

Ba and Ca K-edge XAFS studies on $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$

Toyonari Yaji¹, Kazuyuki Sato², Daiki Kido³, Daisuke Shibata¹, Hirokazu Kitazawa¹, Masao Kimura³, Takeshi Abe^{2,4}, Kiyotaka Asakura^{1*}

¹ SR Center, Ritsumeikan University, Kusatsu, Japan

² Kyoto University, Kyoto, Japan

³ Institute of Materials Structure Science, KEK, Tsukuba, Japan

⁴ Graduate School of Engineering, Kyoto University, Kyoto, Japan

1 Introduction

Fluoride-ion batteries have attracted increasing attention as next-generation energy storage systems due to their high theoretical energy density and the abundance of constituent elements. A key requirement for their realization is the development of solid electrolytes with high fluoride-ion conductivity at ambient conditions. Among candidate materials, $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$ has emerged as a promising system, particularly near the equimolar composition ($x \approx 0.5$), where enhanced ionic conductivity has been observed. While diffraction studies have revealed that the average structure remains fluorite-type, the local structural features that govern ion transport are not fully understood. X-ray absorption fine structure (XAFS) spectroscopy provides a powerful tool for probing the short-range order around specific atomic species. It is therefore well-suited to investigating the structural origin of ionic conduction in this system.[1]

2 Experiment

$\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$ nanoparticles ($x = 0.28, 0.48, 0.74$) were synthesized using a thermal plasma method to ensure homogeneous mixing at the nanoscale. Reference samples of BaF_2 and CaF_2 were also prepared in the same method. XAFS measurements were conducted using BL-9A for the Ca K-edge and AR-NW10A for the Ba K-edge. All measurements were performed in transmission mode at room temperature. EXAFS oscillations were Fourier transformed (FT), and curve fitting (CF) was performed in k -space using reference-based phase and amplitude functions, along with cumulant expansion up to the third order to capture both disorder and anharmonicity.

3 Results and Discussion

Fig. 1 shows the FT of the EXAFS spectra. In pure BaF_2 and CaF_2 , distinct peaks corresponding to cation–anion and cation–cation correlations are observed, reflecting well-ordered structures. In contrast, the $\text{Ba}_{1-x}\text{Ca}_x\text{F}_2$ samples show a significant reduction in peak intensity. Notably, the cation–cation correlation peak nearly disappears at $x = 0.48$, indicating a strong suppression of medium-range order.

Tables 1 and 2 show CF results that revealed the Ba–F and Ca–F bond lengths remain close to those in BaF_2 and CaF_2 , respectively, rather than following Vegard’s rule. This bond-length preservation implies that each cation maintains its preferred local environment, governed by ionic radii and electrostatic interactions. However, accommodating these distinct bond lengths within a single lattice introduces a mismatch with the average crystal

structure. This mismatch leads to geometric frustration, which is relieved by increasing local structural disorder. The enhanced Debye–Waller factors and asymmetric bond distributions indicate large fluctuations in interatomic distances. The disorder is particularly significant at $x = 0.48$, where competition between Ba and Ca environments is strongest. The disappearance of cation–cation correlations further suggests that the lattice becomes highly disrupted at this composition. Such structural disorder plays a crucial role in ionic conduction. The distorted local structure reduces the energy barriers for fluoride-ion migration and facilitates the formation of continuous conduction pathways. Therefore, the enhanced ionic conductivity in $\text{Ba}_{0.48}\text{Ca}_{0.52}\text{F}_2$ can be attributed to the combination of geometric frustration and strong local disorder.

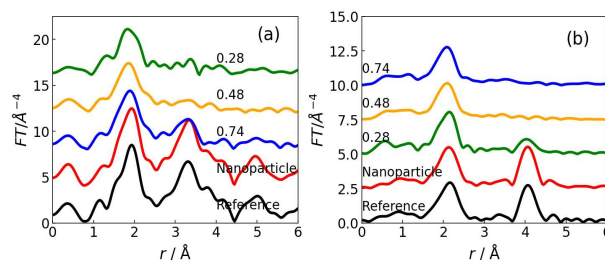


Fig. 1: FT of (a) Ca K-edge and (b) Ba K-edge EXAFS spectra in BCF.

Table 1 Ca K-edge EXAFS CF results for Ca-F

Sample	CN	$r / \text{\AA}$	$\Delta\sigma^2 / \text{\AA}^2$	$C_3 / \text{\AA}^3$
CaF_2	8	2.37	0.0	0.0002
BCF0.74	8	2.38	0.0030	0.0007
BCF0.48	8	2.38	0.0059	0.0009
BCF0.28	8	2.40	0.0063	0.0008

Table 2 Ba K-edge XAFS CF results for Ba-F

Sample	CN	$r / \text{\AA}$	$\Delta\sigma^2 / \text{\AA}^2$	$C_3 / \text{\AA}^3$
BaF_2	8	2.68	0.0	0.0002
BCF0.28	8	2.66	0.0002	0.0004
BCF0.48	8	2.65	0.0021	0.0006
BCF0.74	8	2.65	0.0018	0.0006

Acknowledgement

This paper is based on results obtained from a project, JPNP21006, commissioned by the New Energy and Industrial Technology Development Organization (NEDO).

References

[1] T. Yaji, K. Sato, et al., *Chem. Lett.*, **55** (2026) upag041.

* kytkaskr@fc.ritsumei.ac.jp