Study of $BaGe_5$ by manual electron-diffraction tomography

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The novel tool electron-diffraction tomography [1] was used for a single-crystal structure study of $BaGe_5$ with unit cell parameters *a* = 10.7242(7) Å, *b* = 9.2873(8) Å, *c* = 14.7905(11) Å (refined from X-ray powder diffraction data) [2] and space group *Pmna* (previous electron diffraction study) [3]. The $BaGe_5$ phase was obtained as microcrystalline material (layered crystallites, about 6 – 15 μm length, about 0.5 – 3 μm thickness, Fig. 1 *left*) by decomposition of the high-temperature Ba_8Ge_{43} clathrate-I (stable at 770°C to 810 °C) after annealing at 460 °C [2]. The first attempt to solve its crystal structure from precession electron diffraction data (precession semi-angle 1°) failed [3]. Although, in the meantime the $BaGe_5$ crystal structure has been solved from X-ray powder diffraction data [2, 4], we used $BaGe_5$ to test the manual electron-diffraction tomography technique and learn about all the features and difficulties of the method.

Conventional transmission electron microscopy and manually collected diffraction tomography were performed on a FEI TECNAI 10 (100 KV) microscope, equipped with a 2k CCD camera (TemCam-F224HD from TVIPS). The selected area diffraction (SAED) mode was used for data collection. The aperture area had at the image plane a size of about 450 nm. A small crystal (Fig. 1 *right*) on the holey carbon-coated TEM support grid was selected for data acquisition (without beam precession). The tilt sequence at steps of 1° was performed manually in a total tilt range of 130° (± 65°) using a standard double-tilt holder from GATAN. The collected series data was stored as a set of files in TIF format and converted into MRC stacks, which were further processed using the ADT3D software package [1] for a reconstruction of the diffraction volume. After indexing the 3D-spots in the reciprocal-space lattice of $BaGe_5$, their intensities were integrated and stored as standard *hkl*-files (1412 reflections; 454 unique reflections). In Fig 2, two projections (along *a* and *b* axes) of the three-dimensional reconstructed reciprocal-space diffraction volume of $BaGe_5$ are illustrated. The unit cell parameters resulting from electron-diffraction tomography were *a* = 10.762 Å, *b* = 9.270 Å, *c* = 14.919 Å, α = 89.53°, β = 89.77°, γ = 89.72°.

Structure solution was achieved by direct methods using SIR2008 software [5]. All the atomic positions of $BaGe_5$ structure were obtained by direct methods and were refined with the SHELXL software [6]. The final *R*-value was relative large (R_1 = 0.247; 423 reflections, 40 refined parameters) but reasonable for electron diffraction data without corrections for absorption or residual dynamical effects. The Ba–Ge (3.15 – 4.10 Å) and Ge–Ge (2.38 – 2.66 Å) distances were similar to those obtained by X-ray powder diffractometry methods.

Although, several details of the crystal structure were already discussed before [2, 4], we can mention here that the semiconductor $BaGe_5$ discloses a partially disordered structure related to both clathrate types I and II. It contains germanium vacancies arranged in layers parallel to (010) plane, appearing as a collapsed clathrate-II structure or as a reconstructed clathrate-I realized by crystallographic shear [2].

In summary, we were able to solve the crystal structure of $BaGe_5$ using *hkl*-intensity data acquired by manual electron-diffraction tomography. This success opens new perspectives for our future investigations on micro- and nano-structured intermetallic and other compounds.

