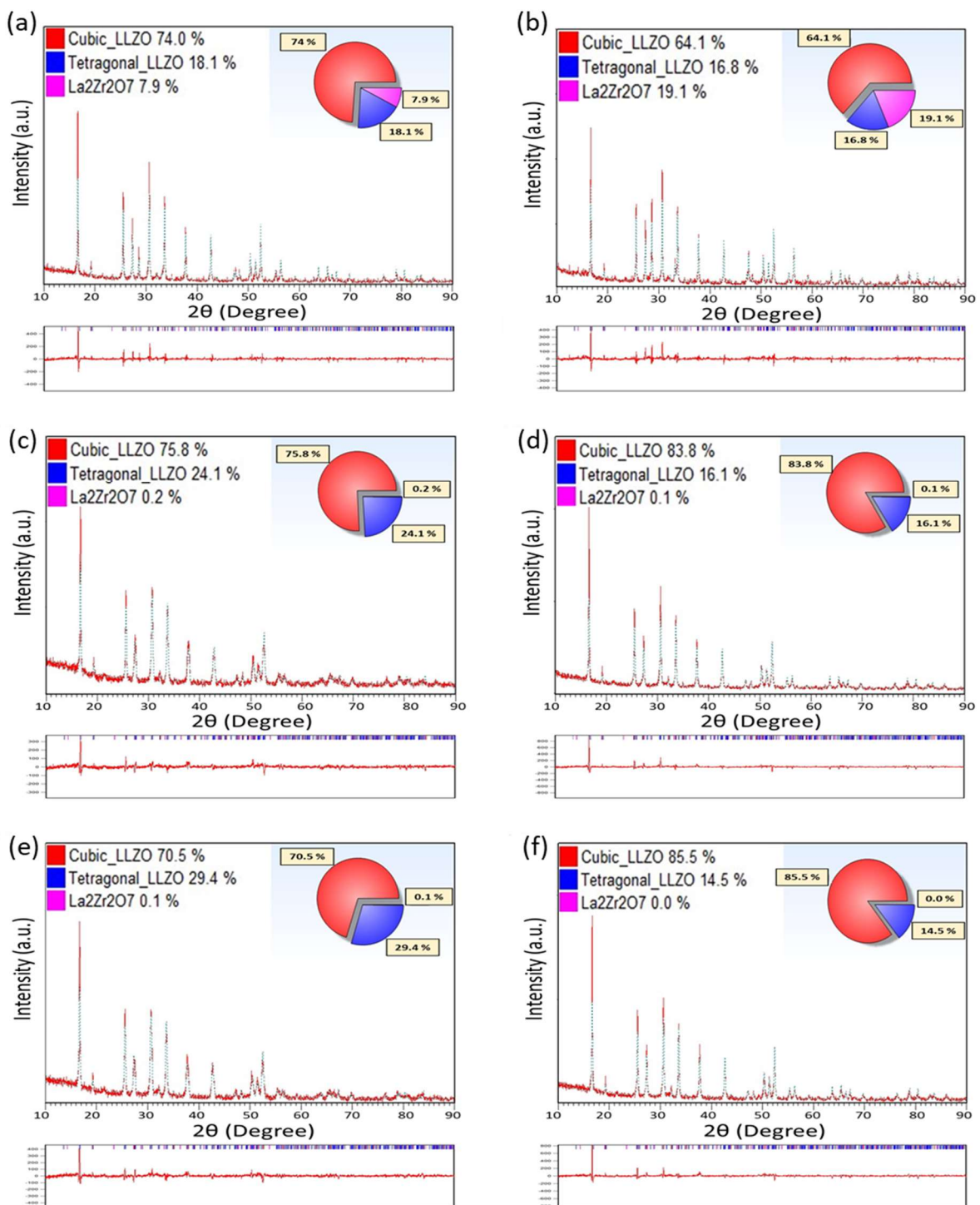




**Figure S2:** XRD Rietveld refinement results of Al-doped LLZO and AGT-doped LLZO powders prepared with Li content of 6.9 mol after the second ball milling process with different rotation speeds (0, 200, 300, 400 and 500 rpm): (a) Al0, (b) AGT0, (c) Al200, (d) AGT200, (e) Al300, (f) AGT300, (g) Al400, (h) AGT400, (i) Al500, and (j) AGT500.

