Revealing Impacts of Anion Defect Species on Fluoride-Ion Conduction of Ruddlesden-Popper Oxyfluoride Ba$_2$ScO$_3$F

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Abstract

Mixed anion oxyfluorides are one of promising candidates of fast fluoride-ion conductor for all-solid-state fluoride-ion batteries. In order to establish scientific guidelines for further development of oxyfluoride-based solid electrolyte, understanding the true impact of anion defect species on ionic conduction is important. In this work, Ruddlesden-Popper oxyfluoride Ba$_2$ScO$_3$F, which can accept relatively high concentration of various types of anion defects, is selected as a target material to reveal defect functionalities. Oxide-ion vacancy (V$_O^-$), fluoride-ion vacancy (V$_F^-$) and interstitial
3 fluoride-ion ($F'_i$) were introduced into $\text{Ba}_2\text{ScO}_3\text{F}$, and the influence of each anion defect on fluoride-ion conduction was investigated. The ionic conductivities in $\text{Ba}_2\text{ScO}_3\text{F}$ were improved by introducing fluoride-ion defects ($V_F'$ or $F'_i$), while not improved by introducing $V'_O$. These suggest that the fluoride-ion migrates by interstitialcy diffusion through the rock-salt structure in Ruddlesden-Popper oxyfluorides, and tuning anion defects species can be rational and effective strategy for the development of fast fluoride-ion conductors based on mixed anion compounds.

1. Introduction

Solid-state batteries (SSBs) are expected to offer higher safety and energy density compared to conventional lithium-ion batteries using flammable liquid electrolytes.\textsuperscript{1,2} Among SSBs, all-solid-state fluoride-ion batteries (ASSFIBs) have been attracted great attention because of their potential of high energy density.\textsuperscript{3-8} For instance, in 2021, Nakano et al. demonstrated that the ASSFIB cell achieved 820 mAh g$^{-1}$ in the first cycle.\textsuperscript{9} For further development of ASSFIBs, solid electrolytes with high ionic conductivity and electrochemical stability are vitally important.
Generally, introducing extrinsic ionic defects is an effective strategy for the development of fast ion conducting solid electrolytes in inorganic crystalline materials. Although this strategy is sometimes available also for fluoride systems such as tysonite-type and fluorite-type fluorides,\textsuperscript{10-17} it is not always effective for many of simple fluorides. For example, unlike in perovskite oxides, such as LaGaO\textsubscript{3}, in which oxide-ion vacancy can be easily introduced,\textsuperscript{18,19} in perovskite fluorides, it is indicated by DFT calculation that fluoride-ion vacancy is difficult to be introduced because of its high formation energy.\textsuperscript{20} This indication was experimentally confirmed in some typical perovskites an perovskite-related fluorides by our preliminary investigations (detailed in SI). To overcome the difficulty of defect control in simple fluorides, the use of mixed-anion compounds as a host material is a promising approach for controlling defect species and concentration.\textsuperscript{21,22} For instance, in oxyhydrides and hydride-halides, it was reported that high concentration of anion defects, consequently high hydride-ion conduction, can be achieved.\textsuperscript{23-31} Considering that the ionic size and effective charge of fluoride-ion is similar to those of hydride-ion, a strategy for developing hydride-ion conducting oxyhydrides may be available for developing high fluoride-ion conducting oxyfluorides. In order to demonstrate this strategy of flexible defect control in oxyfluorides, in this work, Ruddlesden-Popper oxyfluoride Ba\textsubscript{2}ScO\textsubscript{3}F was chose as a host material.\textsuperscript{32} Herein,
we selectively introduce three different types of anion defect species, oxide-ion vacancy \((\nu_0)\), fluoride-ion vacancy \((\nu_F)\), and interstitial fluoride-ion \((F'_i)\) into Ba\(_2\)ScO\(_3\)F, and reveal the influence of each type of anion defect on fluoride-ion conduction.

