Fast fluoride ion conduction of NH₄(Mg₁₋ₓLiₓ)F₃₋ₓ and (NH₄)₂(Mg₁₋ₓLiₓ)F₄₋ₓ assisted by molecular cations

Kota Motohashi¹,² *, Yosuke Matsukawa¹, Takashi Nakamura², Yuta Kimura², Naoaki Kuwata³, Yoshiharu Uchimoto⁴ & Koji Amezawa²

Aiming development of the fast anion conductors, we proposed a new material design using flexible molecular cation as a host cation, and demonstrated it with fluoride ion conduction in NH₄MgF₃ and (NH₄)₂MgF₄ based materials. Dominant fluoride ion conduction with relatively high conductivities of 4.8 × 10⁻⁵ S cm⁻¹ and 8.4 × 10⁻⁶ S cm⁻¹ were achieved at 323 K in (NH₄)₂(Mg₀.₈₅Li₀.₁₅)F₃.ₘ and NH₄(Mg₀.₉Li₀.₁)F₂.ₙ, respectively. It is implied that the molecular cation in the host lattice can assist the anion conduction. Our findings suggest molecular cation-containing compounds can be attractive material groups for fast anion conductors.

Developing high energy density batteries are an urgent issue for establishing environmentally-friendly and sustainable society. All-solid-state fluoride ion batteries (ASSFIBs) are one of promising batteries because of their potential of high energy density¹⁴. The energy density of ASSFIBs is theoretically expected to reach 5000 Wh L⁻¹. However, state-of-the-art ASSFIBs still have many problems, for instance, the gap between theoretical and practical discharge/charge capacities, the poor cycling performance, the high operating temperature, the insufficient operating voltage, and so on³⁶. One major reason for such poor performances of the present ASSFIBs is the lack of suitable solid electrolytes having high ionic conductivity and thermochemical stability. PbSnF₄ shows the highest ionic conductivity, 1.6 × 10⁻³ S cm⁻¹ at room temperature, among already-known solid-state fluoride ion conductors. However, this material is unstable under the high operating voltage due to the narrow potential window.

There are several strategies for development of solid electrolytes. One is the use of highly disordered structure advantageous for high ionic conduction. Another is the introduction of the mobile ionic defects (such as vacancies or interstitial ions) by doping aliovalent ions. Among fluoride ion conductors, PbSnF₄, RbSnF₃, and β-PbF₂ are the materials developed based on the former strategy⁷–⁹. On the other hand, the tsyloni-type La₁₋ₓBaₓF₃₋ₓ and Sn₁₋ₓCaₓF₃₋ₓ and the fluorite-type Sn₁₋ₓKₓF₂ₓ and Ba₁₋ₓLaₓF₂₊ₓ are the materials based on the latter one¹¹–¹⁴. Although various fluoride ion conductors are previously reported¹⁵,¹⁶, further material explorations for sufficiently high fluoride ion conductivity are required to realize ASSFIBs.

Excellent cation conduction has been reported in some materials containing molecular anions such as PO₄³⁻, SiO₄⁴⁻, PS₄⁶⁻, and etc. proton conductors like CsH₂PO₄ and lithium ion conductors like Li₃PO₄-Li₄SiO₄ and Li₃P₅S₁₃ are the typical examples¹⁷–¹⁹. High cation conductivity in these materials is considered to be caused by unique size, structure, and dynamics of molecular ions, resulting in extension of the bottleneck for ionic conduction, reduction of the interaction between the host and carrier ions, and assistance of the ion conduction by the rotation of the molecular ions⁰⁻¹⁴, and so on. Considering these, a similar strategy can be applied to develop novel anion conductors. There had been some attempts to develop new fluoride ion conductors containing molecular ions such as NH₄⁺ in NH₄SnF₄²². However, the role of molecular cations for anion conduction has not been well

¹Graduate School of Engineering, Tohoku University, 6-6 Aramaki Aza Aoba, Aoba-ku, Sendai, Miyagi 980-8579, Japan. ²Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira Aoba-ku, Sendai, Miyagi 980-8577, Japan. ³National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. ⁴Graduate School of Human and Environmental Studies, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan. ⁵Present address: Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan. ⁎email: kota.motohashi@chem.osakafu-u.ac.jp; koji.amezawa.b3@tohoku.ac.jp
examined. It is therefore interesting to systematically investigate the potential of materials containing molecular cations as fast anion conductors.

