

XAFS analysis of novel Prussian blue structure

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Introduction

Prussian blue analogues, $A_xM_A[M_B(CN)_6]_y \cdot zH_2O$ (A is an alkali metal ion and M_A and M_B are metal ions), are consisted of 3-D network, and have nanoporous structures which can accommodate A ions and H_2O molecules (Figure 1). A ion generally occupy just the center of the interstitial site. Various interesting properties have been reported with Prussian blue analogues, lithium ion battery¹, alkali cation exchange effect², negative thermal expansion³, etc. To find novel functionality, the finding of novel structure is important. Recently, we observed powder X-ray diffraction peaks due to superlattice structure in $K_{0.25}Mn[Fe(CN)_6]_{0.75} \cdot 3.5H_2O$ Prussian blue analogue. To construct superlattice structure in Prussian blue analogue, two possible models exist. One is bending of CN bridge, and the other is the dislocation of K ion from the center of the interstitial site. In this work, to clarify the local structure of K ion, X-ray absorption fine structure (XAFS) experiments have been conducted.

Experimental

The sample (**KMF**) was prepared by mixing the aqueous solutions of KCl (1 mol dm⁻³), MnCl₂·2H₂O (2 mmol dm⁻³), and K₃[Fe(CN)₆] (2 mmol dm⁻³). The obtained powder was filtered and washed with water and then dried in air. The reference samples were also prepared by mixing the aqueous solutions of KCl (0.5 mol dm⁻³), MCl₂·6H₂O ($M = Co$ (**KCF**), and Ni (**KNF**); 10 mmol dm⁻³), and K₃[Fe(CN)₆] (10 mmol dm⁻³). Elemental analyses were conducted by inductively coupled plasma (ICP) mass spectrometry for metal elements and standard microanalytical methods for C, H, and N elements.

XAFS measurements with transmission mode were performed at BL-7C and 9A of Photon Factory.

Results and Discussion

The formulae of the obtained samples were $K_{0.25}Mn[Fe(CN)_6]_{0.75} \cdot 3.5H_2O$ (**KMF**), $K_{0.31}Co[Fe(CN)_6]_{0.77} \cdot 3.6H_2O$ (**KCF**) and $K_{0.19}Ni[Fe(CN)_6]_{0.73} \cdot 5.7H_2O$ (**KNF**), respectively. The powder X-ray diffraction patterns suggest that **KMF** had the superlattice structure. On the contrary, **KCF** and **KNF** had ordinary Prussian blue structure. Figure 2 shows the K K-edge XANES spectra of **KMF**, **KCF** and **KNF**. We could not observe EXAFS oscillation even in low temperature (25 K). The XANES peak positions were close with each other, 3613.0 eV (**KMF**), 3613.3 eV (**KCF**), and 3613.3 eV (**KNF**). However, only **KMF** had a shoulder peak. This peak shape difference suggests that the moiety around K ion is quite different in **KMF**.

Considering **KCF** and **KNF** are ordinary Prussian blue structure, K ion occupy just the center of the interstitial site. Hence, the dislocation of K ion in **KMF** is also suggested by XANES spectra.

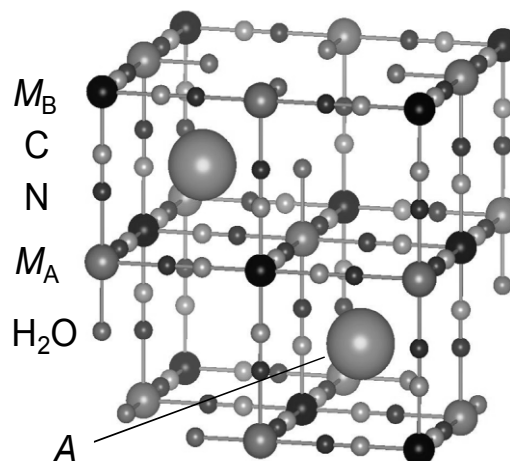


Figure 1 Schematic crystal structure of Prussian blue analogue.

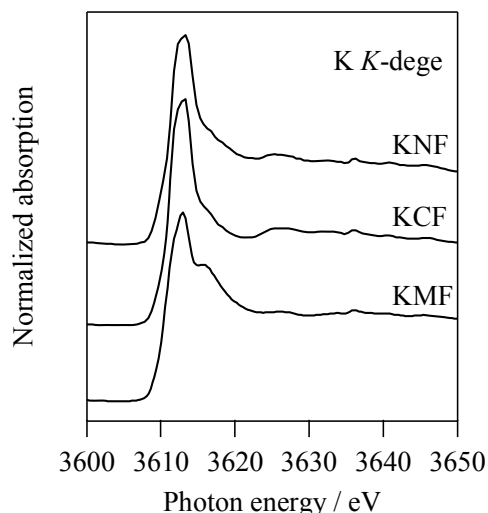


Figure 2 K K-edge XANES spectra for **KMF**, **KCF**, and **KNF**.

References

- [1] T. Matsuda et al., Appl. Phys. Exp. 4, 047101(2011).
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- [3] T. Matsuda et al., Phys. Rev. B 79, 172302 (2009).

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