

Supporting Information

Fast Material Search of Lithium Ion Conducting Oxides Using a Recommender System

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Table S1. Molar fraction of cations and nominal composition of Li-Ge-P of unknown CRCs in $\text{Li}_2\text{O-GeO}_2\text{-P}_2\text{O}_5$ quasi-ternary system.

| Unknown CRC ID | Predicted rating | Li | Ge | P | Nominal composition |
|----------------|------------------|----|----|---|---|
| GP1 | 0.1715 | 3 | 2 | 1 | $\text{Li}_3\text{Ge}_2\text{PO}_8$ |
| GP2 | 0.0722 | 1 | 1 | 1 | LiGePO_5 |
| GP3 | 0.0248 | 2 | 1 | 1 | $\text{Li}_4\text{Ge}_2\text{P}_2\text{O}_{11}$ |
| GP4 | 0.0167 | 1 | 2 | 1 | LiGe_2PO_7 |
| GP5 | 0.0165 | 2 | 3 | 1 | $\text{Li}_4\text{Ge}_6\text{P}_2\text{O}_{19}$ |
| GP6 | 0.0103 | 3 | 1 | 2 | $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$ |

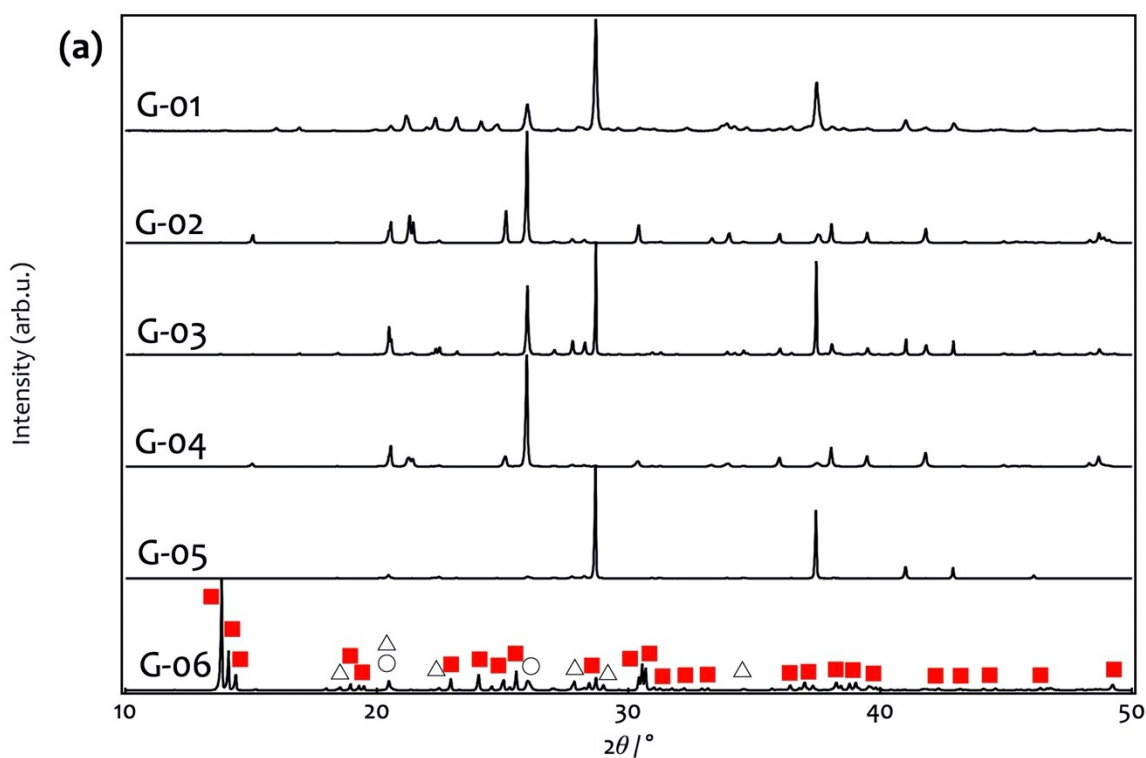


Figure S1 (a). XRD patterns of the obtained products (experimental ID from G-01 to G-06). The squares (■), triangles (Δ), and circles (○) indicate the diffraction peaks from unknown phase I, $\text{Li}_4\text{P}_2\text{O}_7$, and GeO_2 , respectively.