In this study, perovskite and layered perovskite fluorides containing NH₄⁺ as a molecular cation, NH₄MgF₂ and (NH₄)₂MgF₄, are selected as targets of materials. In order to introduce fluoride ion vacancies by the substitution of Li⁺ for Mg⁺, their electrical conduction properties were studied. In comparison, the conductivities of perovskite and layered perovskite containing K⁺ as the A-site cation, K(Mg₀.₉Li₀.₁)F₂.₉ and K₂(Mg₀.₉Li₀.₁)F₃.₉, were examined. Since the ionic radius of K⁺ (1.64 Å) is similar to the effective radius of NH₄⁺ (1.46 Å), the influence of the molecular ions on the ionic conductivity can be discussed.

NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉, were synthesized by solid state reaction methods. The obtained powders and pressed samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) observation, electron probe micro analyzer (EPMA), and nuclear magnetic resonance (NMR) spectroscopy. The thermal stabilities of NH₄MgF₂ and (NH₄)₂MgF₄ were examined by thermogravimetry (TG). The electrical conductivities of the pellets were measured by AC electrochemical impedance spectroscopy (EIS). To confirm the dominant fluoride ion conduction, AC EIS and DC polarization measurements were performed with the fluoride ion conducting cell. In order to cross-check the dominant fluoride ion conduction, electromotive force (emf) measurements of the fluorine concentration cell, M₁F₂Mₓ/sample/MₓF₂M₁, were performed. Details are given in the supplementary information.

Results
Figure 1a,b show the XRD patterns of (a) NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (b) (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉. The most of XRD peaks could be indexed with the cubic (Pm3m) symmetry for NH₄(Mg₀.₈Li₀.₂)F₂.₈ and the tetragonal symmetry (I4/mmm) for (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉. The lattice parameters of NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ were calculated from the diffraction angles and were plotted in Fig. 1c,d as a function of the Li content. Except for the c-axis of (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉, the lattice parameters changed monotonically with the Li content in NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ phases, suggesting that solid solution is formed at least within the compositional range of 0 < x < 0.3 in NH₄(Mg₀.₈Li₀.₂)F₂.₈ and 0 < x < 0.2 in (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉, and the solubility limit of Li is higher than 30 mol% in NH₄(Mg₀.₈Li₀.₂)F₂.₈ and 20 mol% in (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉. Small diffraction peaks of NH₄NO₃ could be found in some compositions, especially in NH₄(Mg₀.₈Li₀.₂)F₂.₈. In order to investigate the state and location of the impurity, the SEM observation and EPMA analysis were carried out. The results for NH₄(Mg₀.₉Li₀.₁)F₂.₈ were presented in Figs. S1. The impurity, possibly NH₄NO₃, was observed as indicated by the yellow circles in Fig. S1. However, since the impurity particles seemed to exist sparsely from the main compound and their amount was not significant, the influences of the impurity on the observed ionic conductivities were supposed as negligibly small.

The SEM images of the cross sections of the pressed samples of NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ were shown in Fig. S2. The pellets seemed dense as just pressed, and the relative densities of all the pellets were approximately 75%.

Figure S3 (a) and (b) show the results of TG measurement. NH₄MgF₂ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ were stable below approximately 443 and 413 K, respectively. As shown in Figs. S3 (c) and (d), XRD analysis indicated that NH₄MgF₂ was decomposed to MgF₂ at around 443 K and (NH₄)₂MgF₄ was decomposed into NH₄MgF₂ and MgF₂ near 413 K forming NH₄F gas.

Figure 2 show Nyquist plots observed with (a) NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (b) (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ at 323 K. Although the results are not given in Fig. 2, only scattered signals were observed in EIS measurements with non-doped NH₄MgF₂, indicating its extremely low electrical conductivity. On the other hand, the Li-doped samples showed typical impedance responses of an ionic conductor with blocking electrodes, e.g. a semicircle in the high frequency region and a sharp spike in the low frequency region. These impedance behaviours suggested ionic conductivity in these samples. The total resistance of the sample including the bulk and grain boundary resistances was determined from the semicircle in high frequency region. Figure 3 shows temperature dependences of the electrical conductivities of NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉. The conductivities were enhanced by Li-doping, but they showed the maximum and decreased with further increasing the Li content. At 323 K, the maximum conductivity was observed at x = 0.1 for NH₄(Mg₀.₈Li₀.₂)F₂.₈ (8.4 × 10⁻⁶ S cm⁻¹) and at x = 0.15 for (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ (4.8 × 10⁻⁵ S cm⁻¹). The decrease in electrical conductivity in highly doped samples is considered to be caused by cluster formation or ordering of fluoride ions and vacancies, and etc.⁵,²⁸ The fact that the conductivities showed the maximum at a certain Li concentration also indicated that the presence of the impurities did not affect the conductivity enhancement of NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉, because the amount of the impurities monotonically increased with increasing the Li concentration.