In Ba\(_2\)ScO\(_3\)F, fluoride- and oxide-ions randomly occupy the apical sites, and oxide-ions selectively occupies the equatorial sites of octahedron around the B-site cation, as shown in Fig. 1 (a).\(^{32,33}\) In addition, interstitial anions \((F'_i\) and \(O''_i)\) can exist at the interstitial site in the rock-salt layer. Therefore, fast fluoride-ion conduction can be expected by vacancy diffusion through the perovskite layer and/or by interstitialcy-like diffusion through the rock-salt layer.\(^{32}\) To investigate the contribution of each possible conduction path, in this work, Ba\(_2\)ScO\(_3\)F-based materials having three different types of anion defect species were synthesized; oxygen-deficient \((\text{Ba}_{2-x}K_x)\text{ScO}_{3-x/2}\)F (Fig. 1 (b)), fluorine-deficient \((\text{Ba}_{2-x}K_x)\text{ScO}_{3}F_1-x\) (Fig. 1 (c)), and fluorine-excess \((\text{Ba}_{2-x}La_x)\text{ScO}_{3}F_1+x\) (Fig. 1 (d)) by the substitution of K\(^+\) or La\(^{3+}\) for Ba\(^{2+}\).

\[
\text{K}_2\text{O} \xrightarrow{\text{Ba}_2\text{ScO}_3\text{F}} 2\text{K}'_\text{Ba} + 0'O + \nu_0' \text{at apical or equatorial sites} \quad (1)
\]

\[
\text{KF} \xrightarrow{\text{Ba}_2\text{ScO}_3\text{F}} \text{K}'_\text{Ba} + F'_F + \nu'_F \text{at apical site} \quad (2)
\]

\[
\text{LaF}_3 \xrightarrow{\text{Ba}_2\text{ScO}_3\text{F}} \text{La}'_\text{Ba} + 2F'_F + F'_i \quad (3)
\]
Depending on type of introduced anion defects, following anion conduction can be expected. By the introduction of $V_0^-$ at equatorial site, diffusion of anion, presumably oxide-ion, through the perovskite layer is selectively enhanced. On the contrary, anion diffusion through the rock-salt layers is enhanced by the introduction of $V_F^-$ or $V_0^-$ at apical site because the anion vacancy would be introduced along the rock-salt layer. If interstitial fluoride-ion $F_i^-$ were introduced, interstitialcy diffusion of fluoride-ion selectively enhanced through the rock-salt layer. Based on above consideration, in this work, not only evaluating ionic conductivity but also identifying major charge carrier species were performed, since both oxide- and fluoride-ion are potentially mobile.

2. Experimental

2.1. Synthesis and characterization

All samples in the series $(\text{Ba}_{2-x-y-z} \text{K}_{x+y} \text{La}_z)\text{ScO}_{3-y/2} \text{F}_{1-x-z}$ were synthesized from $\text{BaCO}_3$ (99.99 %, Rare Metallic Co. Ltd., Japan), $\text{KF}$ (99 %, Fujifilm Wako Pure Chemicals Co., Ltd., Japan), $\text{BaF}_2$ (99.9 %, Kojundo Chemical Laboratory Co., Ltd., Japan), $\text{LaF}_3$ (99.9 %, Kojundo Chemical Laboratory Co., Ltd., Japan), and $\text{Sc}_2\text{O}_3$ (99.9 %, Kojundo Chemical Laboratory Co., Ltd., Japan) by solid-state reactions. These reagents
were mixed in appropriate stoichiometric ratios in Ar atmosphere. The mixtures were calcined at 1175 - 1348 K for 72 hours in Ar atmosphere with an intermediate grinding and pelletization, and then crushed and ground by ball-milling at 250 rpm for 1 hour (P-6, Fritsch Japan Co., Ltd., Japan). The obtained powders were characterized by X-ray diffraction with Cu K\(\alpha\) radiation (XRD, D2 Phaser, Bruker AXS, Germany), scanning electron microscopy observation (SEM, JSM-7800F, JEOL, Japan) and energy dispersive X-ray spectrometry (EDS).

