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Non-uniform Distribution of Doped Carrier in a Na-doped CaB_6 Bulk Material Observed by EPMA-SXES

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Recently realized commercial X-ray fluorescence spectroscopy instrument for soft X-rays and extreme ultraviolet radiation, form 50 eV to 2000 eV, has a better or a comparable energy resolution with those of EPMA by using aberration corrected gratings and a two order better acquisition rate due to its parallel detection system by using a CCD detector [1,2]. Radiations in this energy range usually carry not only elemental but also chemical information, because those are generated by electronic transitions from valence bands (bonding electrons) to a shallow inner-shell core-hole state generated by an electron beam irradiation [3]. Here, EPMA-SXES (JXA-8230 with SS-94000SXES) study on a correlation between distributions of doped-atom and doped carrier in Na-doped CaB_6 bulk material is reported.

CaB_6 is a member of metal hexaboride MB_6 material, which is based on a network of B_6-clusters. When an M atom can supply two electrons to B_6-network, the valence bands (VB) of B_6-network is fully occupied and becomes a *n*-type semiconductor as in the case of CaB_6 [4]. For producing a *p*-type character CaB_6, Na-doping had been conducted and succeeded [5]. EDS analysis of the *p*-type CaB_6 showed an inclusion of a few % of Na. Doped Na atoms occupy Ca site. As one Na atom can transfer one electron to B_6-network, Na-doping can be a hole-doping based on the rigid band-structure scheme.

Figure 1 shows (a) secondary electron (SE) image, (b) Ca-Ll,η intensity (150-154 eV) map, (c) B-K intensity (170-188 eV) map and (d) map of the top part of B-K intensity (187-188 eV) which corresponds to the top of the valence band. In the SE image, a contamination in the upper left region is only noticed. The area showed carbon K-emission intensity, not shown here. The Ca-Ll,η intensity map of (b) shows a non-uniformity in Ca atom distribution. As doped Na-atoms occupy Ca-atom sites, the Ca-deficient region observed should be a highly Na-substituted region. Unfortunately, X-ray emission signal from Na atoms cannot be detected with the present spectrometer. B K-emission intensity of (c) shows a little decrease in the Na-substituted region. On the other hand, the map of the top part of B-K intensity of (d) shows an intensity in this region. B K-emission spectrum of the Na-doped region showed a little different intensity distribution compared to that of surrounding region. Furthermore, the spectrum shift in higher energy side was also noticed. Thus, the intensity increase in (d) can be understood as a shift of B K-emission intensity in higher energy side due to a larger binding energy of B 2*p* level, chemical shift, caused by the hole doping for B_6-cluster network. The observed localization of doped carrier in (d) may be reasonable owing to a charge compensation of doped Na-atoms.

This experimental result shows that the high energy-resolution soft X-ray mapping with an appropriate energy window can show not only elemental distribution but also chemical state distribution or doped carrier distribution of bulk materials [6].

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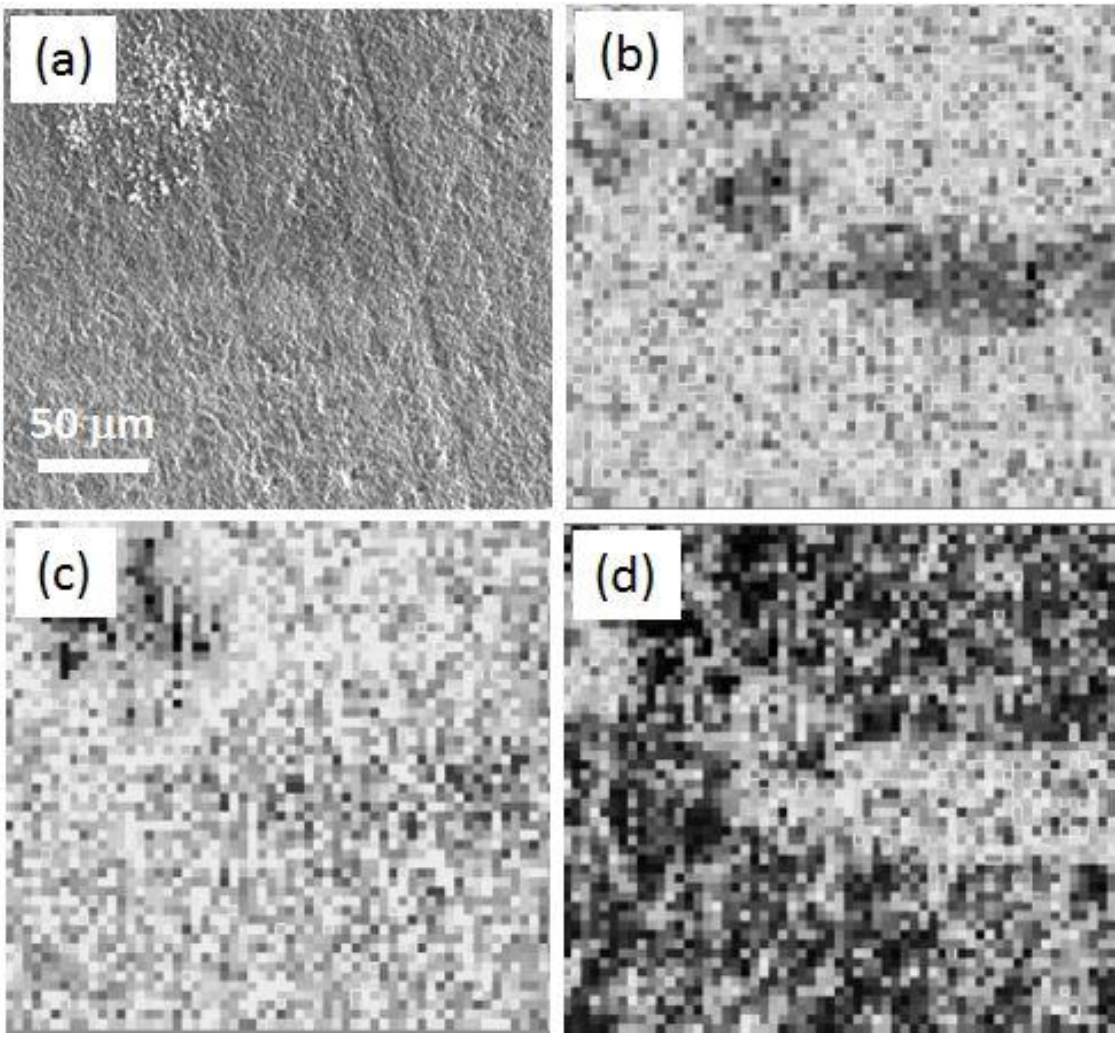

Figure 1. (a) secondary electron image of Na-doped CaB_6 bulk specimen. (b) Ca-Ll,η emission intensity map. (c) B-K emission intensity map. (d) B-K emission intensity setting an energy window at the top region of the spectra.

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