In order to confirm dominant fluoride ion conduction in the investigated materials, we prepared a blocking cell consisting of Pb/PbSnF₄/sample/PbSnF₄/Pb. Since PbSnF₄ is an almost pure fluoride ion conductor, this cell conducts only fluoride ion under steady-state DC bias, while the AC conductivity of the cell includes the contribution of all mobile carriers in the sample. Thus, if the conductivities measured by AC EIS and DC polarization methods are comparable, it can be concluded the dominant carrier is fluoride ion. The voltage transient curves observed in DC polarization measurements with a Pb/PbSnF₄/sample/PbSnF₄/Pb at various temperatures are shown in Figs. S4b–e and S5b–h. The measured voltages were considerably increased immediately after the DC polarization and then gradually increased with time. From the impedance spectra shown in Figs. S4(a) and S5(a), the relaxation times for electrical conduction in NH₄(Mg₀.₈Li₀.₂)F₂.₈ and (NH₄)₂(Mg₀.₈Li₀.₁5)F₃.₉ were faster than 10⁻⁴ s. Thus, the gradual increase of the voltage might be mainly caused by the formation...
of resistive interphases by the decomposition of PbSnF$_4$ at the PbSnF$_4$/current-corrector interface. Therefore, the DC conductivity of the blocking cell was evaluated from the current and the voltage drop observed at 1 s after applying DC current. Figure 4 shows temperature dependence of conductivities of NH$_4$(Mg$_{1-x}$Li$_x$)$_2$F$_{3-x}$ and (NH$_4$)$_2$(Mg$_{1-x}$Li$_x$)$_3$F$_{4-x}$ measured by AC EIS and DC polarization methods with a Pb/PbSnF$_4$/sample/PbSnF$_4$/Pb cell. The conductivities by AC EIS and DC polarization methods were comparable to those of NH$_4$(Mg$_{1-x}$Li$_x$)$_2$F$_{3-x}$ and (NH$_4$)$_2$(Mg$_{1-x}$Li$_x$)$_3$F$_{4-x}$. Thus, it can be concluded that the dominant carrier was fluoride ion both in NH$_4$(Mg$_{1-x}$Li$_x$)$_2$F$_{3-x}$ and (NH$_4$)$_2$(Mg$_{1-x}$Li$_x$)$_3$F$_{4-x}$.

In Fig. 3, the conductivities of conventional fluoride ion conductors are shown by dash-dotted lines. The fluorides investigated in this work exhibited relatively high ionic conductivity, although not as high as that of the best fluoride ion conductor, PbSnF$_4$. It is also noteworthy that pressed samples of NH$_4$(Mg$_{1-x}$Li$_x$)$_2$F$_{3-x}$ and (NH$_4$)$_2$(Mg$_{1-x}$Li$_x$)$_3$F$_{4-x}$ showed relatively high conductivities without sintering. This can be a great advantage for...
the fabrication of all-solid-state batteries. The activation energies of $\text{NH}_4(\text{Mg}_{1-x}\text{Li}_x)\text{F}_3$, as summarized in Table S1. The activation energies of $\text{NH}_4(\text{Mg}_{1-x}\text{Li}_x)\text{F}_3$ and $(\text{NH}_4)_2(\text{Mg}_{1-x}\text{Li}_x)\text{F}_4$ were approximately 0.3–0.4 eV higher than those of the reported typical fluoride ion conductors.