References

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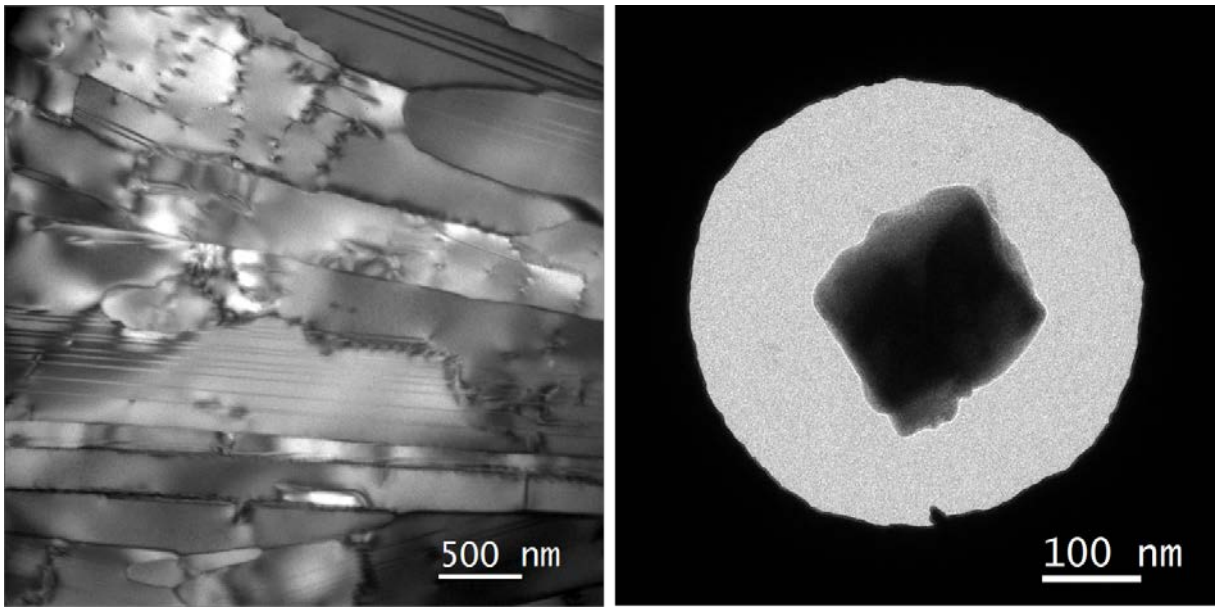

Figure 1. *(left) Bright field TEM image showing elongated crystallites of $BaGe_5$, several of them with stacking faults. (right) Crystal fragment (200x190x90 nm) used for the electron-diffraction tomography study.*

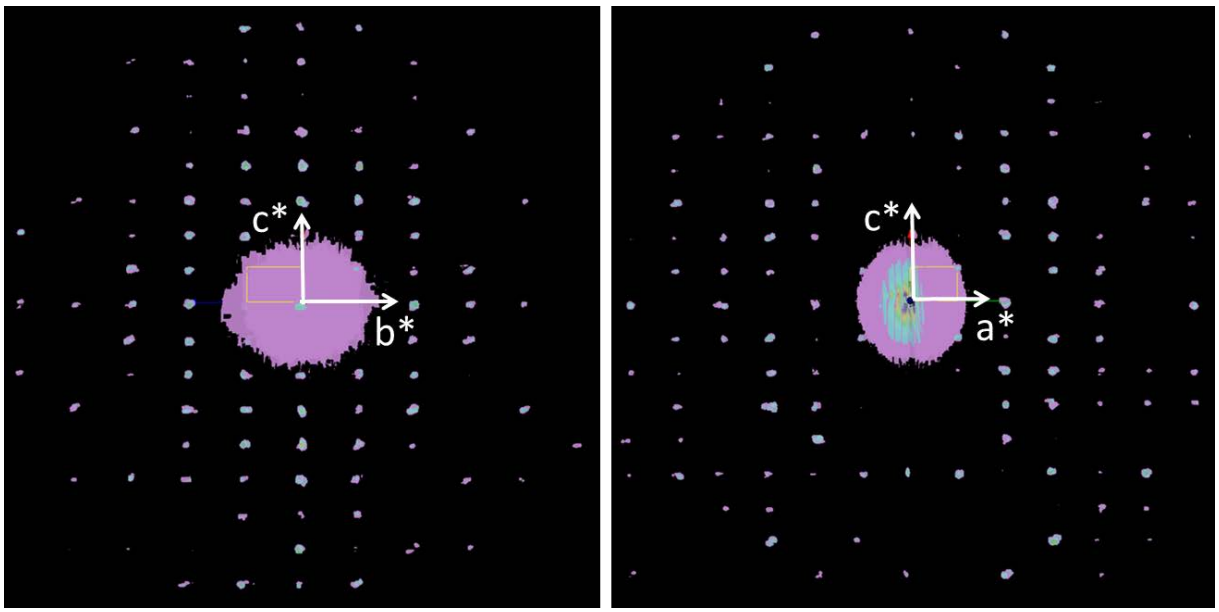

Figure 2. *Projections of the reciprocal volume along [100] (left) and [010] (right) directions. It can be recognized that the spot intensity distribution has symmetry revealing a kinematical character.*