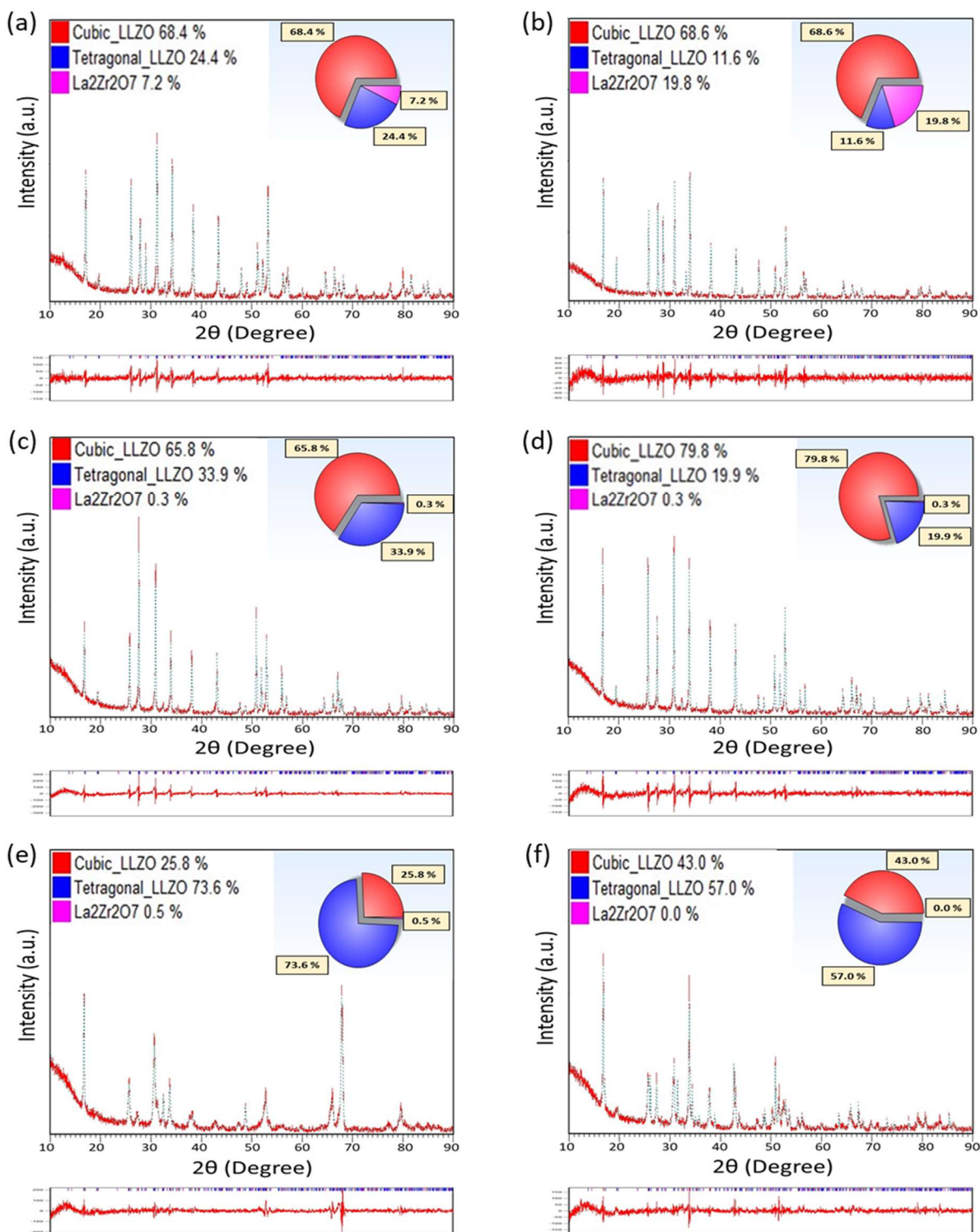


**Figure S3:** SEM images of the Al/Ga/Ta-doped LLZO powders after the second ball milling process at (a) 0 rpm, (b) 200 rpm, (c) 300 rpm, (d) 400 rpm, and (e) 500 rpm for 2 h.



**Figure S4:** XRD Rietveld refinement results of powder samples after the second ball milling process at 200 rpm for 2 h: (a) Al<sub>6.9</sub>, (b) AGT<sub>6.9</sub>, (c) Al<sub>7.7</sub>, (d) AGT<sub>7.7</sub>, (e) Al<sub>8.4</sub>, and (f) AGT<sub>8.4</sub>.





