Phase and Orientation analysis of Bismuth Germanium Oxide (BGO) on evaporated aluminum

Introduction

Understanding and control of crystallographic texture (distribution of crystallographic orientations) is desirable in many areas of materials science. Many functional materials are polycrystalline, and information on grain orientations and sizes is very relevant for their functional properties. Engineering of the processing methods may enhance the properties of such functional materials. The ability to characterize the texture of the materials at the nanoscale can thus be relevant to engineering applications such as aerospace, ceramics, semiconductors, steel and alloys and many others.

This technical note describes the use of TESCAN TENSOR for nanoscale orientation and phase analysis of BGO ($Bi_{12}GeO_{20}$) on evaporated aluminum. $Bi_{12}GeO_{20}$ has a relatively large lattice parameter of 10.1Å, and Al a much smaller lattice parameter of 4.1Å, and thus this sample is well suited to illustrate the methodology to analyse phase and orientation using electron diffraction patterns.

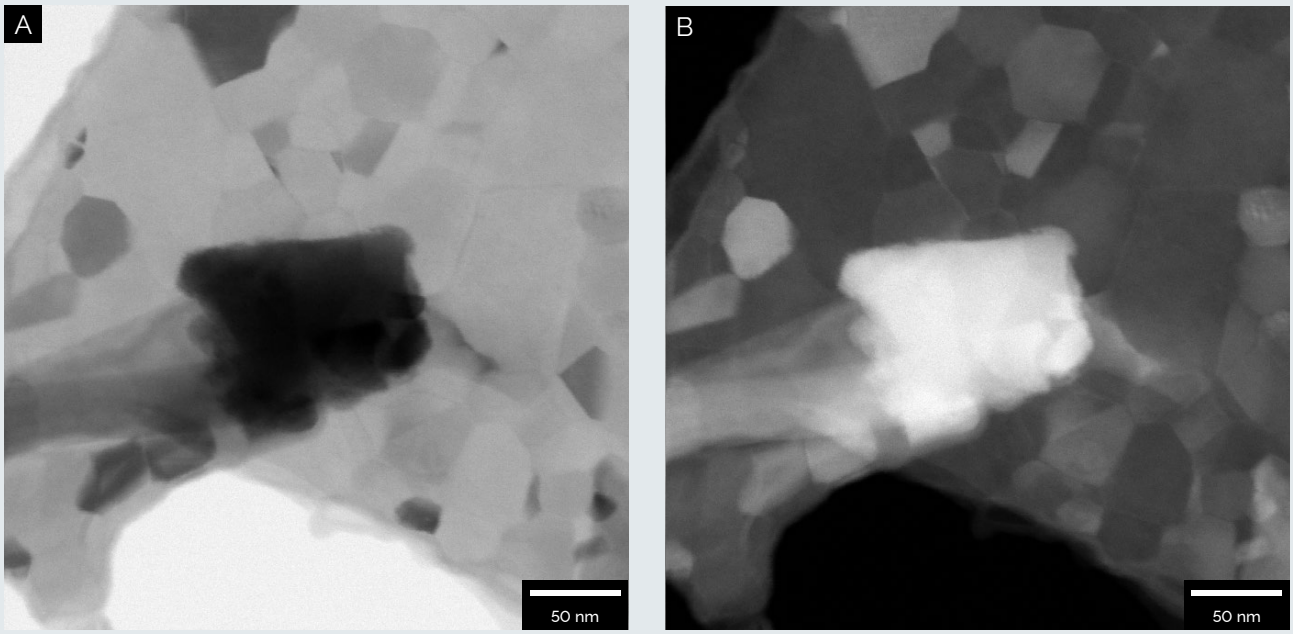


Figure 1: – **A)** STEM BF and **B)** ADF image of $Bi_{12}GeO_{20}$ on evaporated aluminum

Methods

Electron Diffraction Patterns of crystalline materials contain information about the lattice parameters and the orientation of the crystal (grain). By scanning a beam over the Region of Interest (ROI), and acquiring diffraction patterns for each beam (pixel) position, information can be deducted about the phase and orientation of the material under investigation. The extraction of phase and orientation information is achieved by matching the diffraction patterns with hkl templates (from corresponding cif files) of the phases expected to be present in the sample. The template with the best match to the acquired diffraction pattern is selected and tagged to the pixel in the scanning diffraction dataset. This methodology is commonly referred to as ACOM-TEM analysis (Automated Crystal Orientation and phase Mapping) [Rauch et al., 2008]. The combination of scanning the probe over the sample with diffraction acquisition is known as 4D-STEM. The result of this experiment is a generated 4D data cube, which can be analysed in real time or after the measurement is finished. The methodology enables to compute properties of underlying materials, such as texture (grain orientation), phase distribution, grain size or subgrain features such as twinning.

