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

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A practical material search using a recommender system is demonstrated to obtain novel lithium ion conducting oxides. The synthesis of unknown chemically relevant compositions (CRCs) proposed by the recommender system and their related materials effectively reveals two kinds of novel lithium ion conductors using different approaches. In the Li_2O-GeO_2-P_2O_5 system, $Li_6Ge_2P_4O_{17}$ is found, which has the same composition as the recommended unknown CRC. Less-than-10-time synthesis following the ranking order in the diagram provides evidence of the discovered new phase. In the other quasi-ternary diagram of the Li_2O-ZnO-GeO_2 system, $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ is discovered by a combination of a recommender system and synthetic chemistry, because the composition of the novel phase is different from that of the recommended unknown CRC. Here too, the required time for material discovery is reduced to one-third of that required for random search without the recommender system. Phase identification and elemental analysis suggest that these discovered materials could have unique compositions and crystal structures. The room-temperature (~300 K) ionic conductivity (10^{-9}–10^{-6} S·cm^{-1}) of the novel phases can be improved by compositional and structural optimisations. The recommender system could emerge as a practical material search tool for enhancing the discovery rate of solid lithium ion conductors.

Introduction

All-solid-state energy storage devices attract much attention due to their high safety, reliability, and long calendar life.[1-4] A lithium battery with all-solid configurations is considered to be among the most promising next-generation energy devices, which possesses high power and energy density.[3, 4] In this battery system, characteristics of the solid electrolyte are key to determining the electrochemical properties.[5] Thus, sulfide-based materials with high ion conductivity (ranging from 10^{-4} to 10^{-2} S·cm^{-1})[3, 6-9] are widely used, despite sulfides being reactive with moisture in the air.[10] Although the oxide solid electrolytes have relatively high stability when in contact with water,[11, 12] their low ionic conductivity (~10^{-6} to 10^{-3} S·cm^{-1})[12-16] prevents their practical use in battery systems. Therefore, a search for lithium ion conducting oxide materials is required. In research on sulfide-based solid electrolytes, an important breakthrough was made from a step-by-step material search in the Li_2S-GeS_2-P_2S_5 quasi-ternary system and phase-diagram description.[2, 17, 18] Since the discovery of the thio-LISICON family in the Li_3PS_4-Li_4GeS_4 binary system in 2001, 10 years passed until $Li_{10}GeP_2S_{12}$ (LGPS) was discovered,[2] which has a totally different crystal structure from the thio-LISICON materials and a superionic conductivity > 10^{-2} S·cm^{-1}.

As an important innovation for material search over the last decade, computational calculation and machine learning methods have attracted much attention as they have the potential to markedly reduce the time required for material search.[19-24] Notably, the expected materials are generated experimentally in some cases, such as an electrode material and a semiconductor.[20, 21] However, even in successful examples, prior structural knowledge and/or exhaustive first principle calculations are required to determine the target material. A materials search based on known structures was also demonstrated.[23, 25] However, the proposed materials with expected ionic conductivities have not yet been obtained.[26, 27]

As the LGPS superionic conductor demonstrated, a material with a completely new composition and structure could become a flagship material to enable the further development of solid electrolytes.[2, 3] Therefore, the prediction of compositions in the absence of structural information is also necessary for materials searches. Recently, Seko et al. proposed the recommender system to search for novel inorganic