In the case of the layered perovskite structure, interstitial anions sometimes can be mobile, as interstitial oxygens in $\text{Ln}_2\text{NiO}_{4+}$ $(\text{Ln} = \text{rare earth})$. Based on this idea, the introduction of interstitial fluoride ions was tried for the layered perovskite $(\text{NH}_4)_2\text{MgF}_4$ by partially substituting trivalent cation $\text{Sc}^{3+}$ for $\text{Mg}^{2+}$. However, as shown in Fig. S6, this trial was not effective for improving the ionic conductivity of $(\text{NH}_4)_2\text{MgF}_4$.

In order to demonstrate the influence of the molecular cations on the anionic conductivity, $\text{K}(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$ having the same crystal structures was prepared. The lattice constant of $\text{K}(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$ was 3.989 Å which was comparable with $\text{NH}_4(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$, 4.072 Å. The electrical conductivities of $\text{K}(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$ and $\text{K}(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{3.9}$ were considerably low, 5.2 × 10$^{-6}$ S cm$^{-1}$ at 789 K and 7.3 × 10$^{-5}$ S cm$^{-1}$ at 717 K, respectively (Fig. S7). This demonstrated that $\text{NH}_4^{+}$ in the host lattice can assist the fluoride ion conduction. At this moment, the reason for the conductivity enhancement by the substitution of $\text{K}^{+}$ for $\text{NH}_4^{+}$ is not clear. One likely hypothesis is that the rotational motion of $\text{NH}_4^{+}$ assists the fluoride ion conduction. Figure 5 presents $^1$H NMR spectra of $\text{NH}_4(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$ and $(\text{NH}_4)_2(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{3.9}$ at various temperatures. A peak was observed at 9 ppm for both $\text{NH}_4(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{2.9}$ and $(\text{NH}_4)_2(\text{Mg}_{0.9}\text{Li}_{0.1})\text{F}_{3.9}$. This peak gradually narrowed as temperature increased. As already
discussed, the dominant charge carrier in both of NH4(Mg0.8Li0.2)F2.8 and (NH4)2(Mg0.8Li0.2)F3.8 is confirmed to be fluoride ion, meaning the conduction of NH4+ or proton is negligible. Thus, the narrowing of the 1H NMR peak seen in Fig. 5 is considered due to the rotational or reorientational motions of NH4+. Actually, in (NH4)2MgF4, the rotational motion of NH4+ was suggested in literature. The rotation of NH4+ can induce extension of the bottleneck for anion conduction, reduction of the interaction between the host and carrier ions, or assistance of anion hopping, as happened in cation conductors containing molecular anions. Such influences by the molecular cation might enhance the fluoride ion conduction in NH4MgF3 and (NH4)2MgF4 based materials.

In this work, we succeeded to achieve relatively high fluoride ion conductivities in compounds containing molecular cations, NH4(Mg1-xLix)F3-x and (NH4)2(Mg1-xLix)F4-x, by introducing fluoride ion vacancies. It was suggested that the molecular cation in the host lattice might assist anion conduction. The findings of this works suggested that compounds containing molecular cations can be new host materials for fast anion conductors.

**Conclusion**

NH4(Mg0.8Li0.2)F2.8 and (NH4)2(Mg0.8Li0.2)F3.8 were found to exhibit relatively high fluoride ion conductivities of 8.4 × 10^{-6} (x = 0.1) and 4.8 × 10^{-5} (x = 0.15) S cm^{-1} at 323 K, respectively. The major conduction carrier was identified as fluoride ion. This work demonstrated that compounds containing molecular cations, like hybrid organic–inorganic perovskites, can be a promising material group for noble anion-conducting materials.
Methods
Synthesis and characterization. NH₄(MgₓLi₁₋ₓ)F₃₋ₓ and (NH₄)ₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ were synthesized from 3MgCO₃·3H₂O (99.9%, Kojundo Chemical Laboratory Co., LTD., Japan), NH₄F (97.0 %, Wako Pure Chemical Industries, Ltd., Japan), and LiNO₃ (99.9%, Wako Pure Chemical Industries, Ltd., Japan) by a solid state reaction. For the synthesis of the compounds, excess amount of NH₄F was required to compensate the evaporation of NH₄F during the calcination. Figure S8 shows the products obtained with different molar ratios of NH₄MgF₃. When the mixing ratio was 1:7, the single phase of the perovskite NH₄MgF₃ was obtained, while impurities including MgF₂ were observed with the mixing ratios below 1:6, suggesting the lack of NH₄⁺⁺. Considering these results, raw material powders were mixed with a molar ratio of Mg₂Li : F = (1-x) : x : 7. The mixture was calcined at 453 K for NH₄(MgₓLi₁₋ₓ)F₃₋ₓ and 433 K for (NH₄)ₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ for 2–8 h under Ar gas flow. In order to remove remaining NH₄F, the mixtures were additionally calcined at 433 K for NH₄(MgₓLi₁₋ₓ)F₃₋ₓ and 413 K for (NH₄)ₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ for 1–5 h.