Analysis of phase and orientation is performed routinely by multimodal EDS and EBSD methods on SEM or FIB/SEM systems, with micron to sub-micron spatial resolution. 4D-STEM allows orientation analysis down to the nanometer scale.

TESCAN TENSOR provides state-of-the-art integrated, precession-assisted, analytical 4D-STEM capabilities to yield phase and orientation information at the true nanoscale. The workflow for 4D-STEM data acquisition and processing is straightforward., and users with limited TEM experience can produce a range of STEM, 4D-STEM and tomography measurements without weeks of exhaustive training on the adjustment and alignment of electron optical parameters.

TESCAN TENSOR analytical 4D-STEM is precession-assisted, which enhances the information that can be obtained from a diffraction pattern, and hence improves the quality of phase and orientation maps. Precession of the electron beam around the optical axis extends diffraction space to yield more higher order reflections, and averages out the effects of dynamical diffraction, which allows matching of the acquired precession electron diffraction patterns with templates from kinematical diffraction models. Precession can be switched on or off, based on priority of indexing quality (precession ON), or spatial resolution (precession OFF).

Results

STEM imaging and 4D-STEM Orientation and Phase mapping was used to characterize BGO dropcasted on the thin film of evaporated aluminum. For STEM imaging, a convergence semi-angle of 6.5mrad and current of 100pA was used. Large images of 3000x3000 pixels were acquired in approximately 30 seconds. Orientation and Phase analysis was performed with a convergence angle of 1.5mrad, 40pA beam current, and a precession angle of 0.5°, on a 200 x 200 pixel scanning transmission electron diffraction dataset that took approximately 3 minutes to acquire.

STEM imaging

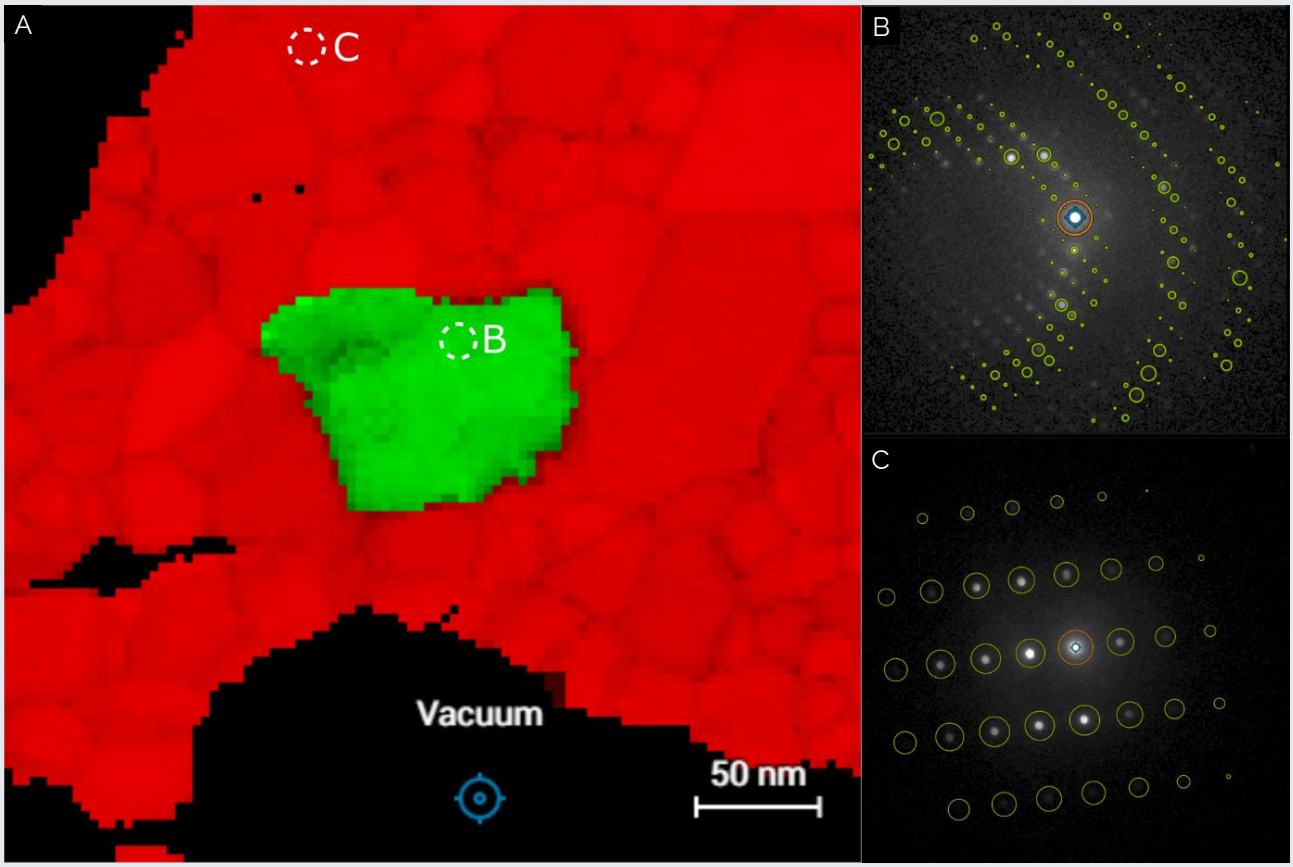
STEM Bright Field (BF) and Annular Dark Field (ADF) images show the BGO particle on the Aluminum film (Fig. 1). The BGO particle yields high intensity on the ADF detector, and can be readily identified, as shown in Figure 1B.