**Figure S5:** XRD Rietveld refinement results of pellets: (a) Al<sub>6.9</sub>, (b) AGT<sub>6.9</sub>, (c) Al<sub>7.7</sub>, (d) AGT<sub>7.7</sub>, (e) Al<sub>8.4</sub>, and (f) AGT<sub>8.4</sub>.



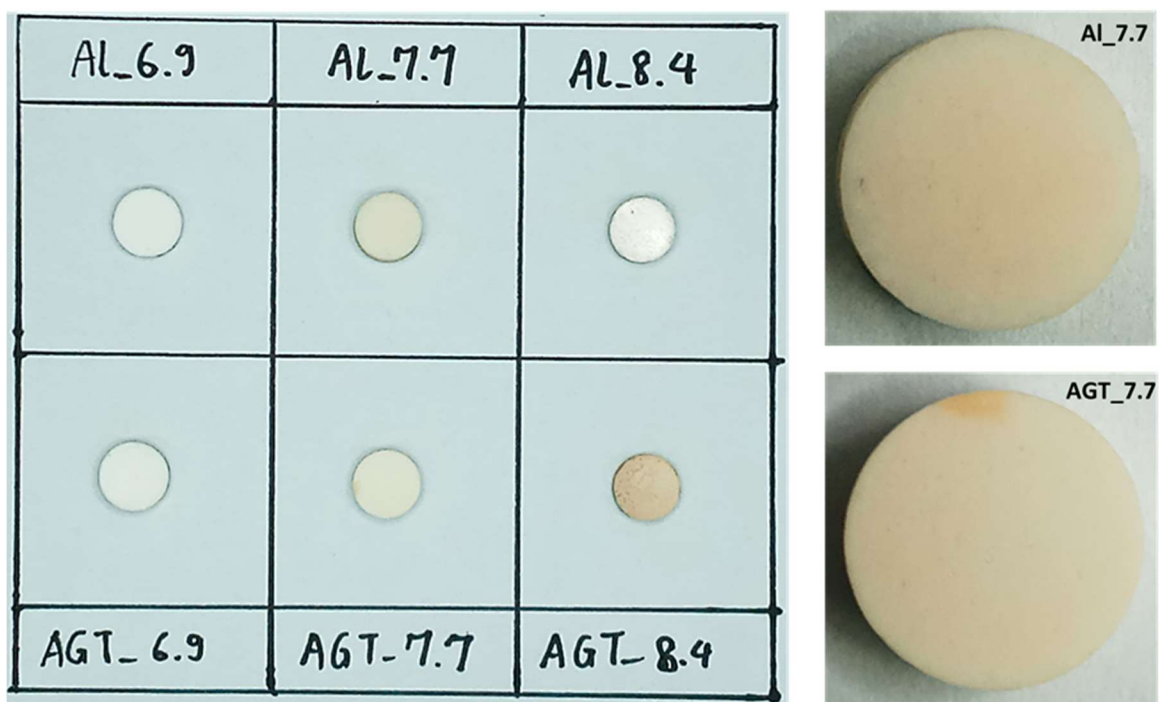


Figure S6: Digital image of pellets.