K(MgₓLi₁₋ₓ)F₃₋ₓ and Kₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ were synthesized from KF (99%, Wako Pure Chemical Industries, Ltd., Japan), MgF₂ (99.9% up, Kojundo Chemical Laboratory Co., LTD., Japan), and LiF (99.98%, Sigma-Aldrich Japan, Japan) by solid state reaction. Powders of reagents were mixed in a stoichiometric ratio, and milled in Ar atmosphere by a planetary ball milling (P-6, Fritsch Japan Co., Ltd., Japan) at 600 rpm for 12 h. The mixtures were sintered at 923 K for K(MgₓLi₁₋ₓ)F₃₋ₓ and 873 K for Kₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ for 10 h in Ar atmosphere.

The obtained samples were characterized by X-ray diffraction (XRD, D2 Phaser, Bruker AXS, Germany), scanning electron microscopy observation (SEM, JSM-7800F, JEOL, Japan), and electron probe micro analyzer (EPMA, JXA-8530F, JEOL, Japan). The thermal stability of the obtained samples was evaluated by thermogravimetry (TG, Cahn D200, Thermo Fisher Scientific K. K., Japan).

1H NMR measurements were performed using NMR spectrometer (ECA300, JEOL, Japan) with a resonance frequency of 282.8 MHz at 298–373 K. The chemical shifts were calibrated by Si(CH₃)₄.

Electrical conductivity measurements. The obtained NH₄(MgₓLi₁₋ₓ)F₃₋ₓ and (NH₄)ₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ powders were pelletized at 200 MPa by a cold isostatic pressing method. Au thin film electrodes were sputtered on the both sides of the dense pellets. Electrical conductivities were evaluated from AC electrochemical impedance spectroscopy (EIS) at 303–343 K in N₂ gas with 30–50 mV of amplitude with frequency of 4.0 × 10⁷ to 1 Hz by using the impedance analyzer (Alpha-A, Novoncontrol Technologies GmbH & Co. KG, Germany).

The powders of K(MgₓLi₁₋ₓ)F₃₋ₓ and Kₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ were pelletized at 200 MPa by a uniaxial pressure, and sintered at 1073 or 873 K for 10 h. Electrical conductivities of K(MgₓLi₁₋ₓ)F₃₋ₓ and Kₓ(MgₓLi₁₋ₓ)Fₓ⁺⁺ were evaluated from AC EIS at room temperature ~ 788 K in Ar atmosphere by using a potentiostat (VersaSTAT, Princeton Applied Research, USA).

To confirm the dominant fluoride ion conduction, DC polarization measurements were performed by using the blocking cell consisting of Pb/PbSnF₄/sample/PbSnF₄/Pb at room temperature ~ 423 K under vacuum. Schematic illustration of the blocking cell was given in Fig. S9. The current for DC polarization measurements was 78 K. The chemical shifts were calibrated by Si(CH₃)₄.

Received: 21 October 2021; Accepted: 28 March 2022
Published online: 08 April 2022