Phase mapping

Once the STEM images are acquired, the operator selects the Orientation/Phase measurement by a single click of a button. Optical adjustments, and their alignments, including precession, are automatically performed. 4D STEM data are now ready to be acquired and processed in real-time. The total time of data acquisition and processing was 7 minutes.

The phase map is shown in Figure 2A The red phase corresponds to aluminum, and the green phase to BGO. The map is a combination of phase distribution and phase reliability. Bright colors indicate high confidence in indexing for phase analysis (indicated by a high matching factor), and dark colors indicate lower confidence. The diffraction patterns from positions B and C on the phase map are shown in Figure 2B, C.

The green circles around the diffraction spots in Figure 2B, C show the expected diffraction spots calculated from the theoretical structure model. We refer to these as templates. The best fitting template then identifies the phase at each pixel in the image. Diffraction patterns from the green areas (BGO, see figure 2B) have much smaller spacing between individual diffraction spots compared to diffraction patterns from the red areas (Al, see figure 2C). The difference between diffraction spot density from BGO and Al is clearly very large, and for this reason BGO on Al provides a clear example of how both phase and orientation information can be obtained from a scanning diffraction dataset. This 4D-STEM technique can be applied to phases with similar symmetry of the unit cell, and lattice spacing differences as small as 5%.