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Electronic Supplementary Information (ESI) available: Figures S1 – S5 and Tables S1 – S6. See DOI: 10.1039/x0xx00000x materials.[28, 29] In this system, via a machine-learning approach using prior knowledge (e.g., the Inorganic Crystal Structure Database (ICSD),[30] the International Centre for Diffraction Data (ICDD),[31] or Springer Materials (SpMat)[32]), unknown chemically relevant compositions (CRCs) of undiscovered crystals that can be formed were estimated. The recommender system demonstrated high discovery performance for unknown CRCs, whereby the unknown CRCs were proposed with expectant probability or predicted rating, which can be related to the discovery rate for novel materials. The performance of the predicted rating given by the machine learning techniques was examined using two datasets. One was denoted dataset (A) and used for machine learning while the other, denoted dataset (B), was not used for learning but to evaluate the performance thereof. The unknown CRCs obtained during the machine learning were examined to determine whether or not they could be found in dataset (B). Results showed that the discovery rate of those unknown CRCs was slightly lower but nearly proportional to the predicted ratings for ternary, quaternary, and quinary compositions[28]; i.e., approximately 50% of the unknown CRCs, which had predicted ratings of 0.5-0.6, were discovered in dataset (B). Therefore, the predicted rating is a good indicator by which to search for unknown materials. Since the estimated unknown CRCs do not contain information or requirements for the crystal structure to be formed, novel materials with a unique composition and crystal structure may be obtained. Thus, this method can be a powerful tool for a quick search of flagship lithium ion conducting oxides. However, although the discovery rate and predictive power of the system were investigated using existing databases and DFT calculations, respectively, there is limited literature for a synthetic experiment-based feasibility test of unknown CRCs to date.[33] In this study, aiming to evaluate the novel material search method using unknown CRC data from the recommender system, the proposed unknown CRCs of the top 100000 oxides were considered as candidates for the material search. Two representative quasi-ternary diagrams were examined, where lithium superionic conductor (LISICON)-related phases are reported (i.e., Li_2O-GeO_2-P_2O_5[34, 35] and Li_2O-ZnO-GeO_2[36, 37]; **Figure 1**). Finally, novel lithium ion conducting oxides with an unknown crystal structure and composition were discovered in the systems.

Experimental section

Machine Learning Methodology

For the material search in this study, quasi-ternary diagrams of the Li_2O-GeO_2-P_2O_5 and Li_2O-ZnO-GeO_2 systems were selected (**Figure 1**). In these diagrams, $Li_{3.25}Ge_{0.25}P_{0.75}O_4$ ($\sigma_{298\ K}$ = ~10^{-6} $S{\cdot}cm^{-1}$)[35, 38] and $Li_{14}Zn(GeO_4)_4$ ($\sigma_{298\ K}$ = ~10^{-7} $S{\cdot}cm^{-1}$)[39] were respectively found between Li_4GeO_4 and Li_3PO_4, and Li_4GeO_4 and Zn_2GeO_4. The $Li_{14}Zn(GeO_4)_4$ is a representative composition of LISICON.[36, 37] The unknown CRC data are obtained by machine-learning with the compositional descriptor-based recommender system using the random forest classifier.[29] The datasets for machine-learning were sourced from ICSD, while other compositions not nominated in the database are regarded as the no-entry data. The unknown CRCs with a predicted rating larger than 0.007 in the quasi-ternary diagram were regarded as target compositions. The recommender system considers two different possible states of germanium oxidation (divalent and tetravalent). Since electric insulation is required for the solid electrolyte, we considered only the tetravalent state of germanium; therefore, only metal molar fractions of the predicted composition were employed. The nominal composition is, therefore, re-described as lithium is monovalent, germanium is tetravalent, and zinc is divalent.

Material Synthesis

The starting materials, Li_2CO_3 (≧99.95%, KANTO CHEMICAL CO., INC.), GeO_2 (99.995%, Kojundo Chemical Laboratory Co. Ltd.), $NH_4H_2PO_4$ (>99%, Wako Pure Chemical Industries Ltd., Japan), and ZnO (≧99.9%, NAKALAI TESQUE, INC.) were mixed using an