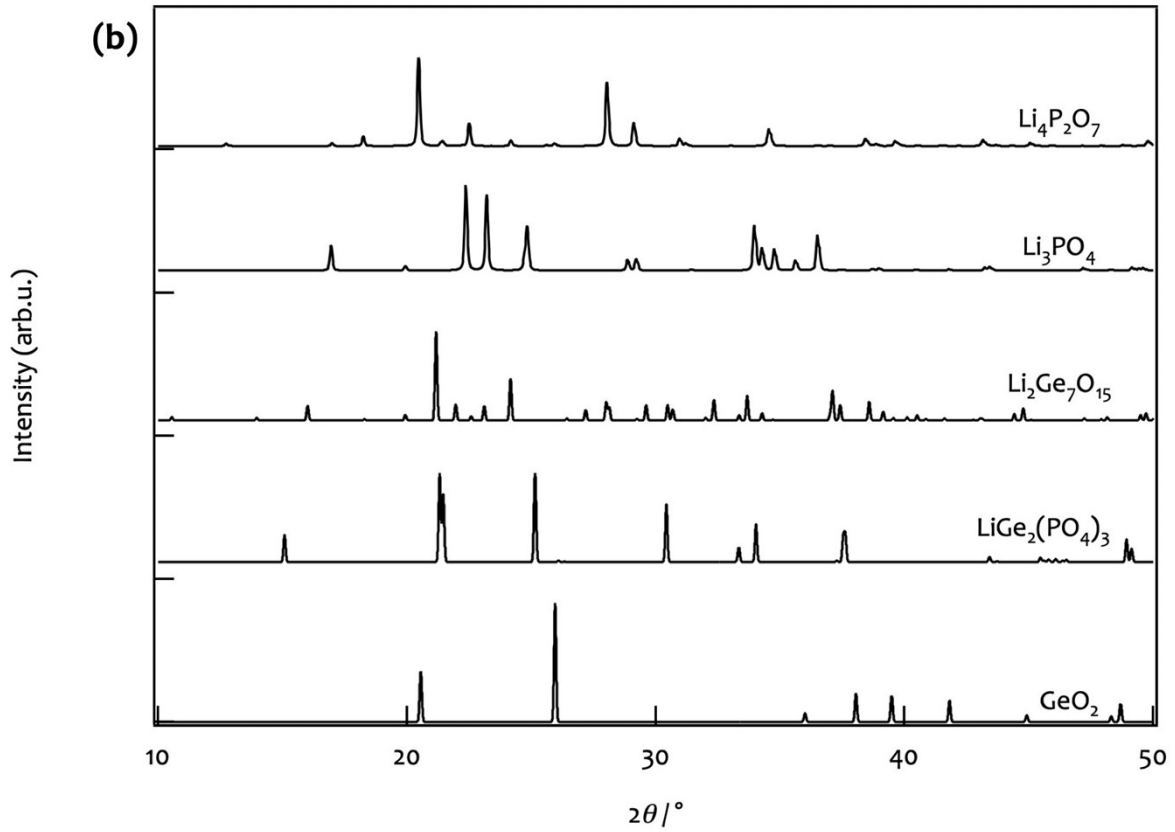


Figure S1 (b). XRD patterns of the detected known phases for material search in the $\text{Li}_2\text{O}-\text{GeO}_2-\text{P}_2\text{O}_5$ quasi-ternary system.

Table S2. Summary of the searched materials in the $\text{Li}_2\text{O}-\text{GeO}_2-\text{P}_2\text{O}_5$ quasi-ternary system.

| Experimental ID | Unknown CRC ID | Identified phases |
|-----------------|----------------|---|
| G-01 | GP1 | $\text{Li}_2\text{Ge}_7\text{O}_{15}$ Li_3PO_4 GeO_2 |
| G-02 | GP2 | $\text{LiGe}_2(\text{PO}_4)_3$ $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| G-03 | GP3 | Li_3PO_4 $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| G-04 | GP4 | $\text{LiGe}_2(\text{PO}_4)_3$ $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| G-05 | GP5 | Li_3PO_4 $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| G-06 | GP6 | Unknown I $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |

Table S3. Summary of the synthetic conditions for $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$ (unknown CRC ID 6) in the Li_2O - GeO_2 - P_2O_5 quasi-ternary system.

| Experimental ID | Li excess (mol%) | Synthesis temperature $T / ^\circ\text{C}$ | Identified phases |
|-----------------|------------------|--|--|
| G-06 | 5 | 900 | Unknown I $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| F-01 | 0 | 700 | Unknown I $\text{LiGe}_2(\text{PO}_4)_3$ $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| F-02 | 0 | 750 | Unknown I $\text{LiGe}_2(\text{PO}_4)_3$ $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| F-03 | 0 | 780 | Unknown I |
| F-04 | 0 | 800 | Unknown I |
| F-05 | 0 | 850 | $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |
| F-06 | 0 | 900 | $\text{Li}_4\text{P}_2\text{O}_7$ GeO_2 |