References
1. Reddy, M. A. & Fichtner, M. Batteries based on fluoride shuttle. J. Mater. Chem. A. 11, 17059–17062. https://doi.org/10.1039/D2TA0824B (2021).
2. Gschwind, F. et al. Fluoride ion batteries: Theoretical performance, safety, toxicity, and a combinatorial screening of new electrodes. J. Fluor. Chem. 182, 76–90. https://doi.org/10.1016/j.jfluchem.2015.12.002 (2016).
3. Rongeet, C., Reddy, M. A., Witter, R. & Fichtner, M. Nanostructured fluorite-type fluorides as electrolytes for fluoride ion batteries. J. Phys. Chem. C. 117, 4943–4950. https://doi.org/10.1021/jp3117825 (2013).
4. Zhang, D. et al. Understanding the reaction mechanism and performance of 3d transition metal cathodes for all-solid-state fluoride ion batteries. J. Mater. Chem. A. 9, 406–412. https://doi.org/10.1039/D0TA08824B (2021).
5. Mohammmd, L., Witter, R., Fichtner, M. & Reddy, M. A. Room-temperature, rechargeable solid-state fluoride-ion batteries. ACS Appl. Energy Mater. 1, 4766–4775. https://doi.org/10.1021/acsenergymater.8b00848 (2018).
6. Bhata, H. et al. Conductivity optimization of tysonite-type LaₓBaₓFₓ⁺⁺ solid electrolytes for advanced fluoride ion battery. ACS Appl. Mater. Interfaces. 9, 23707–23715. https://doi.org/10.1021/acsami.7b04936 (2017).
7. Hull, S. Superionic: Crystal structures and conduction processes. Rep. Prog. Phys. 67, 1233. https://doi.org/10.1088/0034-4885/67/7/005 (2004).
8. Yamane, Y., Yamada, K. & Inoue, K. Mechanochemo synthesis and order-disorder phase transition in fluoride ion conductor Rb₂PbF₄. Solid State Ionics 179, 605–610. https://doi.org/10.1016/j.ssi.2008.04.022 (2008).
9. Réau, J. et al. Etude des propriétés structurales et électriques d’un nouveau conducteur anionique: PbSnF₄. Mater. Res. Bull. 13, 877–882. doi:10.1016/0025-5408(78)90097-1 (1978).
10. Murakami, M. et al. High anionic conductive form of PbSnF₄. Chem. Mater. 31, 7704–7710. https://doi.org/10.1021/acschemmater.9b02623 (2019).
11. Rongeet, C., Reddy, M. A., Witter, R. & Fichtner, M. Solid electrolytes for fluoride ion batteries: Ionic conductivity in polycrystalline fluorite-type fluorides. ACS Appl. Mater. Interfaces. 6, 2103–2110. https://doi.org/10.1021/am0521888 (2014).
12. Duédonné, B. et al. Exploring the SnₓCaₓF₉₋ₓ system: solid solution as a solid-state electrolyte: Relationships between structural features and F⁻ Ionic conductivity. J. Phys. Chem. C. 119, 25170–25179. https://doi.org/10.1021/acs.jpcc.5b05016 (2015).
13. Patro, L. N. & Haritharan, K. Ionic transport studies in Snₓₓ₋ₓKₓ₂Fₓ₋ₓ type solid electrolytes. Mater. Res. Bull. 47, 2492–2497. https://doi.org/10.1016/j.materresbull.2012.05.006 (2012).
14. Duvöl, A., Bednařík, J., Šepelák, V. & Hejtánš, P. Mechanosynthesis of the fast fluoride ion conductor Ba₂LaₓF₁ₓ₋ₓ: From the fluorite to the tysonite structure. J. Phys. Chem. C. 118, 7117–7129. https://doi.org/10.1021/acs.jp110018 (2014).
15. Motohashi, K., Nakamura, T., Kimura, Y., Uchimoto, Y. & Amezawa, K. Influence of microstructures on conductivity in Tysonite-type fluoride ion conductors. Solid State Ionics 338, 113–120. https://doi.org/10.1016/j.ssi.2019.05.023 (2019).

16. Patro, L. N. & Harirahan, K. Fast fluoride ion conducting materials in solid state ionic: An overview. Solid State Ionics 239, 41–49. https://doi.org/10.1016/j.ssi.2013.03.009 (2013).

17. Baranov, A. I., Khiznichenko, V. P., Sandler, V. A. & Shuvalov, L. A. Frequency dielectric dispersion in the ferroelectric and superronic phases of CsH2PO4. Ferroelectrics 81, 183–186. https://doi.org/10.1080/00150198808008840 (1988).

18. Hui, Y. W., Raanick, I. D. & Huggins, R. A. Ionic conductivity of lithium orthosilicate-lithium phosphate solid solutions. J. Electrochem. Soc. 124, 1240–1242. https://doi.org/10.1149/1.2133537 (1977).

19. Tachez, M., Malugani, J. P., Mercier, R. & Robert, G. Ionic conductivity of and phase transition in lithium thiophosphate Li3PS4. Solid State Ionics 14, 181–185. https://doi.org/10.1016/0167-2738(84)90097-3 (1984).