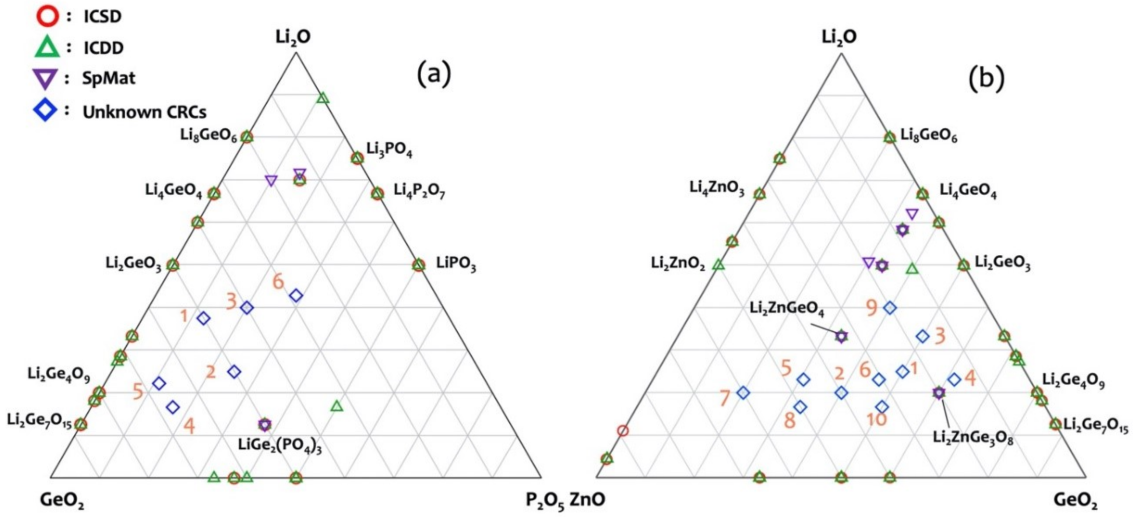

Figure 1 Quasi-ternary diagrams of (a) Li_2O-GeO_2-P_2O_5 and (b) Li_2O-ZnO-GeO_2 systems, with recorded compositions in different databases (ICSD, ICDD, and SpMat) and unknown CRCs from recommender system.

agate mortar and pestle in the appropriate molar ratios. In the starting materials, a 5 mol% excess lithium source was used to compensate for lithium loss during high temperature sintering. In some cases, no excess lithium was applied to optimise the synthesis conditions. All mixtures were then subjected to a planetary ball milling process for 30 min at 100 rpm, followed by a 24 h milling at 380 rpm. The obtained powders were pressed into a pellet, and then heated at 700–900 °C for 12 h. The pellets were cooled to approximately 25 °C naturally or by quenching with liquid nitrogen.

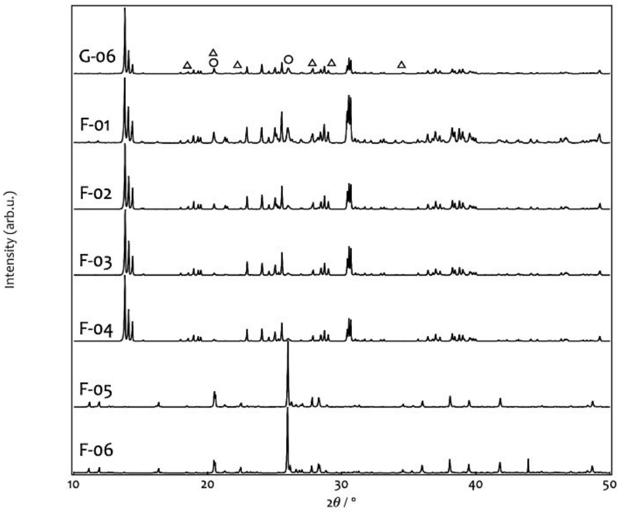

Figure 2. X-ray diffraction patterns of the obtained samples with a composition around unknown CRC ID 4. Circle (○), and triangle (△) indicate the diffraction peaks from GeO_2 and $Li_4P_2O_7$, respectively.

Phase Identification and Ionic Conductivity Measurements

The samples were characterised by powder XRD using a Rigaku SmartLab powder X-ray diffractometer with Cu Kα radiation (45 kV, 200 mA). The diffraction data were collected at 25 °C in a 2ϑ range of 10–50° with a step width of 0.01°. The XRD patterns were indexed using PDXL software (Rigaku, The Woodlands, TX). The morphologies and elemental distributions of the synthesised samples were investigated by scanning electron microscopy (SEM; JEOL JSM-6610LV) and energy dispersive X-ray spectroscopy (EDS; JEOL JED-2300). The ionic conductivity was determined using an alternating current (AC) impedance method in the frequency range of 1 Hz to 10 MHz using a frequency response analyser of Solartron 1260 (Solartron) or E4990A (Keysight Technologies). A disk-shaped sample (~1 mm thick, ~6 mm diameter) was prepared for conductivity measurements. Gold paste electrodes were coated on the surface of the disk prior to heating under vacuum at 150 °C for 3 h. Data were collected between 25 and 300 °C.

Results and discussion

A material search in the Li_2O-GeO_2-P_2O_5 quasi-ternary system provided a new material of $Li_6Ge_2P_4O_{17}$, which has the same composition as that of the recommended unknown CRC; this system was selected since a variety of lithium superionic conductors exists in the analogous sulfide system (Li_2S-GeS_2-P_2S_5).[2, 6, 18] **Table S1** summarises target compositions of the unknown CRCs in the Li_2O-GeO_2-P_2O_5 system. **Figure S1** shows X-ray diffraction (XRD) patterns of the obtained products and related materials recorded in ICSD. The obtained samples with experimental IDs from G-01 to G-05 show only the known materials. However, G-06 shows the characteristic pattern indicating the formation of an unknown phase I, which cannot be indexed using the known crystal phase. Although the small peaks assigned to $Li_4P_2O_7$ and GeO_2 were also confirmed (**Table S2**), dominant diffraction peaks from the unknown phase I indicate that it could be comparable to the expected nominal composition of $Li_6Ge_2P_4O_{17}$.