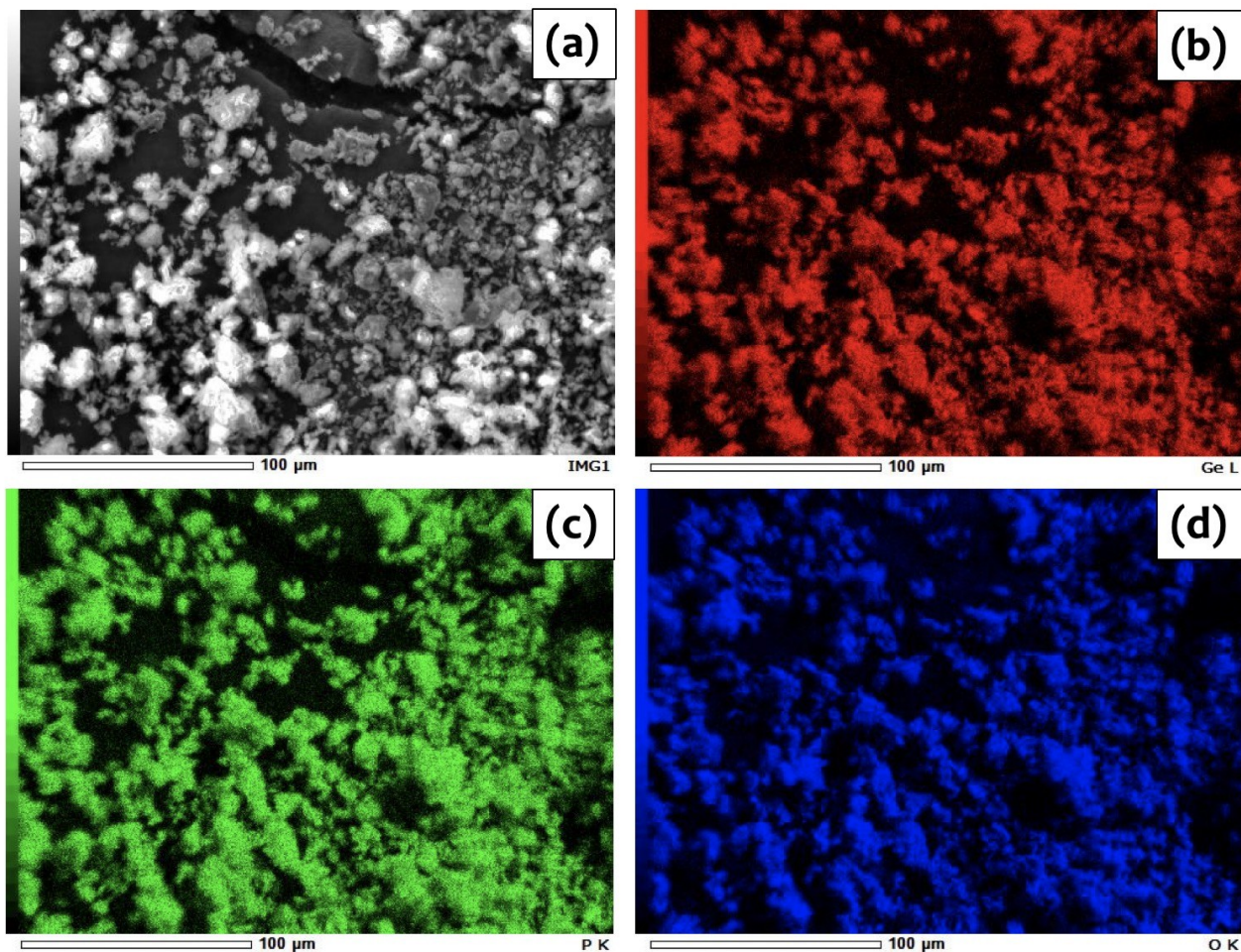


Figure S2. (a) SEM image of $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$. EDX mapping results of (b) Ge, (c) P, and (d) O for $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$.

Table S4. Molar fraction of cations and nominal composition of Li-Zn-Ge of unknown CRCs in the Li_2O - ZnO - GeO_2 quasi-ternary system.

| Unknown CRC ID | Predicted rating | Li | Zn | Ge | Nominal composition |
|----------------|------------------|----|----|----|--|
| ZG1 | 0.1467 | 2 | 1 | 2 | $\text{Li}_2\text{ZnGe}_2\text{O}_6$ |
| ZG2 | 0.0914 | 1 | 1 | 1 | $\text{Li}_2\text{Zn}_2\text{Ge}_2\text{O}_7$ |
| ZG3 | 0.0156 | 4 | 1 | 3 | $\text{Li}_4\text{ZnGe}_3\text{O}_9$ |
| ZG4 | 0.0135 | 3 | 1 | 4 | $\text{Li}_6\text{Zn}_2\text{Ge}_8\text{O}_{21}$ |
| ZG5 | 0.0099 | 3 | 3 | 2 | $\text{Li}_6\text{Zn}_6\text{Ge}_4\text{O}_{17}$ |
| ZG6 | 0.0095 | 3 | 2 | 3 | $\text{Li}_6\text{Zn}_4\text{Ge}_6\text{O}_{19}$ |
| ZG7 | 0.0093 | 2 | 3 | 1 | $\text{Li}_2\text{Zn}_3\text{GeO}_6$ |
| ZG8 | 0.0092 | 2 | 3 | 2 | $\text{Li}_2\text{Zn}_3\text{Ge}_2\text{O}_8$ |
| ZG9 | 0.0086 | 4 | 1 | 2 | $\text{Li}_4\text{ZnGe}_2\text{O}_7$ |
| ZG10 | 0.0077 | 2 | 2 | 3 | $\text{Li}_2\text{Zn}_2\text{Ge}_3\text{O}_9$ |