20. Amezawa, K., Maekawa, H., Tomii, Y. & Yamamoto, K. Protonic conduction and defect structures in Sr-doped LaPO4. J. Solid State Chem. 145, 233–240. https://doi.org/10.1016/S0022-4531(01)00963-8 (2001).

21. Famprikis, T. et al. A new superionic plastic polymorph of the Na+ conductor Na5PS4. ACS Mater. Lett. 1, 641–646. https://doi.org/10.1021/acsmaterialslett.9b00322 (2019).

22. Sorokin, N. I., Rakov, E. G., Fedorov, P. P. & Zakalyukin, R. M. Synthesis and electrical properties of ammonium fluorostannates (II). Russ. J. Appl. Chem. 76, 497–499. https://doi.org/10.1021/0A0585625331 (2003).

23. Charpin, P., Roux, N. & Ehretsmann, J. Fluorures doubles de magnésium et d’ammonium. C. R. Acad. Sc. Paris. 267, 484–486 (1968).

24. Kieslich, G., Sun, S. & Cheetham, A. K. Solid-state principles applied to organic-inorganic perovskites: New tricks for an old dog. Chem. Sci. 5, 4712–4715. https://doi.org/10.1039/C4SC02211D (2014).

25. Arachi, Y., Sakai, H., Yamamoto, O., Takeda, Y. & Inamishai, N. Electrical conductivity of the ZrO2-Ln2O3 (Ln=lanthanides) system. Solid State Ionics 121, 133–139. https://doi.org/10.1016/S0167-2738(98)00540-2 (1999).

26. Charpin, P., Roux, N. & Ehretsmann, J. Fluorures doubles de magnésium et d’ammonium. C. R. Acad. Sc. Paris. 267, 484–486 (1968).

27. Mohammad, L., Chable, I., Witter, R., Fichtner, M. & Reddy, M. A. Synthesis of fast fluoride-ion-conductive fluoride-type Ba1-xSbxF2+x (01 ≤ x ≤ 04): A potential solid electrolyte for fluoride-ion batteries. ACS Appl. Mater. Interfaces. 10, 17239–17256. https://doi.org/10.1021/acsami.8b04108 (2018).

28. Diedonné, B. et al. The key role of the composition and structural features in fluoride ion conductivity in tysonite Ce1-xSr1xF4 solid solution. Dalton Trans. 46, 3761–3769. https://doi.org/10.1039/C6DT04714A (2017).

29. Fujisaki, F. et al. Mechanical synthesis and structural properties of the fast fluoride-ion conductor PbSnF4. J. Solid State Chem. 253, 287–293. https://doi.org/10.1016/j.jssc.2017.06.007 (2017).

30. Jorgensen, J. D., Dabrowski, B., Pei, S., Richards, D. R. & Hinks, D. G. Structure of the interstitial oxygen defect in La2NiO4+x Phys. Rev. B. 40, 2187–2199. https://doi.org/10.1103/PhysRevB.40.2187 (1989).

31. Subias, G., Palacios, E., Blasco, J. & García-Ruiz, J. Phase transition and crystal structures of (NH4)3MgF4. J. Phys. Condens. Matter. 10, 8971–8982. https://doi.org/10.1088/0953-8984/10/46/004 (1998).

32. Yamada, K., Sagara, T., Yamane, Y., Ohkita, H. & Okuda, T. Superprotonic conductor CsH2PO4 studied by 1H, 31P NMR and X-ray diffraction. Solid State Ionics 175, 557–562. https://doi.org/10.1016/j.ssi.2004.03.042 (2004).

Acknowledgements
This work was partly supported by JST-Mirai Program JPMJMI18E2 and Grant-in-Aid for JSPS Fellow Grant number 20J12230, Japan.

Author contributions
K.M. contributed the following: funding acquisition, investigation, data curation, and writing original draft. Y.M. performed the experiments. T.N., and Y.K. discussed the results and wrote—review and editing manuscript. N.K. discussed the result of NMR measurement. Y.U. prepared the measurement environment. K.A. contributed the following: conceptualization, funding acquisition, resources, and writing—review and editing. The ideas and experiments were conceived, planned, and analyzed by all co-authors under the supervision of K. A. All the authors have given approval to the final version of the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary Information The online version contains supplementary material available at https://doi.org/10.1038/s41598-022-09835-0.

Correspondence and requests for materials should be addressed to K.M. or K.A.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher’s note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© The Author(s) 2022