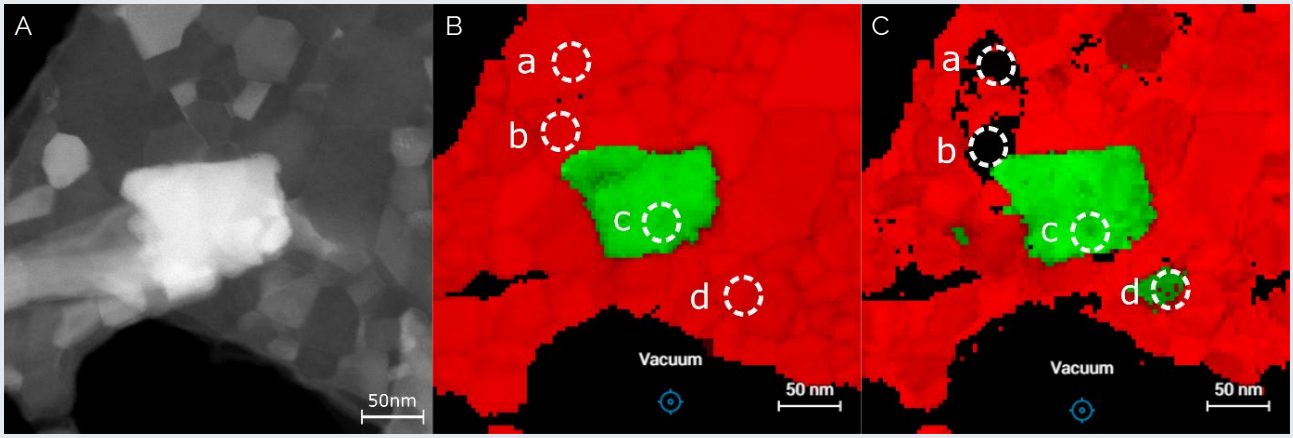
▲ **Figure 2: A)** Phase map of $Bi_{12}GeO_{20}$ on Evaporated aluminum acquired with precession (precession angle 0.5°) **B)** diffraction pattern corresponding to BGO crystal with template overlay **C)** diffraction pattern corresponding to Al crystal with template overlay

Advantage of precession

The added value of precession can be demonstrated by comparing the phase maps calculated from precessed and non-precessed diffraction patterns. The map acquired without precession on Figure 3C suffers from poor phase matching confidence (dark areas in point a and b) and false indexing of the phases, e.g., point d wrongly indexed as BGO. The map acquired with precession, Figure 3B, shows only one BGO particle, with bright colors of the phase map indicating high confidence of phase matching.

To illustrate the challenges of phase mapping without precession, we picked four locations a, b, c, d from Figure 3B and C. For each of these points, a comparison of the diffraction patterns acquired with and without precession is shown in Figure 4. It can be seen that, in all of the locations, the diffraction patterns acquired with precession provide more spots and better signal to noise ratio. Figure 4e shows the same diffraction patterns as Figure 4d, with templates projected on the patterns. Since only a few spots are visible for this location, the template matching wrongly selects the BGO structure when precession is not used. The diffraction pattern with precession, with significantly more diffracted spots, is indexed correctly using the Al template.

This shows that using even relatively small precession angles of 0.5° assists greatly to improve the quality of phase maps.



▲ **Fig. 3: A)** STEM ADF image of $Bi_{12}GeO_{20}$ on Evaporated aluminium **B)** Phase map of $Bi_{12}GeO_{20}$ on Evaporated aluminium acquired with precession (precession angle 0.5°) **C)** Phase map of $Bi_{12}GeO_{20}$ on Evaporated aluminium acquired without precession using our hybrid-pixel detector Dectris Quadro. Red – Al, Green - $Bi_{12}GeO_{20}$