Table S5. Summary of the searched materials in the Li₂O-ZnO-GeO₂ quasi-ternary system.

| Experimental ID | Unknown CRC ID | Cooling method | Identified phases |
|-----------------|----------------|----------------|--|
| Z-01 | ZG1 | Natural | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ |
| Z-02 | ZG1 | Quench | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ |
| Z-03 | ZG2 | Natural | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Zn ₂ GeO ₄ |
| Z-04 | ZG2 | Quench | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Zn ₂ GeO ₄ |
| Z-05 | ZG3 | Natural | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Li ₂ GeO ₃ |
| Z-06 | ZG4 | Natural | Unknown II Li ₂ ZnGe ₃ O ₈ Li ₂ GeO ₃ |
| Z-07 | ZG4 | Quench | Unknown II Li ₂ ZnGe ₃ O ₈ Li ₂ GeO ₃ |
| Z-08 | ZG5 | Natural | Li ₂ ZnGeO ₄ Zn ₂ GeO ₄ ZnO |
| Z-09 | ZG5 | Quench | Li ₂ ZnGeO ₄ Zn ₂ GeO ₄ ZnO |
| Z-10 | ZG6 | Natural | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Zn ₂ GeO ₄ |
| Z-11 | ZG6 | Quench | Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Zn ₂ GeO ₄ |
| Z-12 | ZG7 | Natural | Li ₂ ZnGeO ₄ ZnO |
| Z-13 | ZG7 | Quench | Li ₂ ZnGeO ₄ ZnO |
| Z-14 | ZG8 | Natural | Li ₂ ZnGeO ₄ Zn ₂ GeO ₄ ZnO |
| Z-15 | ZG8 | Quench | Li ₂ ZnGeO ₄ Zn ₂ GeO ₄ ZnO |
| Z-16 | ZG9 | Natural | LISICON Li ₂ ZnGeO ₄ Li ₂ GeO ₃ |
| Z-17 | ZG9 | Quench | LISICON Li ₂ ZnGeO ₄ Li ₂ GeO ₃ |
| Z-18 | ZG10 | Natural | Unknown III Li ₂ ZnGeO ₄ Li ₂ ZnGe ₃ O ₈ Zn ₂ GeO ₄ Li ₂ O |

