Nanophase separation in $K_{1-x}Ca_xC_8$ revealed by X-ray fluorescence holography

Graphite intercalated compounds (GICs) have garnered significant attention due to their novel physical properties, such as superconductivity. In 1965, the first GIC superconductor was discovered in K-doped graphite, KC_8 [1], whose superconducting transition temperature, T_c, was 0.55 K. Among various GICs, the highest value of T_c is 11.5 K, observed in CaC_6 [2]. In addition to single-element intercalations, binary-element intercalations have been explored to achieve higher T_c superconductors. Recently, $K_{1-x}Ca_xC_y$ (T_c = 6.5–11.5 K for $0.33 \leq x \leq 1$) has been synthesized by one of the authors, Kubozono [3]. By X-ray diffraction (XRD), the interlayer distance between graphene layers was estimated to be 5.35 Å, which is the same as that of KC_8. This result implies that intercalated elements with larger radii increase the interlayer distance and determine the *c*-axis length. The structures of KC_8 and CaC_6 are shown in Figs. 1(a,b), respectively. For this reason, the crystal structure of $K_{1-x}Ca_xC_8$ has been assumed to be KC_8-type. Matsui *et al.* characterized a $K_{1-x}Ca_xC_y$ sample using surface-sensitive photoelectron holography to investigate the structure in detail. However, only K holograms could be measured due to the condensation of K atoms on cleaved surfaces [4]. Therefore, we applied bulk-sensitive X-ray fluorescence holography (XFH) to this system to determine the entire structure by measuring both Ca and K holograms [5].

XFH provides three-dimensional (3D) atomic images around specific elements emitting fluorescent X-rays, enabling the determination of local atomic arrangements within a short to intermediate range of up to a few nanometers around these emitting atoms. This technique is particularly effective for identifying the location of impurity sites and local lattice distortions around impurity atoms. Therefore, XFH discovered unexpected local structures around the additive atoms [6].

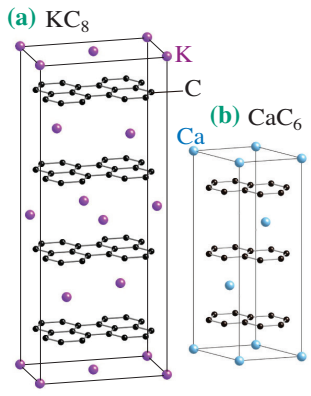

Fig. 1. Crystal structures of **(a)** KC_8 and **(b)** CaC_6.

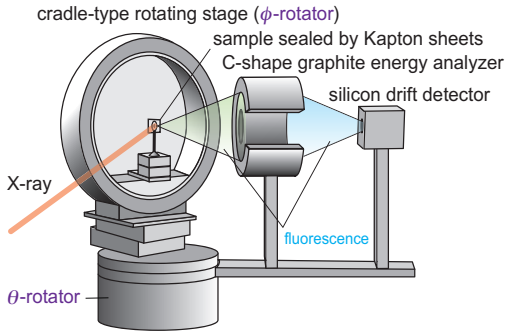

Fig. 2. XFH experimental setup with cradle-type stage.

The $K_{1-x}Ca_xC_8$ samples were prepared using the liquid alloy method. A superconducting quantum interference device (SQUID) measurement found a T_c of ~9.0 K. XRD obtained the lattice parameters and the distance between the graphene layers was 5.35 Å, which is close to the pure KC_8 structure. The X-ray fluorescence spectrum identified the sample composition as $K_{0.7}Ca_{0.3}C_8$. Intriguingly, it shows a high T_c even at such low calcium concentrations.

XFH measurements in inverse mode were conducted at SPring-8 **BL39XU**. The sample size was approximately $2.0 \times 2.0 \times 0.50$ mm^3. To prevent the oxidation of the sample in the atmosphere, the sample was sealed using Kapton sheets in a glove box. The K-*K*α (3.3 keV) and Ca-*K*β (4.0 keV) lines were used for the hologram measurements, as the Ca-*K*α (3.7 keV) line overlapped with the K-*K*β (3.6 keV) lines. Here, we used a C-shaped graphite energy analyzer specifically designed for 3–5 keV X-ray fluorescence [7]. A cradle-type rotating stage was used to collect XFH signals (Fig. 2). Due to the present sample's thinness and composition of light elements, incident X-rays could easily pass through. This stage prevents the incident X-rays passing through the sample from being backscattered by the sample holder. The K-*K*α and Ca-*K*β fluorescent X-rays were collected using an energy-dispersive silicon drift detector via the C-shaped graphite energy analyzer.

