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Characterization of LiBC by phase-contrast scanning transmission electron microscopy

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ABSTRACT

LiBC was used as a model compound for probing the applicability of phase-contrast (PC) imaging in an aberration-corrected scanning transmission electron microscope (STEM) to visualize lithium distributions. In the LiBC structure, boron and carbon are arranged to hetero graphite layers between which lithium is incorporated. The crystal structure is reflected in the PC-STEM images recorded perpendicular to the layers. The experimental images and their defocus dependence match with multi-slice simulations calculated utilizing the reciprocity principle. The observation that a part of the Li positions is not occupied is likely an effect of the intense electron beam triggering Li displacement.

1. Introduction

The determination of Li positions and the corresponding site occupancy is an important task, for example in a comprehensive characterization of battery materials. However, to detect lithium is difficult owing to the comparatively low mass of this element. This is particularly true for electron microscopy as the contrast in most imaging methods strongly depends on the scattering potential of the atom type that is increasing with the atomic number (Huang and Ikuhara, 2012).

Although it was found possible to identify Li positions in $LiCoO_2$ by HRTEM (Shao-Horn et al., 2003), scanning transmission electron microscopy (STEM) bright field (BF) methods have recently provided more promising results. In particular, annular bright field STEM (ABF-STEM) represents a powerful tool to image the positions of light elements besides heavy ones (Okunishi et al., 2012). Even the direct visualization of the hydrogen positions in the metal hydrides VH_2 (Findlay et al., 2010) and YH_2 (Ishikawa et al., 2011) was reported. In this variant of BF-STEM, a disk is placed in the center of the BF detector so that beams traveling directly on the optical axis are blocked and do not contribute to the image. Successful examples from battery research are the detection of the lithium positions in the crystal structures of LiV_2O_4 (Oshima et al., 2010; Lee et al., 2011), $LiFePO_4$ (Gu et al., 2011) and $LiMn_2O_4$ (Lee et al., 2013).

Phase-contrast STEM (PC-STEM) represents a further variant of BF-STEM using a small BF detector in which the image is mainly formed by the interference of beams diffracted toward the optical axis (Rose, 1974). The required large illumination angle can be achieved by correcting the spherical aberration of the objective lens. A contrast is then generated that is similar to that of a HRTEM image according to the principle of reciprocity. Here the positions of electron source and detector in the ray path as well as the corresponding illumination and detection angles are interchanged (Cowley, 1969). Today, PC-STEM imaging represents an increasingly important alternative to the well-established HRTEM method (Krumeich et al., 2013). With both methods, the image contrast is coherently generated and thus depends not only on illumination and collection angles but also on defocus and specimen thickness. PC-STEM is also a suitable technique for the detection of light element positions, as demonstrated firstly for O in $SrTiO_3$ (Pennycook et al., 2006). Motivated by these intriguing results, we evaluated the PC-STEM method for the characterization of LiBC, a compound consisting of light elements only (Wörle et al., 1995).

LiBC is an interesting compound regarding different aspects. Boron and carbon form planar hetero graphite layers (in the following designated as BC layers) of the isoelectronic hexagonal BN type (Fig. 1). These BC six-ring layers are stacked ecliptically such that B and C alternate along the *c* axis. The stacking type is different from that in graphite but alike to that in Li_xC (Juza and Wehle, 1965; Winter et al., 1998). Li is intercalated between these layers ($P6_3/mmc$; $a = 275.2$ pm; $c = 705.8$ pm) (Wörle et al., 1995). The structure can be described as an intercalated hetero graphite $Li^+(BC)^-$ according to the Zintl–Klemm concept (Nesper, 1990). The high theoretical capacity of 1165 mAh g^{-1} for the exchange of all Li renders LiBC a promising candidate as battery material. However, a reversible Li exchange does not occur; instead, new covalent bonds are formed upon Li removal. Furthermore, NMR studies revealed

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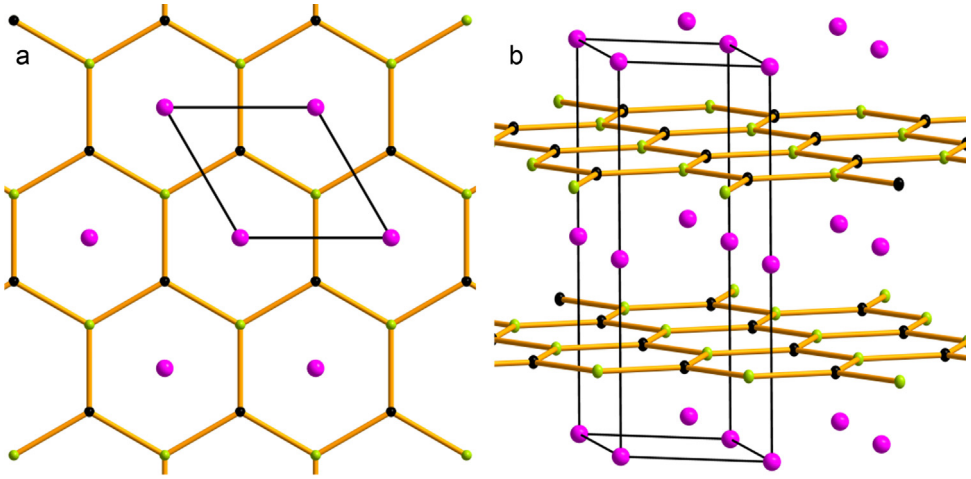

Fig. 1. Structure of LiBC. (a) Projection along [0 0 0 1]. (b) Side view. Lines connecting the B and C positions are drawn to emphasize the hetero graphite layers. For both projections, unit cells are outlined.