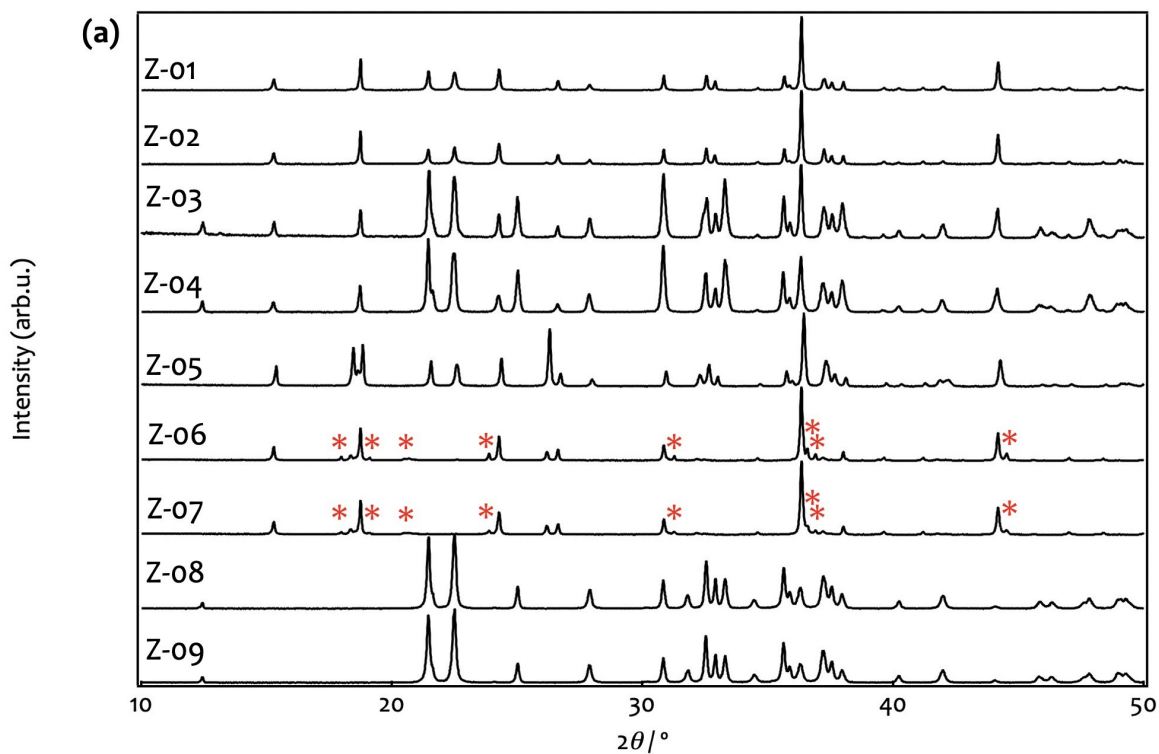


Figure S3 (a). XRD patterns of the obtained products with experimental IDs from Z-01 to Z-09. The asterisks (*) indicate the diffraction peaks from unknown phase II.

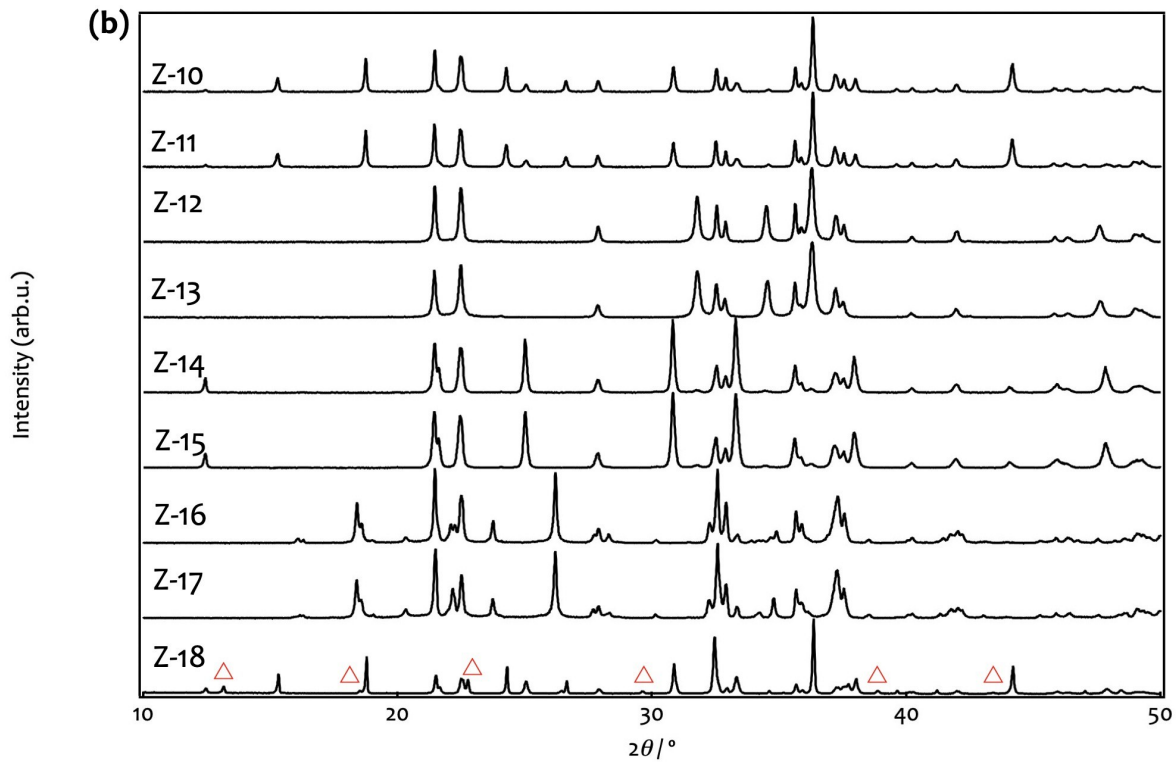


Figure S3 (b). XRD patterns of the obtained products with experimental IDs from Z-10 to Z-16. Triangles (Δ) indicate the diffraction peaks from unknown phase III.

