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Elucidating structural order and disorder phenomena in mullite-type $Al_4B_2O_9$ by automated electron diffraction tomography

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ABSTRACT

The crystal structure and disorder phenomena of $Al_4B_2O_9$, an aluminum borate from the mullite-type family, were studied using automated diffraction tomography (ADT), a recently established method for collection and analysis of electron diffraction data. $Al_4B_2O_9$, prepared by sol-gel approach, crystallizes in the monoclinic space group $C2/m$. The *ab initio* structure determination based on three-dimensional electron diffraction data from single ordered crystals reveals that edge-connected AlO_6 octahedra expanding along the **b** axis constitute the backbone. The ordered structure (*A*) was confirmed by TEM and HAADF-STEM images. Furthermore, disordered crystals with diffuse scattering along the **b** axis are observed. Analysis of the modulation pattern implies a mean superstructure (*AAB*) with a threefold **b** axis, where *B* corresponds to an *A* layer shifted by ½**a** and ½**c**. Diffraction patterns simulated for the *AAB* sequence including additional stacking disorder are in good agreement with experimental electron diffraction patterns.

1. Introduction

One-dimensional structures, such as nanowires, nanotubes, and nanobelts, gained considerable attention in material research and solid-state chemistry due to their potential applications [1] in electronics, optics and mechanics. Aluminum borate nanorods are important mullite-type ceramic raw materials with high temperature stability, low temperature expansion, excellent mechanical properties and corrosion resistance [2–5]. The most frequently investigated aluminum borates in the Al_2O_3-B_2O_3 system include $Al_{18}B_4O_{33}$ ($9Al_2O_3$:$2B_2O_3$), Al_5BO_9 ($5Al_2O_3$:B_2O_3) and $Al_4B_2O_9$ ($2Al_2O_3$:B_2O_3) [6,7]. Mullite-type aluminum borates can be prepared by solid-state reaction at high temperature [2,6]. In addition, other approaches, such as sol-gel synthesis, one-step combustion method, and thermal evaporation, have been applied to improve the formation and properties [3,7,8]. One of the characteristic properties of mullite-type structures are linear edge-sharing octahedral chains, which are connected parallel to each other by different inter-chain units controlling the growth of nanowires and nanorods [4,9]. Threefold and fourfold coordinated B atoms in the inter-chain units increase complexity, and disorder phenomena can be often observed in mullite-type structures.

$Al_4B_2O_9$ shows a structure similar to boralsilite ($Al_{16}B_6Si_2O_{37}$) [10]. The structure of $Al_4B_2O_9$ was first investigated by Scholze et al. [11]. An orthorhombic lattice was proposed by the author with a=14.8(2) Å, b=15.1(2) Å, c=5.6(1) Å, and Z=8, with reflection conditions indicating space groups *Cmm*2, *Cm*2*m*, *C*222, or *Cmmm*. Mazza et al. [12] described the structure of a metastable analogue with similar composition in space group *Pbam* with a pseudo tetragonal symmetry. Fischer et al. [7] investigated the crystal structure of $Al_4B_2O_9$ using a combination of NMR spectroscopy and X-ray powder diffraction. The structure was determined to have a monoclinic unit cell in space group $C2/m$ close to the orthorhombic lattice. The initial structure was derived based on the closely related boralsilite structure and refined with Rietveld methods from X-ray powder diffraction data. Similar

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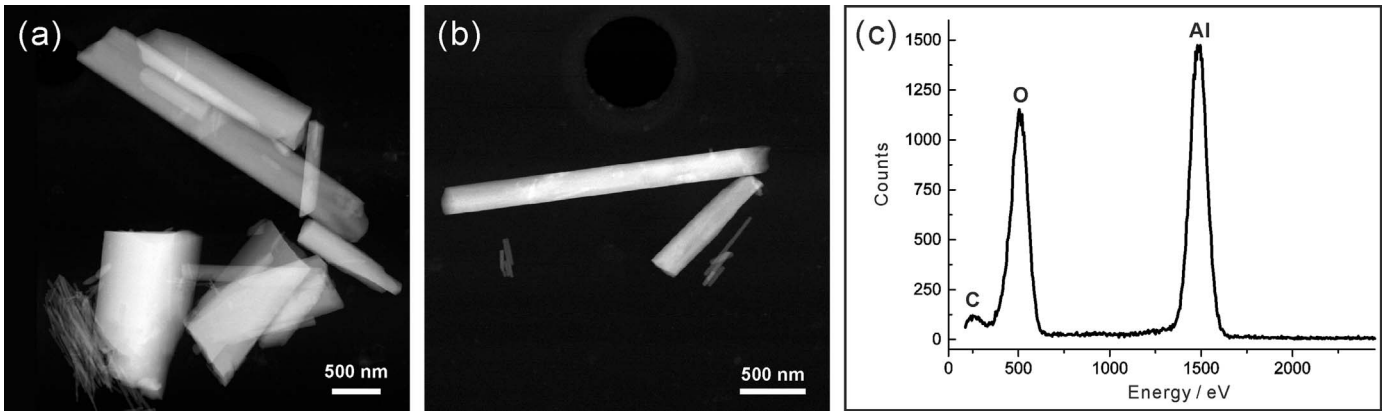

Fig. 1. STEM images and EDX spectrum of $Al_4B_2O_9$: (a) overview of nanorods; (b) single separate nanorods; (c) EDX spectrum of $Al_4B_2O_9$.