Synthetic conditions (i.e., excess mol% lithium and sintering temperature) were optimised for $Li_6Ge_2P_4O_{17}$ (**Table S3**). Synthetic temperatures at 780 and 800 °C without excess lithium provided the purest unknown phase I (**Figure 2**). Lower and higher temperature conditions triggered impurity formation and decomposition, respectively. The SEM and EDX

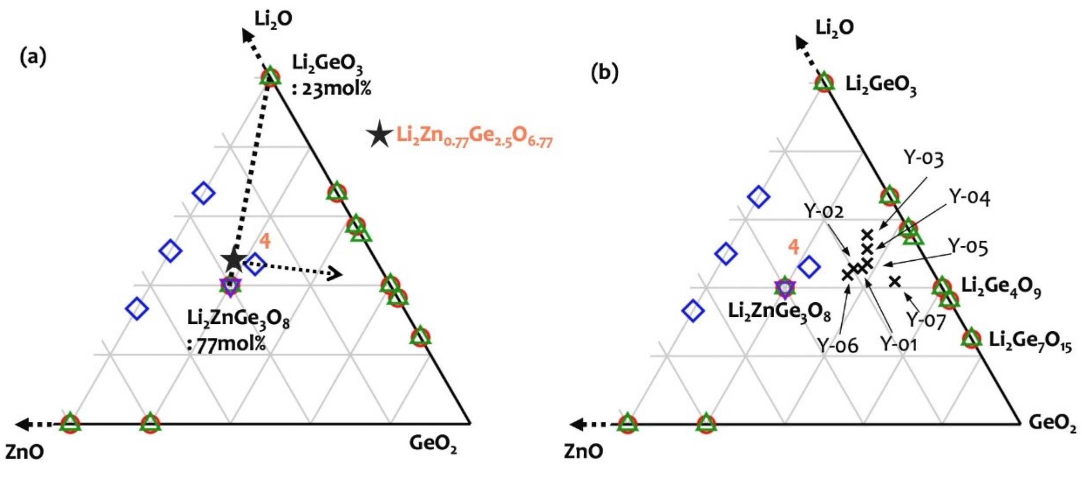

Figure 3. Magnified images of the quasi-ternary diagram of the Li_2O-ZnO-GeO_2 system around unknown CRC ID 4.

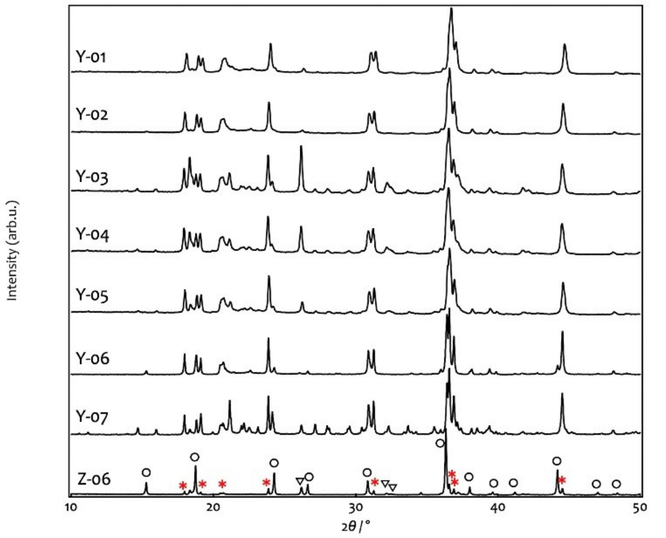

Figure 4. X-ray diffraction patterns of the obtained samples with a composition around unknown CRC ID 4. Asterisk (*), circle (○), and inverted triangle (▽) indicate the diffraction peaks from unknown phase II, $Li_2ZnGe_3O_8$, and Li_2GeO_3, respectively.