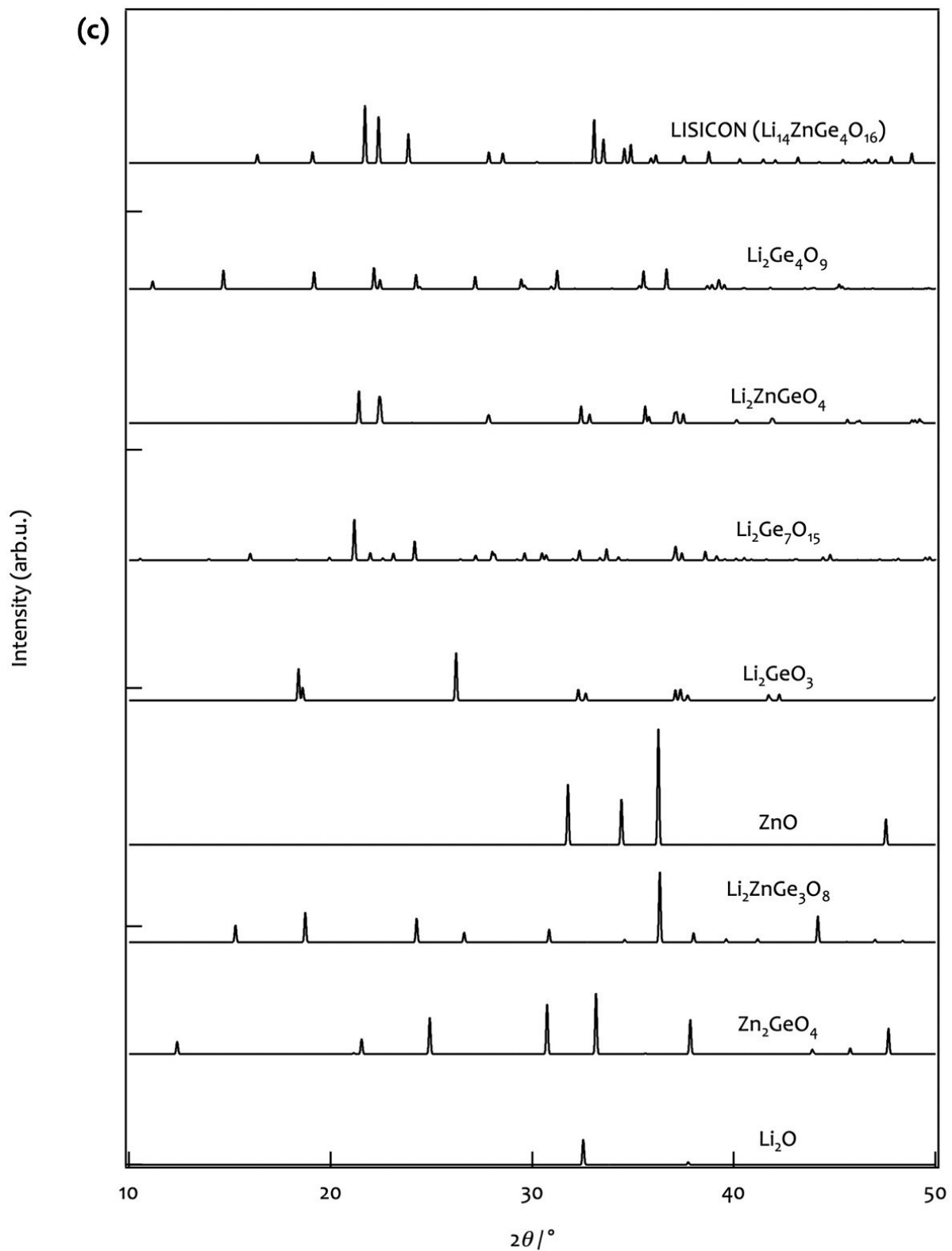


Figure S3 (c). XRD patterns of the detected known phases for material search in the Li₂O-ZnO-GeO₂ quasi-ternary system.

Table S6. Summary of the searched materials in the Li₂O-ZnO-GeO₂ quasi-ternary system with a composition around unknown CRC ID 4.

| Experimental ID | Li | Zn | Ge | Nominal composition | Identified phases |
|----------------------------|------|------|------|--|---|
| Z-06 (unknown CRC ID 4) | 3 | 1 | 4 | Li ₆ Zn ₂ Ge ₈ O ₂₁ | Unknown II Li ₂ ZnGe ₃ O ₈ Li ₂ GeO ₃ Unknown II |
| Y-01 | 3 | 0.6 | 4.4 | Li ₃ Zn _{0.6} Ge _{4.4} O _{10.9} | Li ₂ GeO ₃ Li ₂ Ge ₄ O ₉ Li ₂ Ge ₇ O ₁₅ |
| Y-02 | 3 | 0.65 | 4.35 | Li ₃ Zn _{0.65} Ge _{4.35} O _{10.85} | Unknown II Unknown II |
| Y-03 | 2.8 | 0.3 | 3.3 | Li _{2.8} Zn _{0.3} Ge _{3.3} O _{8.3} | Li ₂ GeO ₃ Li ₂ Ge ₄ O ₉ Li ₂ Ge ₇ O ₁₅ Unknown II |
| Y-04 | 5.2 | 0.7 | 6.7 | Li _{5.2} Zn _{0.7} Ge _{6.7} O _{16.7} | Li ₂ GeO ₃ Li ₂ Ge ₄ O ₉ Li ₂ Ge ₇ O ₁₅ Unknown II |
| Y-05 | 1.2 | 0.2 | 1.7 | Li _{1.2} Zn _{0.2} Ge _{1.7} O _{4.2} | Li ₂ GeO ₃ Li ₂ Ge ₄ O ₉ Li ₂ Ge ₇ O ₁₅ |
| Y-06 | 2.67 | 0.33 | 4 | Li _{2.67} Zn _{0.33} Ge ₄ O _{9.665} | Unknown II Li ₂ ZnGe ₃ O ₈ Unknown II |
| Y-07 | 2.33 | 0.33 | 4 | Li _{2.33} Zn _{0.33} Ge ₄ O _{9.495} | Li ₂ GeO ₃ Li ₂ Ge ₄ O ₉ Li ₂ Ge ₇ O ₁₅ |