2.2. Conductivity measurements

The obtained powders were pelletized at 200 MPa by a cold isostatic pressing, and sintered at 1348 K for 24 hours. The relative density of the obtained compacts was approximately 70%. Au thin film electrodes were sputtered on the both sides of the sintered compacts. Electrical conductivities were measured by two-terminal AC electrochemical impedance spectroscopy (EIS) technique in Ar atmosphere from room temperature to 891 K with amplitude voltage of 50 - 300 mV and frequency of 7.0\(\times\)10\(^6\) - 1 Hz by using a potentiostat (SP-300, Bio-Logic Science Instruments Ltd., France).
To confirm the contribution of fluoride-ion conduction to whole ionic conduction, AC EIS and DC polarization measurements were performed by using the fluoride-ion conducting cell consisting with composite electrode of NiF$_2$-Ni / a pure fluoride ion conductor La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ (LBF) / (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ / LBF / NiF$_2$-Ni. In the EIS measurements, AC amplitude voltage 300 mV of with frequency of 7.0×10$^6$ - 1 Hz was applied.

3. Results

3.1. Material characterization

Figure 2 presents XRD patterns of Ba$_2$ScO$_3$F, (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F, and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$. The broad peak observed between 20 and 40 degrees were due to the sample holder. The XRD patterns of the obtained samples were indexed as the layered-perovskite Ba$_2$ScO$_3$F with space group of $I4/mmm$, although small diffraction peaks of the starting material BaCO$_3$ was found in some compositions. The lattice volumes of (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F, and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$ were shrunk compared with that of Ba$_2$ScO$_3$F by the substitution of La$^{3+}$ for Ba$^{2+}$ and expanded by the substitution of K$^+$ for Ba$^{2+}$ (Table 1). These volume changes are mainly caused by the size
The difference of cation; La$^{3+}$ (1.22 Å), K$^+$ (1.55 Å), and Ba$^{2+}$ (1.47 Å). The SEM observation and EDS analysis confirmed uniform distribution of the constituent elements, as shown in Fig. S2, suggesting that Ba$^{2+}$ was successfully substituted by K$^+$.

3.2. Conductivity measurements

Figures 3 shows Nyquist plot observed with Ba$_2$ScO$_3$F at 656 K. Similar semicircular spectra were observed with all prepared samples. The ion-blocking behavior was not clearly observed with ours sintered compacts, possibly because the compacts were not dense enough and ion-blocking was not sufficient with the Au film electrodes on such imperfectly-dense compacts. The total ionic conductivity of the sample was calculated from the semicircle in high frequency region. Figure 4 shows temperature dependences of the electrical conductivities of Ba$_2$ScO$_3$F, (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F, and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$. Compared with Ba$_2$ScO$_3$F, the conductivity was increased in (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$ and (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, while was decreased or comparable in (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F. The fluorine-excess composition, (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$, in which interstitial fluoride-ion is expected to be introduced in the rock-salt layer, showed the highest conductivity among the prepared samples, and the
conductivity was 3.3 times higher than that of non-doped Ba$_2$ScO$_3$F at 673 K. Similarly, fluorine-deficient (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ achieved 3.8 times higher electrical conductivity than non-doped sample at 673 K, $2.9 \times 10^{-8}$ S cm$^{-1}$. The values of activation energy for the investigated samples were summarized in Table 2. The activation energy was different for each material. This implied that the ion conduction mechanism differs depending on the type of anion defect introduced.