analysis for F-04 confirmed a homogeneous element distribution of Ge, P, and O in the entire region (**Figure S2**). This mono-phasic characteristic indicates that the composition of the unknown phase I could be $Li_6Ge_2P_4O_{17}$, corresponding to the unknown CRC ID GP6. In this diagram, we discovered a novel phase of $Li_6Ge_2P_4O_{17}$ by just six trials and synthetic optimisation using the unknown CRC data from recommender system. This new phase has a unique composition and crystal structure different from those of the related materials in the databases (ICSD, ICDD, and SpMat). Meanwhile, there are many related candidates to be examined for a classical materials search approach (e.g., $LiPO_3$-Li_4GeO_4, $Li_4P_2O_7$-Li_4GeO_4, and Li_2GeO_3-$LiPO_3$); thus, the recommender system clearly enhanced the efficiency of material discovery rate in this case.

During the material search in the other quasi-ternary diagram of the Li_2O-ZnO-GeO_2 system, where the original LISICON ($Li_{14}Zn(GeO_4)_4$) was included,[36] $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ was found using a combination of the recommender system and synthetic chemistry. Experimental information for the unknown CRCs listed in **Table S4** in the Li_2O-ZnO-GeO_2 system are summarised in **Table S5**. **Figure S3** shows XRD patterns of the obtained products. Phase identification using PDXL revealed that the dominant products can be assigned to the known materials (e.g., Li_2ZnGeO_4, $Li_2ZnGe_3O_8$, or Li_2GeO_3; Table S5). For the series of synthetic compounds, no dependence of the formed phases on cooling was observed. Small diffraction peaks from unknown phases were observed for experimental IDs Z-06, Z-07, and Z-18, corresponding to unknown CRC IDs 4 and 10. In both cases, known phases were dominant in diffraction intensities; therefore, the unknown phases II and III may possess compositions different from the nominal composition. Consequently, the latter case (unknown phase III) should have no lithium composition (Zn-Ge-O) because the Li_2O phase is confirmed (**Table S5**). Therefore, we conducted further investigation for the former case (unknown phase II).

Figure 3 exhibits the magnified images of the ternary diagram around unknown CRC ID 4. Using PDXL software, the molar fractions of Li_2GeO_3 and $Li_2ZnGe_3O_8$ were determined to be 23 and 77, respectively. As a result, the imaginary composition of the observed known phases can be determined as $Li_2Zn_{0.77}Ge_{2.5}O_{6.77}$ by the lever rule. Further material search was conducted along the tie line between the nominal composition of $Li_6Zn_2Ge_8O_{21}$ and imaginary composition of $Li_2Zn_{0.77}Ge_{2.5}O_{6.77}$. Seven compositions (**Figure 3b**) were synthesised. Here, a fixed sintering temperature at 850 °C and a natural cooling process were applied for all the samples. **Figure 4** illustrates the XRD patterns of the products, with phase identification results summarised in **Table S6**. In the various conditions examined, the purest unknown phase II was obtained for Y-02. In other cases, the known phases of Li-Ge-O and Li-Zn-Ge-O were detected. SEM and EDX results of the obtained material for Y-02 are shown in **Figure S4**. A homogeneous elemental distribution of Zn, Ge, and O in the entire observed area indicates that the obtained product is a single phase, resulting in the composition of the unknown phase II being $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$. A combination of the recommender system with conventional synthetic chemistry plays a key role in discovering a new material possessing a composition different from the recommended one in this case. Since the unknown phase II exhibited a unique diffraction pattern, which is completely different from those of the related materials in the databases, $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ could have both unique composition and crystal structure.

For assessing the efficiency of the material discovery rate of the recommender system in this phase diagram, we synthesised almost all the regions in the Li_2O-ZnO-GeO_2 system. A phase formation map was then described using our phase identification results in combination with our previous reports.[36, 37] The phase formation map is illustrated in **Figure 5**. It is noteworthy that this is not a phase diagram of the Li_2O-ZnO-GeO_2 system. In the map, the dominant area indicates only the known phase product, except for the area around the unknown CRC ID 4 or 10. Actually, the area of the unknown phase II