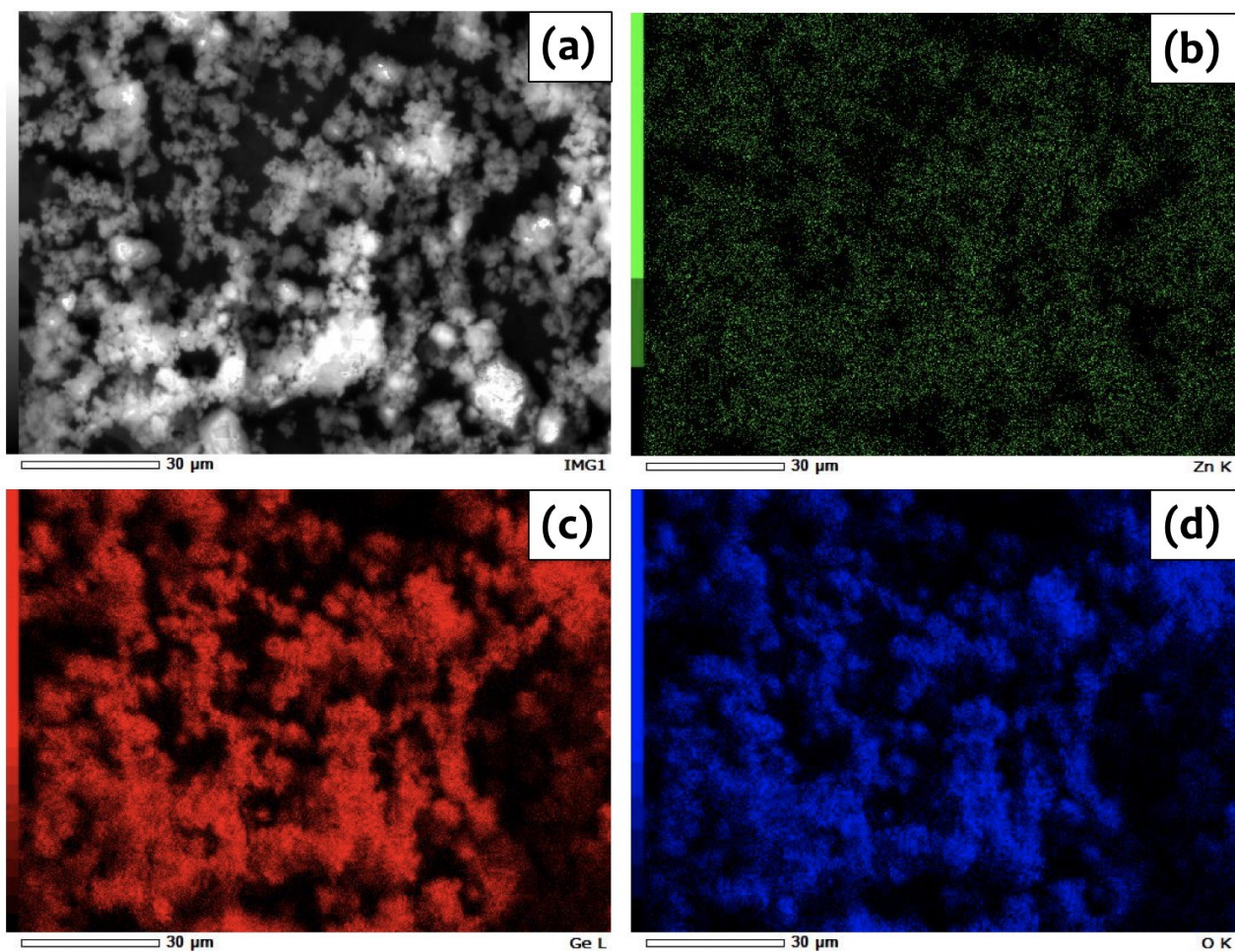


Figure S4. (a) SEM image of $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$. EDX mapping results of (b) Zn, (c) Ge, and (d) O for $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$.