In order to confirm major charge carrier in the Ba$_2$ScO$_3$F-based materials, we prepared a cell consisting of NiF$_2$-Ni / a pure fluoride ion conductor La$_{0.9}$Ba$_{0.1}$F$_{2.9}$ (LBF) / (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ / LBF / NiF$_2$-Ni. Since LBF can be regarded as an almost pure fluoride-ion conductor, this cell conducts only fluoride-ion under steady-state DC bias, whereas the AC conductivity of the cell includes the contribution of all mobile charge carriers in the sample. Thus, if the conductivities measured with this cell by AC EIS and DC polarization methods are comparable, it can be concluded that the major charge carrier is fluoride-ion. The voltage transient curve observed in DC polarization measurements with the NiF$_2$-Ni/LBF/sample/LBF/NiF$_2$-Ni cell at 787 K is shown in Fig. 5 (a). The measured voltages were increased immediately after the DC polarization, and then gradually increased with time. The gradual increase of the voltage might be caused by the formation of resistive NiF$_2$ phase in composite electrode. From the Nyquist plot
shown in Fig. 5 (b), the relaxation times for electrical conduction in (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ was faster than 40 Hz (2.5×10$^{-2}$ s) and that for electrode reaction was slower than this frequency. This is well consistent with DC relaxation behavior. Therefore, the DC conductivity was evaluated from the current and the voltage drop observed at 5.0×10$^{-2}$ s after applying DC current. Figure 5 (c) presents temperature dependence of conductivities of (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ evaluated by AC EIS and DC polarization measurements. Almost comparable electrical conductivities were obtained by both measurements, and the ratios of the conductivities $\sigma_{\text{DC}} / \sigma_{\text{AC}}$ were approximately 0.97 regardless of temperature. Thus, it can be concluded that the doped-Ba$_2$ScO$_3$F dominantly conducts fluoride-ion.

4. Discussion

The ionic conductivities of (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$ were higher than those of stoichiometric Ba$_2$ScOF$_3$ and (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F. As described in the introduction, $V_F^-$, $F'_1$, and $V_{O^\cdot}$ are expected to be introduced in (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$, and (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F, respectively. Thus, the results obtained in this work strongly suggest that introducing appropriate defect species is important for the development of ion conductor based on
mixed-anion compounds. In Ruddlesden-Popper structure compounds, vacancy diffusion through the perovskite structure and interstitialcy diffusion through the rock-salt structure are considered as two main anion diffusion mechanism. Anion vacancy at the apical site of the octahedron around B-site cation enhances both vacancy diffusion through the perovskite structure and interstitialcy diffusion through the rock-salt structure, while anion vacancy at the equatorial site preferentially enhances vacancy diffusion through the perovskite structure. According to the previous report on structural analysis of Ruddlesden-Popper oxyfluoride Ba₂ScO₃F, fluoride-ion preferentially occupies the apical site (2/3 of all apical site), and oxygen preferentially occupies the equatorial site and a part of the apical site (1/3 of all apical site). Such site preferences of fluoride- and oxide-ions suggest that oxide- and fluoride-ion vacancies are prone to exist at the equatorial and the apical sites, respectively. Therefore, the introduction of oxide-ion vacancy enhances vacancy diffusion through the perovskite structure and fluoride-ion vacancy enhances both vacancy diffusion through the perovskite structure and interstitialcy diffusion through the rock-salt structure. As shown in Fig. 4, the conductivity of oxygen-deficient (Ba₁.₉K₀.₁)ScO₂.₉₅F was lower or comparable than that of the stoichiometric Ba₂ScO₃F, suggesting insignificant fluoride-ion conduction via vacancy diffusion through the perovskite structure. On the contrary,
(Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$, in which $V_F^-$ and $F'_i$ are considered to be introduced, respectively, showed higher fluoride-ion conductivity than stoichiometric Ba$_2$ScO$_3$F. This suggests that interstitialcy diffusion through the rock-salt structure is effective for fluoride-ion conduction in the Ruddlesden-Popper oxyfluorides.

From these discussions, it is revealed that, in Ruddlesden-Popper oxyfluorides, interstitialcy diffusion through the rock-salt structure is preferable for fluoride-ion conduction, and that the introduction of defects which enhances interstitialcy diffusion can effectively improve fluoride-ion conductivity. In mixed-anion compounds, it is worth noting that introducing appropriate defect species depending on diffusion mechanism is essentially important, although flexible defect control is possible. This work clearly demonstrated the importance of defect control in mixed-anion compound-based solid electrolytes.