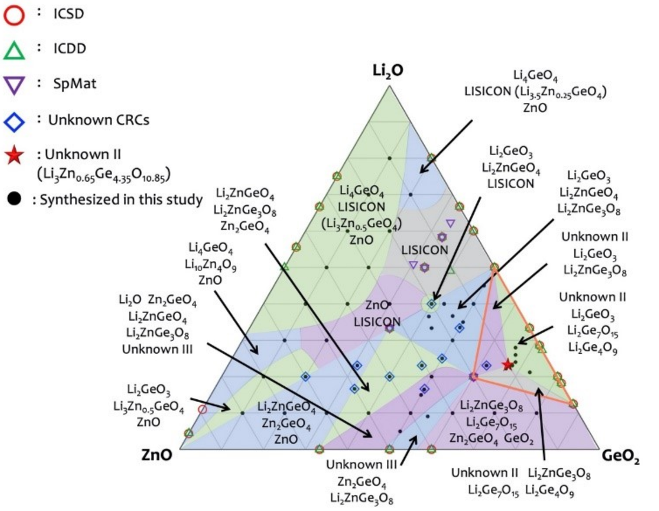

Figure 5. Phase identification results in the quasi-ternary diagram of the Li_2O-ZnO-GeO_2 system with recorded compositions from databases (ICSD, ICDD, and SpMat) and unknown CRCs from the recommender system.

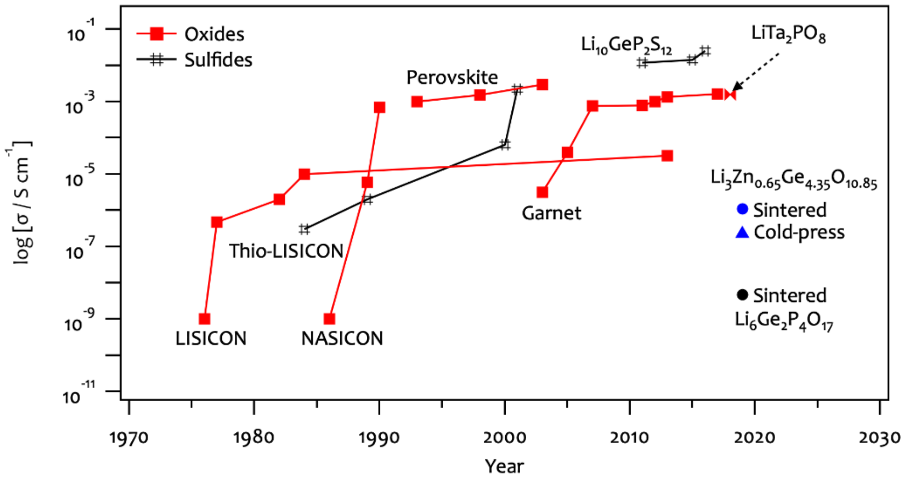

Figure 6. Evolution of ionic conductivity around 25 °C for the representative crystalline lithium ionic conductors.

formation corresponds to 1/13th of the entire diagram area. Therefore, finding the unknown phase II requires much experimentation without any information from the recommender system, e.g., we may find the unknown phase II from 13 trials if the target composition is randomly selected in this system. However, the recommender system provided the direction of this area as rank 4 nominal composition in the system. A rough calculation shows that the ratio of the number of required experiments to achieve the area where the new phase formed is 4 (recommender system)/13 (random search) = 0.31. Therefore, the recommender system could reduce the time required to acquire data, which could in turn reduce by one-third the time (number of experimental trials) required to discover new materials compared with that by a random material search sconducted without any guidelines. In addition, considering the conventional material search methods along the tie line between the known materials, there are many candidates to be investigated (e.g., Li_2ZnO_2-Li_2GeO_3, Li_2GeO_3-$ZnGeO_3$, and Li_4GeO_4-$ZnGeO_3$). As shown here, even the recommended composition did not determine the novel phase precisely; efficient discovery of new materials with unknown composition is demonstrated by applying classical synthetic chemistry methods to determine the target composition of $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$. As demonstrated here, we believe that the material search using the recommender system could enhance the efficiency for novel material discovery.