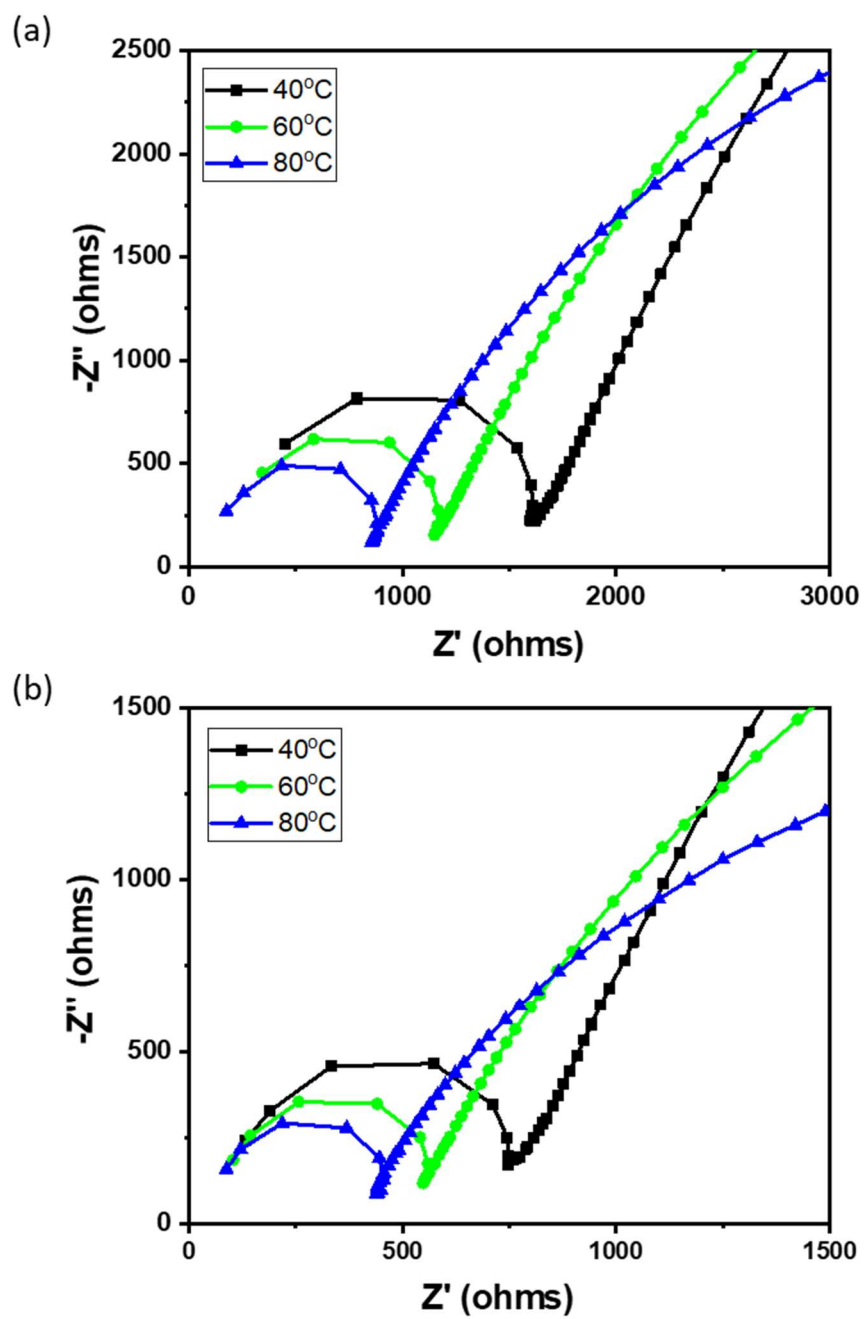
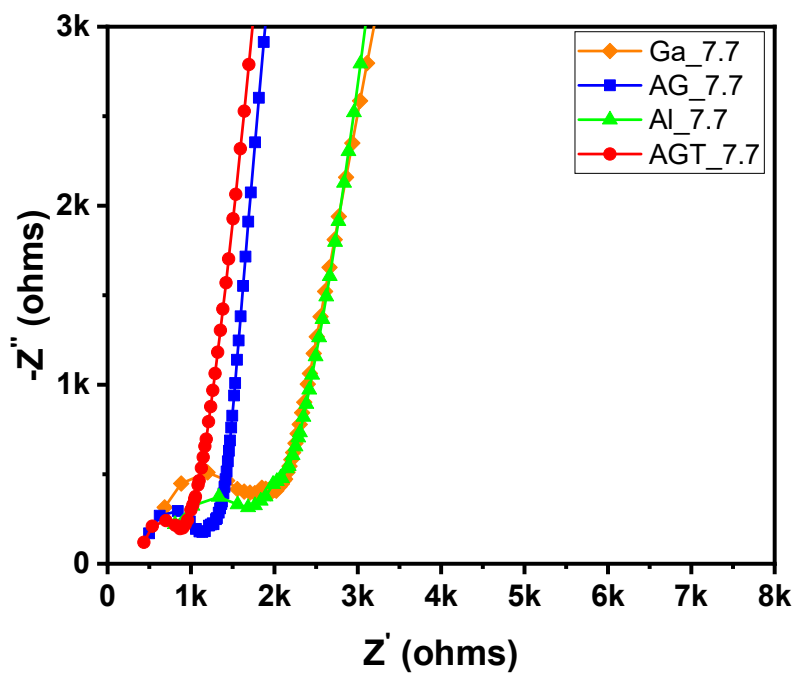