Figures 3(a,b) show the K-*K*α and Ca-*K*β holograms of $K_{0.7}Ca_{0.3}C_8$ recorded at 10.0 keV, presented in orthographic projection. Figure 3(c) displays the atomic images around K on the layer parallel to the (001) plane, reconstructed from the K-*K*α hologram. The K atoms occupy the origin of the image. Atomic images

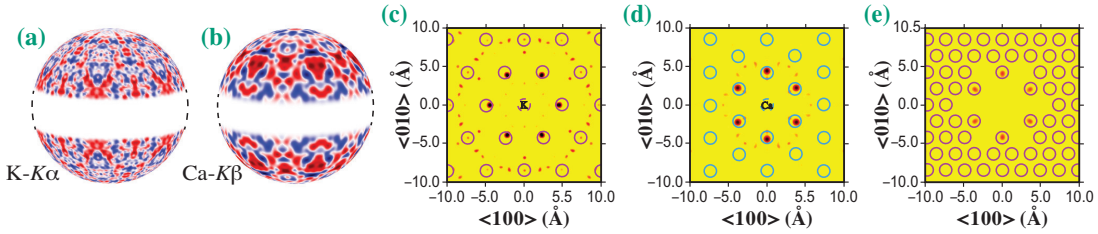

Fig. 3. **(a)** K-*K*α and **(b)** Ca-*K*β holograms of $K_{0.7}Ca_{0.3}C_8$ measured at 10.0 keV. Atomic images parallel to the (001) planes around (a) K and (b) Ca of $K_{0.7}Ca_{0.3}C_8$. **(c)** and **(d)** are reconstructions at the basal plane (z = 0.0 Å). **(e)** is a reconstruction of the plane 1.0 Å above the basal plane.

were shown within the solid red circles, indicating the expected K positions in the KC_8 structure (2×2). However, some weak artifacts were also observed. Figure 3(d) presents atomic images around Ca, reconstructed from the Ca-*K*β hologram, where Ca atoms also occupy the origin of the layer. The expected Ca positions in the CaC_6 structure ($\sqrt{3} \times \sqrt{3} - R30°$) are indicated by solid blue circles. Atomic images were shown within the blue solid circles, indicating that the local structure around Ca retains the CaC_6 structure. These distinct local structures around Ca and K reveal that Ca and K atoms do not form a solid-solution structure, indicating phase separation between the graphene layers.

Among the various reconstructions of the Ca *K*β hologram, meaningful atomic images were identified at z = 1.0 Å (see Fig. 3(e)). While these images could correspond to C, K, or Ca atoms, the possibility of C was excluded due to its low X-ray scattering cross-section. This finding suggests the presence of an additional cation layer 1 Å away from the Ca layer. This layer is composed of K, as Ca and K atoms should be located at different distances from the graphene layer due to their different ionic radii.

Based on these results, we developed the structural model illustrated in Fig. 4. XRD measurements confirmed that the graphene interlayer distance is 5.35 Å, consistent with the KC_8 structure. Therefore, it is believed that the K layer remained in the middle of the C layer. The XFH results indicate that the Ca layer is displaced off-center by 1 Å, suggesting that Ca atoms are closer to one graphene layer. To confirm these considerations, we performed extended X-ray absorption fine structure (EXAFS) measurements for K and Ca in the sample [5]. The results revealed that the distances of Ca-C_{1st} and K-C_{1st} were 2.40 Å and 3.06 Å, respectively, confirming the predictions from XFH. Furthermore, a detailed analysis of the atomic images in Fig. 3(e) revealed an average size of 1 nm for the Ca cluster.

The local structures of Ca and K in $K_{0.7}Ca_{0.3}C_8$ were elucidated using XFH and EXAFS. It was found that Ca and K were phase-separated in the graphite. The CaC_6 and KC_8 phases were separated at the nanometer scale, with Ca clusters displaced off-center by 1 Å. The approach of Ca clusters to graphene layers induces a strong interaction between the Ca 3*d* electrons and phonons in the graphene layer, producing the high superconductivity of $K_{1-x}Ca_xC_y$. The results of this study are essential for exploring high T_c superconducting materials.

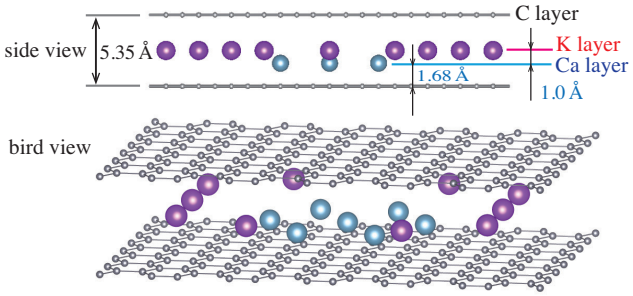

Fig. 4. A 3D structural model obtained from the XFH data.

Naohisa Happo[a,*], Koichi Hayashi[b,c] and Yoshihiro Kubozono[d]

[a] Graduate School of Information Sciences, Hiroshima City University
[b] Research Institute for Interdisciplinary Science, Okayama University
[c] Japan Synchrotron Radiation Research Institute (JASRI)
[d] Department of Physical Science and Technology, Nagoya Institute of Technology

*Email: happo@hiroshima-cu.ac.jp

References

[1] N. B. Hannay *et al.*: Phys. Rev. Lett. **14** (1965) 225.
[2] T. E. Weller *et al.*: Nat. Phys. **1** (2005) 39.
[3] H. T. L. Nguyen *et al.*: Carbon **100** (2016) 641.
[4] F. Matsui *et al.*: Sci. Rep. **6** (2016) 36258.
[5] *N. Happo, A. Kubota, X. Yang, R. Eguchi, H. Goto, M. Ikeda, K. Kimura, Y. Takabayashi, J. R. Stellhorn, S. Hayakawa, K. Hayashi, Y. Kubozono: Chem. Mater. **36** (2024) 4135.*
[6] K. Hayashi *et al.*: J. Phys.: Condens. Matter **24** (2012) 093201.
[7] N. Happo *et al.*: Jpn. J. Appl. Phys. **57** (2018) 058006.