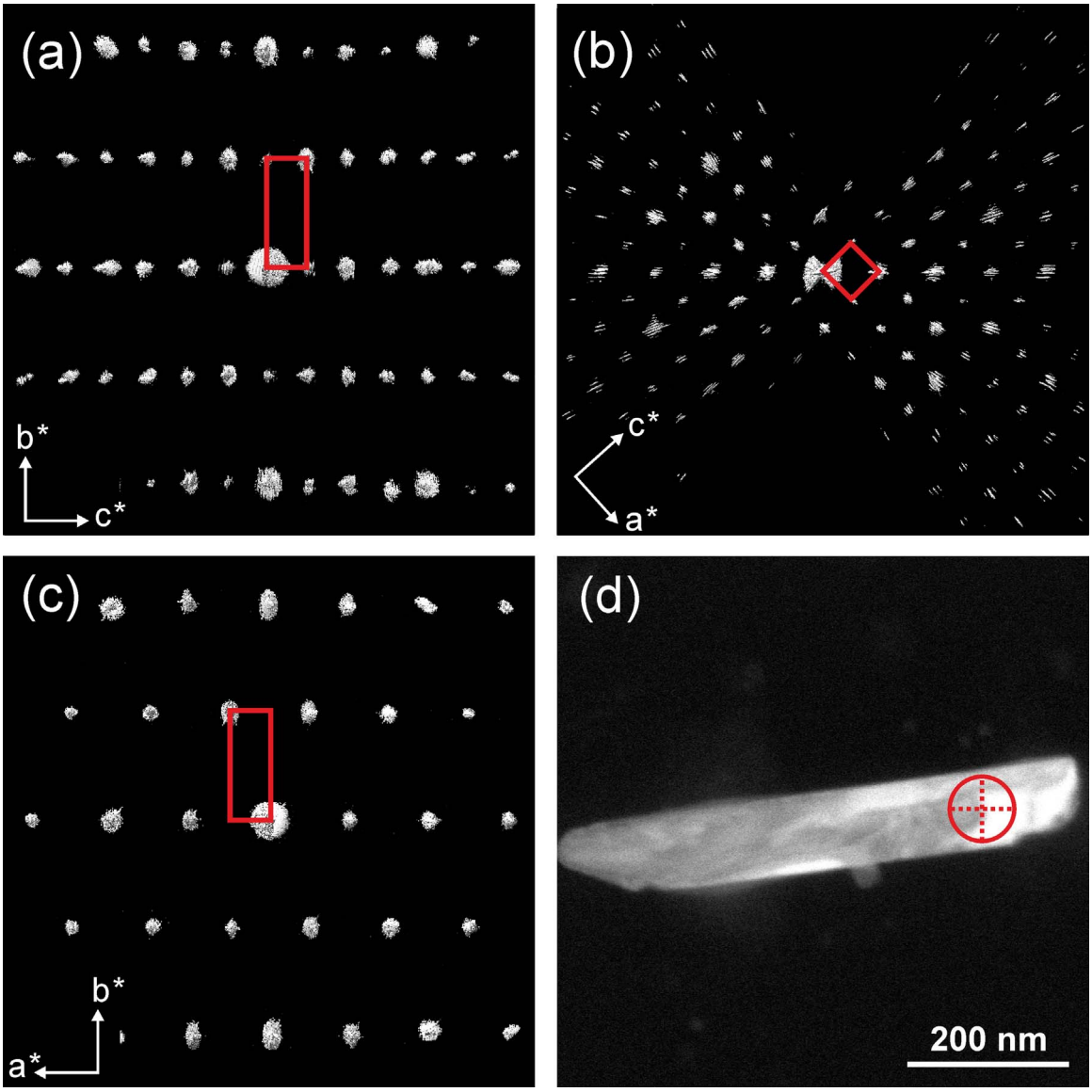

Fig. 2. (a–c) Reconstructed three-dimensional diffraction volume of $Al_4B_2O_9$ obtained by ADT, viewed along the main directions **a***, **b***, **c***. (d) STEM image of a single crystal selected for acquisition of the NED data. The beam position for ADT data collection is marked with a red circle in (d). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

results were obtained from neutron diffraction data [13]. However, some crystal chemical details like the positions of two oxygen atoms (O5 and O10) remained unclear not being resolvable by powder diffraction methods for such a complex structure with disordered O atoms. On the other hand, the achievable crystal size was not suitable for single crystal X-ray diffraction. Additional methods must be applied