STEM-EELS studies of defects and their evolution in the BaTi8O16 hollandite system

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The hollandite system has much intrinsic complexity, with the potential to have tuneable electronic and thermal transport properties, making it an ideal candidate for a thermoelectric material. In order to better understand this complexity, we describe advanced STEM-EELS techniques combined with multislice simulations and report on a number of distinct defects that are likely to impact on the performance of barium titanate hollandite thermoelectrics.

Hollandites have a $A_2B_8O_{16}$ structure, where BO_6 form edge sharing octahedral arranged in square channels containg A cations. An atomic column-resolved HAADF micrograph of [001] oriented $BaTi_8O_{16}$ is presented in Figure 1 (a), with the chemical identity of the atoms revealed by column resolved EELS in Figure 1 (b). Z contrast results in the heavy Ba cations columns being the brightest features, located in the middle of rings of eight less intense Ti columns (O is not visible due to its low atomic number). An intriguing aspect of this material system is that the hollandite channels are able to hold varying amounts and types of cations and have also been reported to contain B species defects (1). The resulting disorder and the mobility of the cations is believed to account for the promising thermal conductivity exploited in thermoelectric applications. Evidence of such defects in the Ba channels can be seen in Figure 1 (d), where an expected bright Ba column is missing, highlighted by the line profile over five Ba columns, with the missing column in the centre. Barium titanate hollandites have mutually incommensurate substructures comprising the Ba cations and the surrounding TiO_6 octohedral framework. We describe the structural details and density of a family of such defects.

While hollandites are generally tetragonal, they have been observed in monoclinic form, with β close to 90, when intercalated by certain channel cations. This monoclinic form enables the appearance of a modulated twinning structure, which can also be induced by exposure to an ion or electron beam. We therefore describe both the dynamic formation of this extrinsic structural modification and how damage-free cross-sectional samples can be prepared without the use of ion beam thinning. We present real time observation of the twinning phenomenon, acquired by rapid acquisition of multiple frames during electron-beam exposure during STEM imaging. Quantification of the critical electron dose that initiates the transformation leads to a protocol for imaging the damage-free specimen. In order to image instrinsic defects in the material, rapid acquisition of multiple low-dose frames was again used and aligned using the Smart Align tool (2). This enabling imaging of the defects before significant twinning has occurred.

Our results help in understanding the defects and disorder in barium titanate hollandites and thereby help elucidate the structural reasons for the material's functionality. This is a critical step in the development of $BaTi_8O_{16}$ as a viable thermoelectric.

(1) O. I. Lebedev *et al.*, "Revisiting Hollandites: Channels Filling by Main-Group Elements Together with Transition Metals in $Bi_{2-y}V_yV_8O_{16}$," *Chemistry of Materials*, vol. 29, no. 13, pp. 5558 - 5565, Jul. 2017.

(2) L. Jones *et al.*, "Smart Align - a new tool for robust non-rigid registration of scanning microscope data," *Advanced Structural and Chemical Imaging*, vol. 1, no. 1, Dec. 2015.

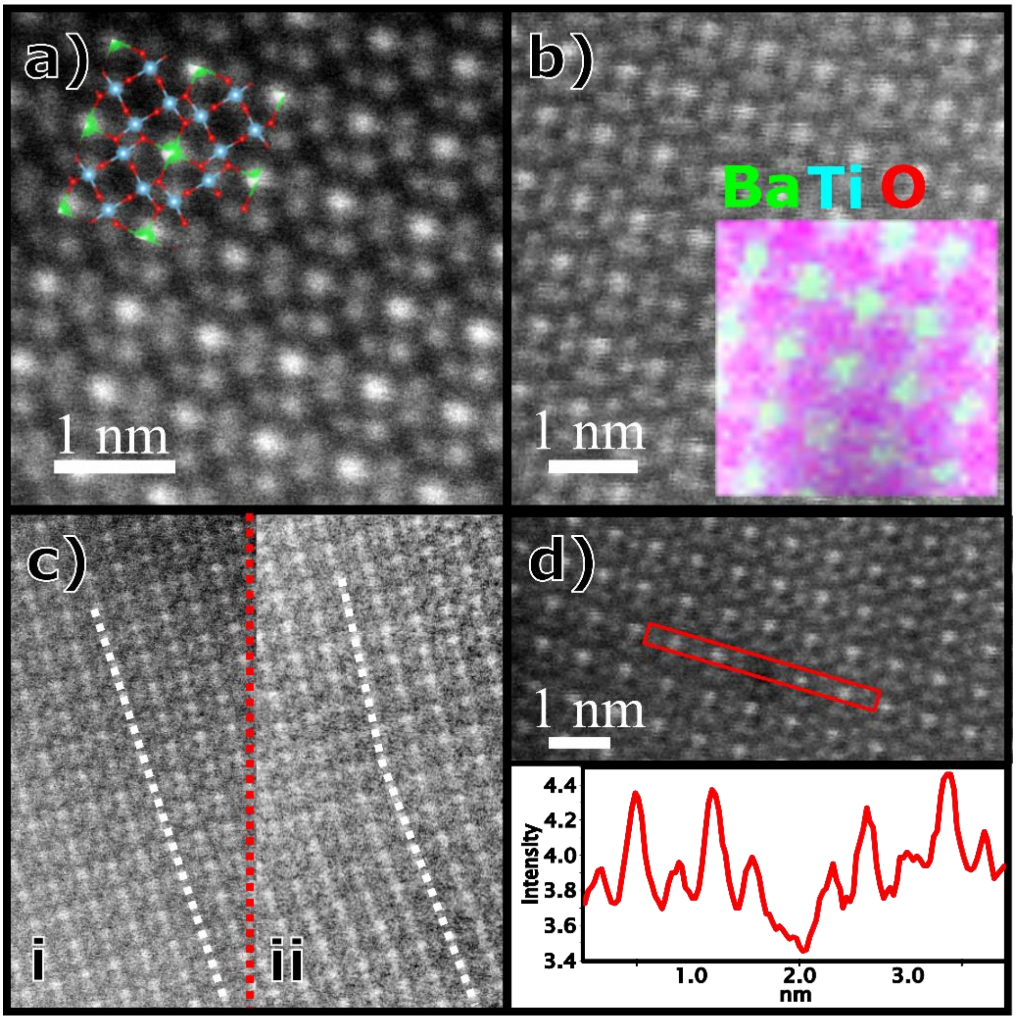

Figure 1 - HAADF-STEM images of $BaTi_8O_{16}$ in [001] direction with (a) structure overlaid (b) Column resolved STEM-EELS (c) i - Before, ii - after e-beam exposure showing evidence of e-beam induced twinning (d) evidence of columnar defect with associated intensity line profile.