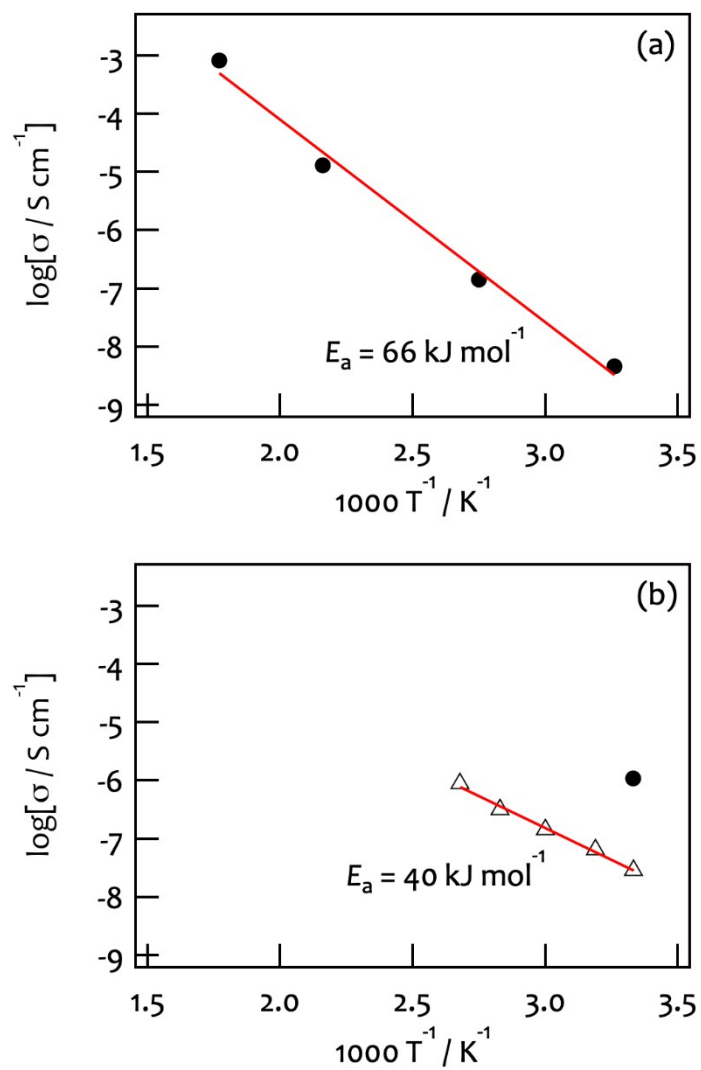


Figure S5. Arrhenius plots of ionic conductivities for the discovered phases (a) $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$ and (b) $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$. Filled circles (●) and triangles (Δ) indicate the values for the sintered pellets at the synthetic temperature and cold-pressed pellet, respectively.

Table S7. Relative density of pellets used for impedance measurements.

| Sample | Relative density (g cm^{-3}) |
|--|---|
| $\text{Li}_6\text{Ge}_2\text{P}_4\text{O}_{17}$ (sintered) | 2.31 |
| $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$ (cold pressed) | 2.62 |
| $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$ (sintered) | 3.08 |

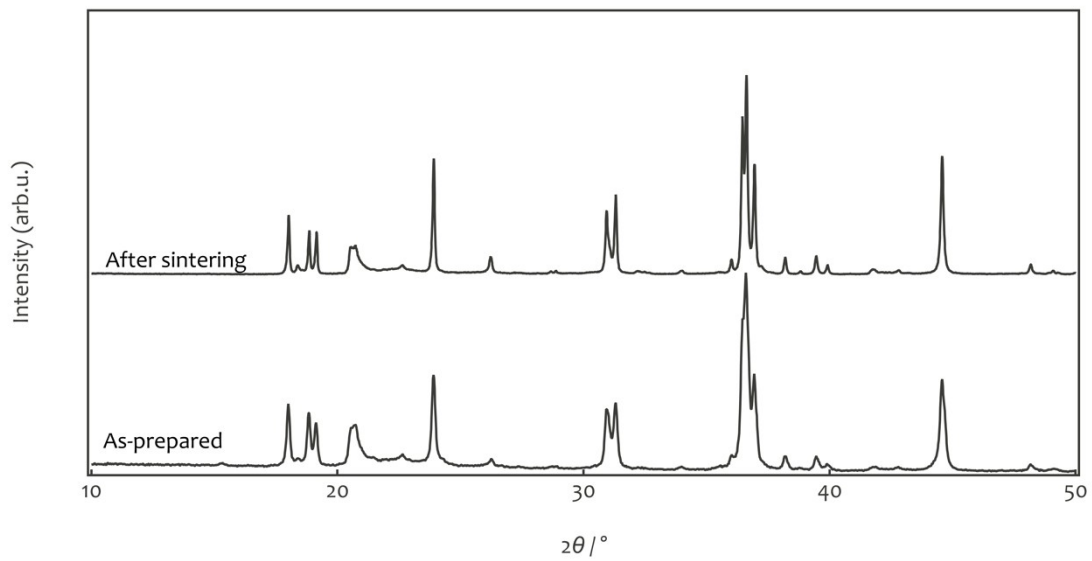


Figure S6. XRD patterns from $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$ used for the impedance measurements, in the as-prepared state and after sintering. The latter sample shows sharper diffraction peaks, indicating the enhancement in the crystallinity of $\text{Li}_3\text{Zn}_{0.65}\text{Ge}_{4.35}\text{O}_{10.85}$.