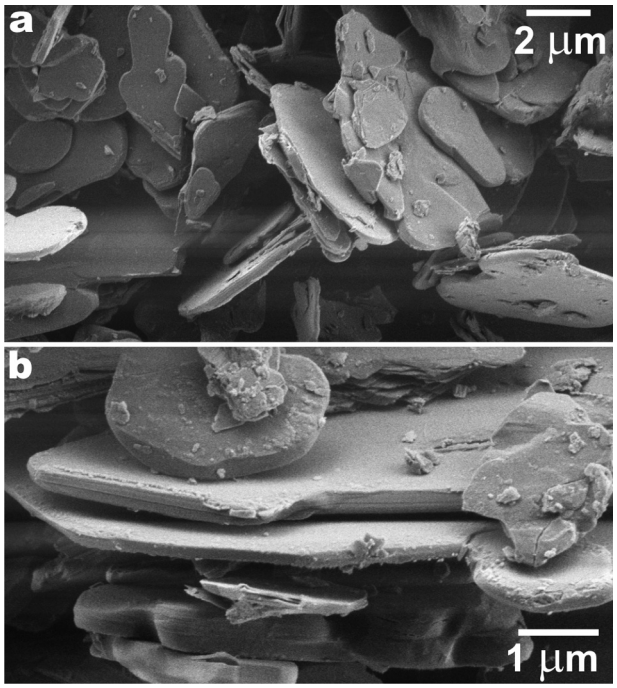

Fig. 2. SEM images of typical LiBC platelets. The grainy surface on top of the platelets can clearly be seen in (b).

a very limited Li mobility even at elevated temperatures of up to 500 K (Langer et al., 2012). This is not surprising as lithium contributes to the strongly stabilized valence band and as such should behave very differently compared to corresponding graphite systems. The aim of this first electron microscopy study of LiBC was to characterize the structure of the BC honeycomb network and the Li distribution with respect to the presence of defects and deviating occupancy.

2. Materials and methods

2.1. Synthesis of LiBC

Platelets of LiBC were synthesized from the elements according to Wörle et al. (1995). The elements (purity > 99.5%) were mixed in a ratio C:B:Li = 1:1:1.2. By using an Li excess, the formation of

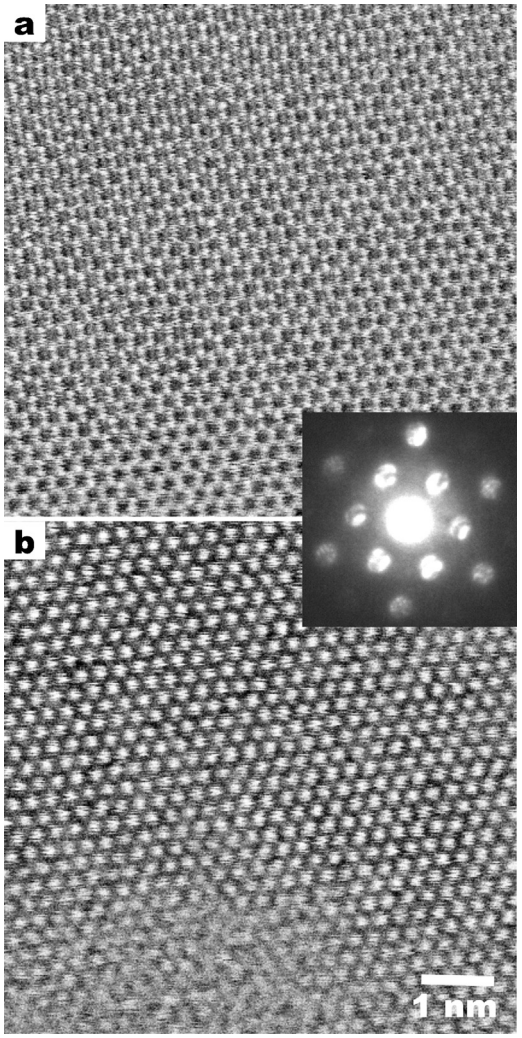

Fig. 3. PC-STEM images (unprocessed) of an area of LiBC (along [0 0 0 1]) recorded at two different defocus values Δf with an experimentally measured difference of ca. 20 nm show a contrast inversion. The lower left part in (b) is already affected by amorphization of the structure in the electron beam. The inset shows a nanodiffraction pattern obtained from the investigated area.

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