Identification of F Defects in $Ba_4Bi_{3-x}Pb_xF_{17-x}$ ($x \leq 0.3$) by EXAFS Measurements

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All-solid-state fluorine ion batteries, which use fluoride ion conductors as solid electrolytes, are expected to achieve high energy density (> 5000 W h L^{-1}) by utilizing multi-electron reactions at the electrodes [1]. However, studies of fluoride ionic conductors have focused mainly on tysonite, fluorite, and perovskite-type structures [2, 3]. Therefore, in order to obtain design guidelines for good fluoride ionic conductors, it is desirable to expand the crystal structure library and elucidate the conduction mechanism.

$Ba_4Bi_3F_{17}$ is a cation order structure that appears within the x = 0.45 ~ 0.50 region of $Ba_{1-x}Bi_xF_{2+x}$ and does not belong to either BaF_2 (space group: *Fm*−3*m*) or BiF_3 (space group: *Pnma*) structures [4]. We found this compound has fluoride ionic conductivity 1.63×10^{-6} S cm^{-1} at 200 ℃, and the conduction pathway may be different from that of the previously reported fluorides. Aliovalent substitution of Pb^{2+} into Bi^{3+} site to form $Ba_4Bi_{3-x}Pb_xF_{17-x}$ ($0.1 \leqq x \leqq 0.4$) can further improve the ionic conductivity, resulting in the 4.95×10^{-5} S cm^{-1} at 200 ℃ for x = 0.3 (Fig. 1). The improvement in ionic conductivity is thought to be attributed to the induction of F^- vacancies and the local crystal structure, but it is unable to extract such information from the laboratory XRD data.

In this study, we perform Ba L3-edge X-ray absorption spectroscopy (XAS) at the BL-4 of SR Center to analyze the local structural changes in $Ba_4Bi_{3-x}Pb_xF_{17-x}$. Fig. 2 shows the radial structure function of $Ba_4Bi_{3-x}Pb_xF_{17-x}$ (x = 0, 0.2) obtained by Fourier transforming from extended X-ray absorption fine structure (EXAFS) oscillation. The extracted oscillation was weighted by k^2, and the Fourier transformation was performed from 1 to 7.4 Å. The major peak appears at 2.0 Å represents the Ba-F interatomic distance, while the height of the peak indicates the coordination number around Ba^{2+}. When Pb^{2+} is introduced (red line in Figure 2), the peak height decreases, indicating a decrease in the coordination number of $Ba_4Bi_{2.8}Pb_{0.2}F_{16.8}$. This can be regarded as the formation of F^- vacancies in the neighborhood of Ba^{2+}. Thus, the EXAFS analysis confirms that in $Ba_4Bi_{2.8}Pb_{0.2}F_{16.8}$, the aliovalent substitution of Pb^{2+} into Bi^{3+} site creates F^- vacancies, resulting in improved ionic conductivity compared to the pristine $Ba_4Bi_3F_{17}$.

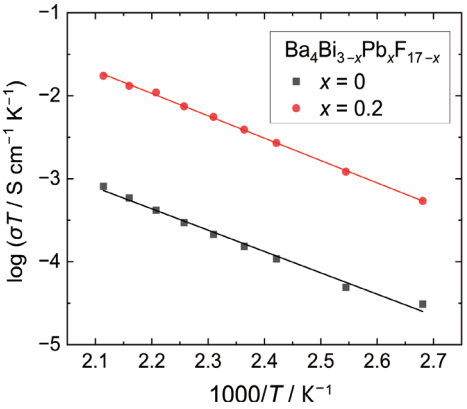

Fig. 1 Arrhenius plots of the sintered $Ba_4Bi_{3-x}Pb_xF_{17-x}$.

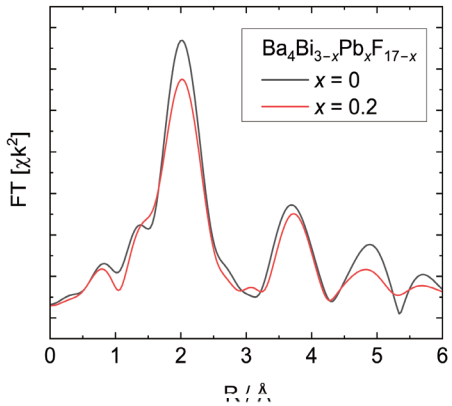

Fig. 2 Radial structure function of Ba L3-edge EXAFS for $Ba_4Bi_{3-x}Pb_xF_{17-x}$.

References

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