Finally, the ionic conductivity of the discovered materials was evaluated by AC-impedance methods. As the bulk and grain boundary contributions could not be separated in the impedance plots, the total conductivities (the sum of the bulk and grain boundary contributions) of the prepared samples were calculated. Sintered pellets of $Li_6Ge_2P_4O_{17}$ and $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ showed an ionic conductivity of 4.7×10^{-9} and 1.1×10^{-6} S·cm^{-1}, respectively, at ~25 °C (**Figure S5**). In the former, this value is lower by three orders of magnitude than that of the related LISICON phase ($Li_{3.25}Ge_{0.25}P_{0.75}O_4$),[35, 38] while in the latter, the value is one order of magnitude higher than that of the related LISICON phase ($Li_{14}Zn(GeO_4)_4$).[39] The clear enhancement in the ionic conductivity of the sintered pellets could be related to the relative pellet density (+18%) and enhancement of crystallinity of the $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ sample (Table S7 and Figure S6). This is also because the higher density and crystallinity could contribute to higher grain boundary and bulk conductivity, respectively. These conductivities are plotted in **Figure 6** with those of representative crystalline lithium conductors, including both oxides and sulfides.[2, 3, 13, 16, 18, 34, 36, 39-57] Although the oxide-based materials have long been studied, their ionic conductivity has remained lower than that for sulfides. Therefore, diverse novel oxides are required as candidates for materials development because the conductivity of crystalline materials can be improved by conventional cation/anion doping due to structure optimisation and introduction of defects.[3] The discovered materials show a relatively low ionic conductivity, even as oxide materials. However, there is room to improve these conductive properties. This claim is also supported by the other studies that demonstrated how unsupervised machine learning proposed some lithium superionic conductors from reported materials.[24] Therefore, as demonstrated herein, a fast material search could be the key to motivating researchers to pursue the development of materials.

Conclusions

A novel material search of lithium ion conducting oxides was conducted based on a recommender system. In the search of the Li_2O-GeO_2-P_2O_5 system, the recommender system directly pointed out a new phase of $Li_6Ge_2P_4O_{17}$, which shows an ionic conductivity of 4.7×10^{-9} S·cm^{-1}. A detailed study on obtaining XRD patterns and classical solid-state chemistry based on phase diagrams contributed to the discovery of $Li_3Zn_{0.65}Ge_{4.35}O_{10.85}$ in the Li_2O-ZnO-GeO_2 system. The novel phase exhibited an ionic conductivity of 1.1×10^{-6} S·cm^{-1} at room temperature. In both cases, the discovery efficiency for the lithium conductors was enhanced by recommender system prediction. As the unknown CRCs with a relatively low predicted rating (< 0.2) were searched in this study, it can be expected that material discovery using the composition with higher predicted ratings would be faster than if this method were not used. Although analysis of the unknown crystal structure is needed for further development, successively providing new material candidates certainly accelerates the research speed of determining solid electrolytes for all-solid-state batteries.

Conflicts of interest

There are no conflicts to declare.

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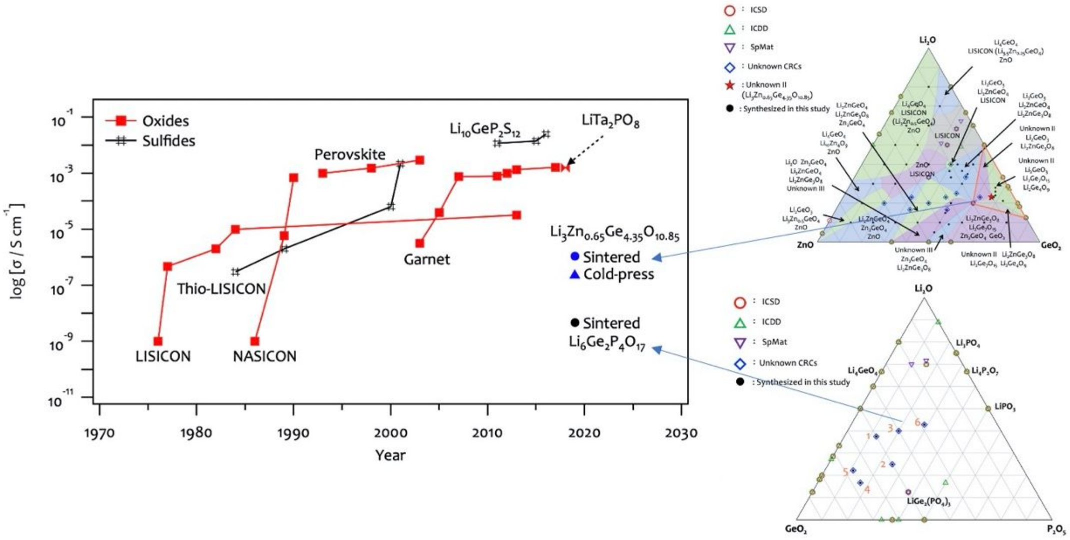

Fast material search using a recommender system is demonstrated to obtain novel lithium ion conducting oxides.