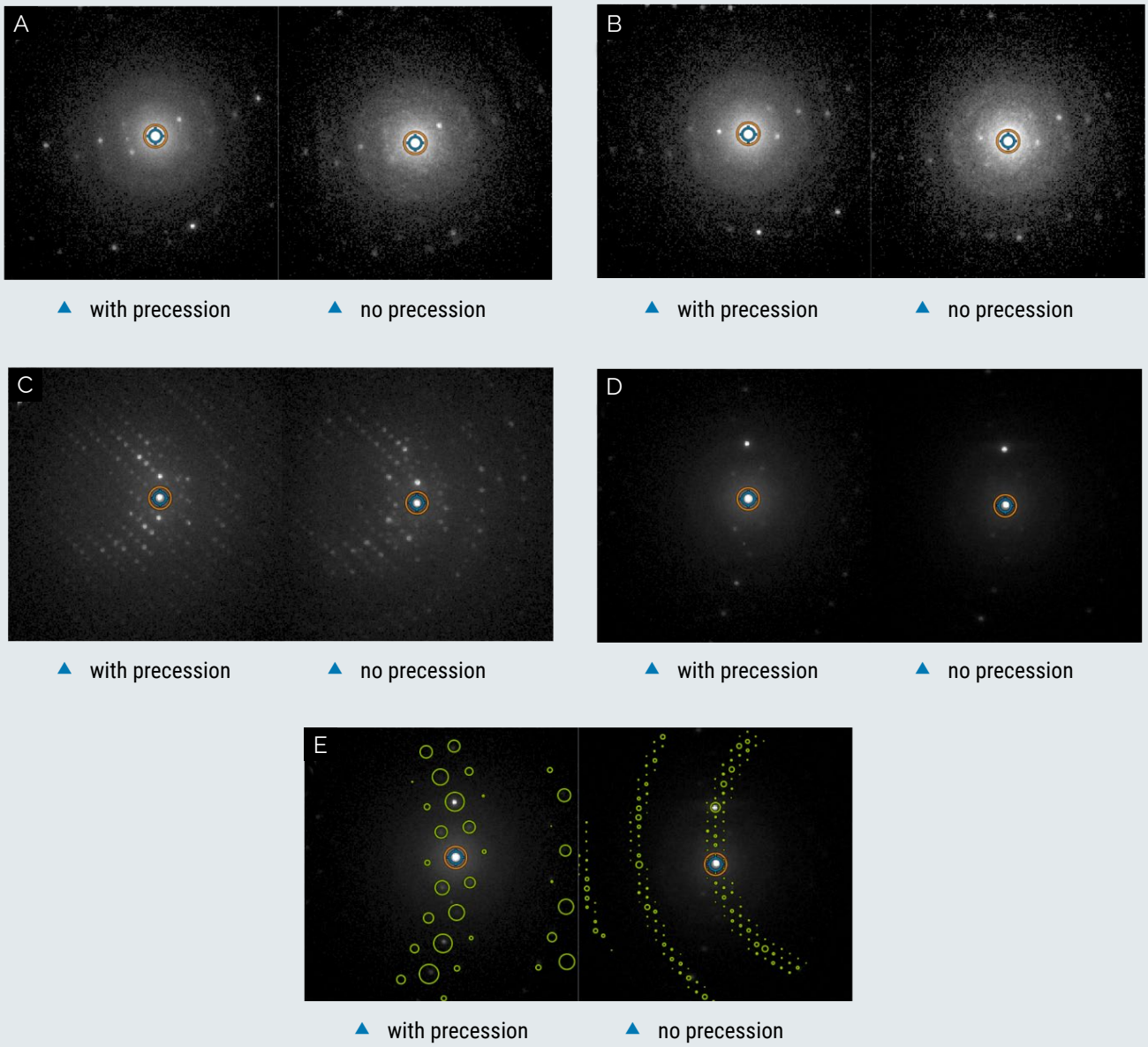
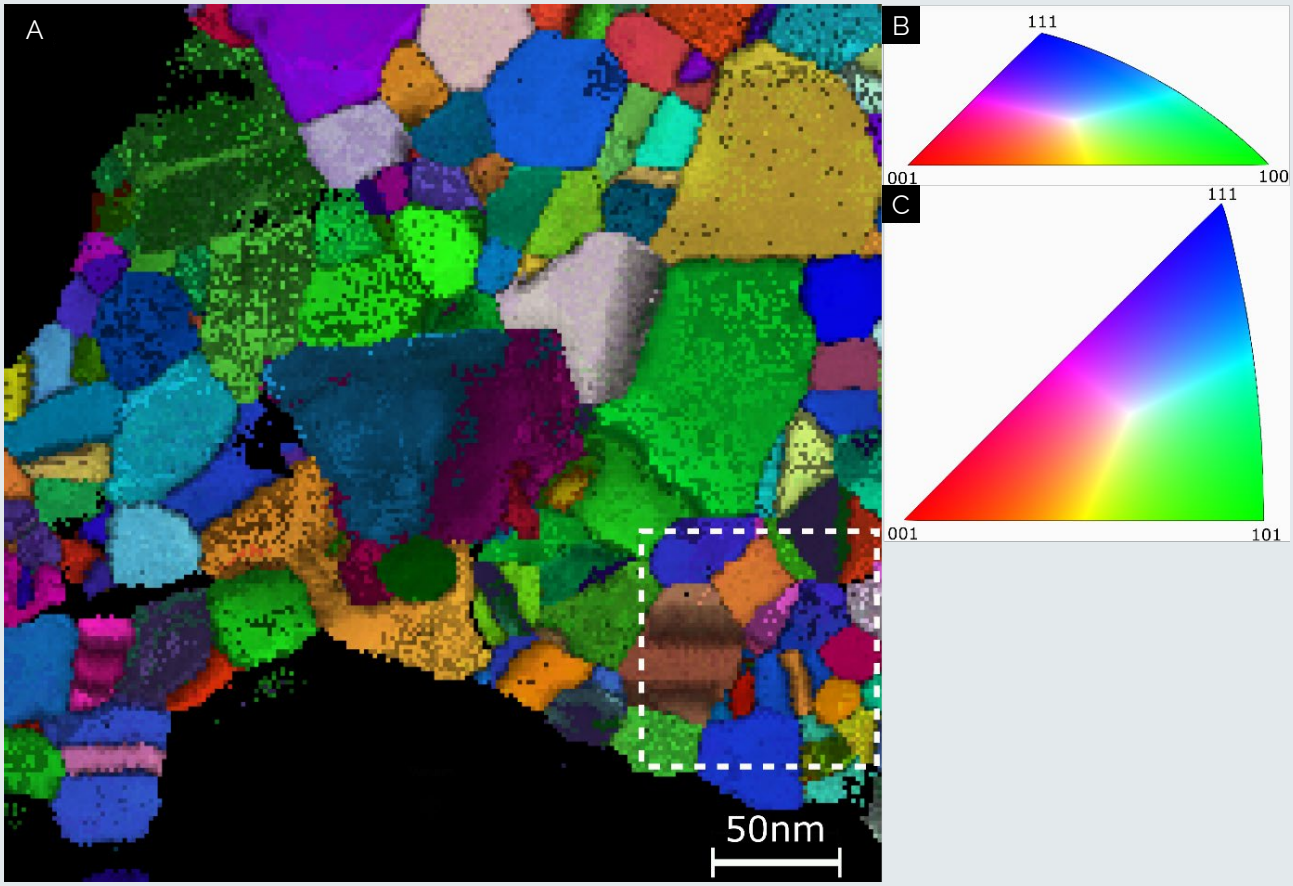


