doi:10.1017/S143192762200191X
Microsc. Microanal. 28 (Suppl 1), 2022

Morphology and Growth Habit of a Novel Flux-Grown Layered Semiconductor $KBiS_2$ Revealed by Lab-based Diffraction-Contrast Tomography

Kejian Qu[1], Hrishikesh Bale[2*], Zachary W. Riedel[3], Junehu Park[3], Leilei Yin[4], André Schleife[3,5] and Daniel P. Shoemaker[3**]

[1.] Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL
[2.] ZEISS Research Microscopy Solutions, Inc. Dublin CA
[3.] Department of Materials Science and Engineering and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL
[4.] Beckman Institute, University of Illinois at Urbana-Champaign, Urbana, IL
[5.] National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign, Urbana, IL
* Corresponding author: hrishikesh.bale@zeiss.com
** Corresponding author: dpshoema@illinois.edu

The discovery of new inorganic materials is sustained by the growth of high-quality single crystals that enable robust characterization of their functional properties typically using techniques like X-ray diffraction. The most effective crystal growth occurs from liquids or gases, based on enigmatic growth mechanisms that are especially tantalizing in the grand challenge of obtaining metastable materials by extracting them from an aggressive growth medium. Reactions in molten fluxes can lead to such kinetically-trapped metastable phases unobtainable by direct combination of elements, [1] and these methods have proven to be prolific in producing new chalcogenide materials in particular. These compounds are typically narrow-gap semiconductors and heavy elements lead to strong spin-orbit coupling, which can lead to topologically protected gaps, such as in $TlBiS_2$ and Bi_2Se_3. Given the nascent field of crystal growth for nontrivial topology, the identification and high-quality growth of these materials is invaluable.

Unfortunately, the reaction vessels obscure the direct visualization of the progression of phase nucleation, growth, and transformation. Some in-situ characterization of flux systems have provided a view of the crystallization and dissolution of phases in reactive fluxes, in particular by powder diffraction, but these methods are poorly suited to probe growths with large crystals.

Here, using the case of a novel flux-grown layered semiconductor crystal, we present results to show how a combination of high resolution X-ray absorption contrast tomography [2] and diffraction contrast tomography [3] can be applied to identify previously-undiscovered materials while simultaneously viewing the crystal morphology and growth habit. Conducting the entire analysis non-destructively enables investigation of the crystals in their native environment while preserving the samples for further subsequent correlative characterization.

Understanding the growth of crystalline materials requires observing the growth habit and grain orientations. Traditional absorption X-ray tomography provides geometric information through which the orientation can be indirectly derived from the facets seen in density contrast. Identifying crystalline phases and their orientations requires diffraction information, which is possible by additionally interrogating the Laue diffraction pattern during sample rotation, as embodied in X-ray diffraction contrast tomography (DCT) [3,4]. We conducted DCT measurements on a lab-based X-ray microscope equipped with the 3D diffraction contrast tomography module enabling us to gather data with similar capabilities as offered at most grain mapping synchrotron beamlines.

The utility of DCT for emerging materials, especially novel crystalline materials intact within their synthesis environment, has never been shown. In this study, we take advantage of the grain visualization capabilities of DCT in combination with the wealth of single-crystal Laue diffraction data to confirm crystal size, shape, orientation and identity simultaneously on a complex $KBiS_2$ single crystal sample. Absorption contrast tomography enables identification of the needle and plate morphologies of rhombohedral KBiS2 that can be attributed to different stages of nucleation and growth, suggesting a screw-dislocation-driven growth mechanism. Applying these measurement techniques to future in-situ studies in extreme environments (especially in aggressive chemical potentials) will allow short-lived, kinetically-trapped phases to be obtained, which has immense potential to accelerate the discovery of new metastable materials.

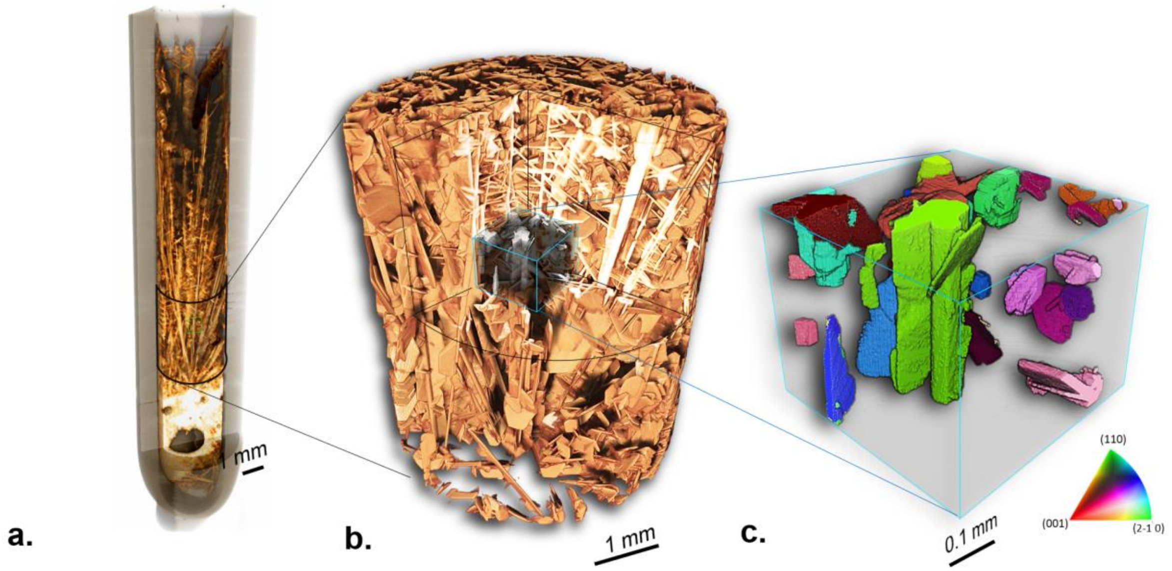

Figure 1. (a) Absorption contrast tomography of the growing $KBiS_2$ crystal within the flux in the reactor vessel. **(b)** Absorption contrast tomography corresponding to the region indicated in (a), with a portion cut to show the needle and rod-shaped crystals. **(c)** LabDCT data showing the crystallographic orientation in in IPF format with the largest central needle-shaped grain in [110] direction.

References:

[1] SE Latturner, Acc. Chem. Res. **51** (2018), p. 40.
[2] SR Stock, Int. Mater. Rev. **53** (2008), p. 129.
[3] W Ludwig et al., J. Appl. Crystallogr. **41** (2008), p. 302–309.
[4] W Ludwig et al., Rev. Sci. Instrum. **80** (2009), p. 033905.