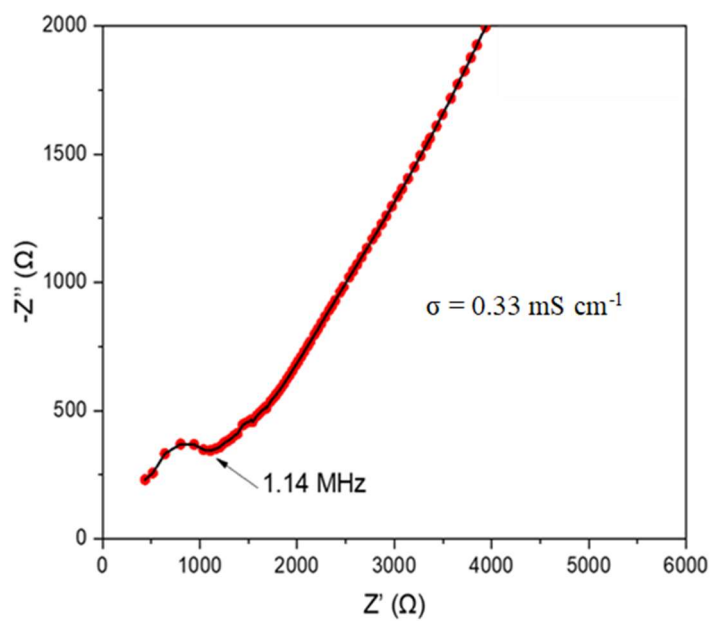
Figure S7: Nyquist plots of (a) Al<sub>7.7</sub> and (b) AGT<sub>7.7</sub> samples at 40–80 °C



**Figure S8:** Nyquist plots of Al-doped LLZO, Ga-doped LLZO, Al/Ga-doped LLZO, and Al/Ga/Ta-doped LLZO pellets with  $\text{Li}^+$  concentration of 7.7 mol.

**Table S2:** Summary of total ionic conductivity at 25 °C of Al-doped LLZO, Ga-doped LLZO, Al/Ga-doped LLZO, and Al/Ga/Ta-doped LLZO pellets with Li<sup>+</sup> concentration of 7.7 mol.

Sample	Al_7.7	Ga_7.7	AG_7.7	AGT_7.7
Ion conductivity ( $\times 10^{-4}$ S cm <sup>-1</sup> )	1.7	2.0	3.2	3.6



**Figure S9:** Nyquist plots of Al-doped LLZO prepared with  $\text{Li}^+$  concentration of 7.7 mol and sintering time of 24 h.

**Table S3:** Comparison of LLZO pellets prepared by fast sintering methods in this work and other studies.

Composition	Sintering method	Sintering temperature (°C)	Sintering time	Ionic conductivity at 25 °C (mS cm <sup>-1</sup> )	Reference
$\text{Li}_{6.45}\text{Al}_{0.05}\text{La}_3\text{Zr}_{1.6}\text{Ta}_{0.4}\text{O}_{12}$	Ultrafast High-temperature Sintering (UHS) with an AC/DC power source	1500	10 s	0.12	[36]
$\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$	Furnace sintering (using Pt crucibles)	1250	40 min	0.64	[32]
$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.45}\text{Ta}_{0.55}\text{O}_{12}$	Sintering with DC power supply and volatile fillers	1327	20 s	1.09	[38]
$\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$	Hot pressing	1000	1 h	0.4	[31]
$\text{Li}_{6.15}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.2}\text{O}_{12}$	Hot pressing	1050	1 h	0.37	[18]
$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.5}\text{Ta}_{0.5}\text{O}_{12}$	Spark plasma sintering	1000	10 min	0.69	[37]



$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	Furnace sintering	1250	40 min	0.17	This work
$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	Furnace sintering	1250	24 h	0.33	This work
$\text{Li}_{6.25}\text{Al}_{0.172}\text{Ga}_{0.072}\text{La}_3\text{Zr}_{1.982}\text{Ta}_{0.018}\text{O}_{12}$	Furnace sintering	1250	40 min	0.36	This work