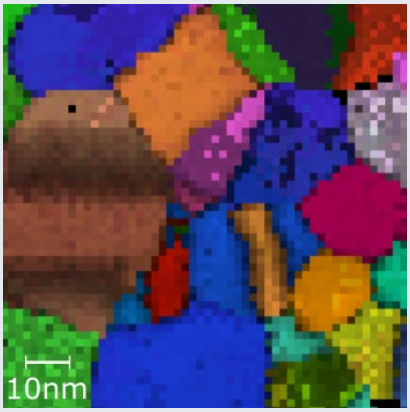
Fig. 4: Diffraction patterns taken with and without precession for location **a)** location a **b)** location b **c)** location c **d)** location d **e)** location d with templates overlayed over the diffraction spots

Orientation mapping

The orientation map is shown in Figure 5A. The color of each grain now indicates its orientation according to the color scheme in the inverse pole figure (Figure 5B, C). The brightness of each pixel indicates the confidence of indexing by a template for orientation analysis. Figure 6 shows a detail of the orientation map, and clearly demonstrates that structural features, such as grains, smaller than 10 nm can be identified.



▲ **Fig. 5: A)** Orientation map of $Bi_{12}GeO_{20}$ on evaporated aluminum acquired with electron beam precession (precession angle 0.5°) **B)** orientation legend of BGO C) orientation legend of Al.



▶ **Fig. 6:** Detail of the orientation map, indicates by the dotted line in Figure 5

Conclusions

TESCAN TENSOR provides integrated 4D STEM capabilities enabling fast nanoscale precession-assisted phase and orientation analysis. Preset measurements and automation of optical adjustments and alignments allows users to interact with the specimen readily, and quickly change from one measurement to the next for fast and effective acquisition of variety of datasets. TENSOR's phase and orientation analysis capabilities have been illustrated on BGO particles dispersed on a thin Aluminum film, ideally suited to explain the methodology of 4D-STEM phase and orientation analysis, thanks to the large difference in lattice spacing between BGO and Al.

Reference:

[Rauch et al., 2008]: Microscopy: the journal of the Quekett Microscopical Club 22(93): S8-S11

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