5. Conclusions

We succeeded to prepare fluoride-ion conductors based on the Ruddlesden-Popper oxyfluoride Ba$_2$ScO$_3$F by introducing various types of anion defects. It was indicated that fluoride-ion conducts in the materials via interstitialcy diffusion through the rock-salt structure. It was also indicated that the introduction of appropriate defect
species, which enhances interstitialcy diffusion, can effectively improve fluoride-ion conductivity. This work demonstrates the importance of defect control for developing anion conduction (conduction of not only F\(^-\) but also other anions like H\(^+\), O\(^{2-}\), and etc.) in mixed-anion compounds.

Author Contributions

K. M. contributed the following: funding acquisition, investigation, data curation, and writing original draft. T. S. performed the experiments. T. N. and Y. K. discussed the results and wrote–review and editing manuscript. 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.
Supporting Information: The Supporting Information is available on the website at DOI: xxxxxxxxxxxxx.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References


Figure 1. Crystal structures of (a) Ba$_2$ScO$_3$F, (b) (Ba$_{2-x}$K$_x$)ScO$_{3-x/2}$F, (c) (Ba$_{2-x}$K$_x$)ScO$_{3-2x}$F, and (Ba$_{2-x}$La$_x$)ScO$_3$F$_{1+x}$ (drawn using VESTA$^{33}$).

Figure 2. XRD patterns of Ba$_2$ScO$_3$F, (Ba$_{1.95}$K$_{0.05}$)ScO$_{3}$F$_{0.95}$, (Ba$_{1.9}$K$_{0.1}$)ScO$_{2.95}$F, and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$. 
Figure 3. Nyquist plot observed with $\text{Ba}_2\text{ScO}_3\text{F}$ measured at 656 K in Ar gas.

Figure 4. Temperature dependences of the electrical conductivities of $\text{Ba}_2\text{ScO}_3\text{F}$, $(\text{Ba}_{1.95}\text{K}_{0.05})\text{ScO}_3\text{F}_{0.95}$, $(\text{Ba}_{1.9}\text{K}_{0.1})\text{ScO}_2\text{F}_{0.95}$, and $(\text{Ba}_{1.95}\text{La}_{0.05})\text{ScO}_3\text{F}_{1.05}$. 
Figure 5. (a) Voltage transient curve observed in DC polarization method and (b) Nyquist plot observed in AC EIS method with a NiF$_2$-Ni/La$_{0.9}$Ba$_{0.1}$F$_{2.9}$/sample/La$_{0.9}$Ba$_{0.1}$F$_{2.9}$/NiF$_2$-Ni cell. (c) Temperature dependence of conductivities of (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$ evaluated from the results of AC EIS and DC polarization measurements.

**Table 1.** Lattice parameters of the prepared Ba$_2$ScO$_3$F, (Ba$_{1.95}$K$_{0.05}$)ScO$_3$F$_{0.95}$, (Ba$_{1.9}$K$_{0.1}$)ScO$_2$F$_{0.95}$, and (Ba$_{1.95}$La$_{0.05}$)ScO$_3$F$_{1.05}$. Space group: $I4/mmm$.

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<th>$c$ / Å</th>
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<td>4.144(1)</td>
<td>13.577(4)</td>
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<td>233.242(147)</td>
<td>4.146(1)</td>
<td>13.569(5)</td>
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<td>233.301(147)</td>
<td>4.145(1)</td>
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<tr>
<td>(Ba$<em>{1.95}$La$</em>{0.05}$)ScO$<em>3$F$</em>{1.05}$</td>
<td>232.536(164)</td>
<td>4.144(1)</td>
<td>13.541(3)</td>
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Table 2. Activation energies of the prepared $\text{Ba}_2\text{ScO}_3\text{F}$, $(\text{Ba}_{1.95}\text{K}_{0.05})\text{ScO}_3\text{F}_{0.95}$, $(\text{Ba}_{1.9}\text{K}_{0.1})\text{ScO}_2.95\text{F}$, and $(\text{Ba}_{1.95}\text{La}_{0.05})\text{ScO}_3\text{F}_{1.05}$.

<table>
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<th>Sample</th>
<th>Activation energy / eV</th>
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