Characterization of the metastable phase $BaGe_5$

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During a reinvestigation of the Ba–Ge system, the metastable phase $BaGe_5$ was discovered [1]. Quenched Ba_8Ge_{43} (high temperature clathrate phase stable at 770 – 810 °C) decomposes into $BaGe_5$ and Ge by annealing at 450 – 608 °C. $BaGe_5$ transforms further into the equilibrium phases $BaGe_{25}$ and Ge by heating at 609 to 770 °C. In as-cast Ba_8Ge_{43} samples, in addition to Ba_8Ge_{43} ($BaGe_{5.375}$) phase, the minority phases $BaGe_5$, Ba_6Ge_{25} ($BaGe_{4.17}$) and Ge are observed. Single phase Ba_8Ge_{43} samples are difficult to obtain with conventional quenching in water. In the present investigation, $BaGe_5$ was characterized by X-ray powder diffraction (XRPD), selected area (SAED) and precession (PED) electron diffraction, and transmission electron microscopy (TEM). Powder particles or FIB thin cuts (FEI Quanta 200 3D dual beam) were used for the TEM work performed on Philips CM20 and Tecnai 10 (max. precession angle 1.2°) electron microscopes.

After annealing of quenched Ba_8Ge_{43} at 460 °C for a few hours, thin curly germanium precipitates from the Ba_8Ge_{43} matrix, the matrix transforming in many flaky $BaGe_5$ particles which are too thin to obtain consistent single-crystal SAED patterns. Similar microstructures were observed in some regions of as-cast samples (at grain boundaries precipitate larger Ge crystals bordered by Ba_6Ge_{25}). In metallographic polished samples, $BaGe_5$ can be easily identified by using polarized light, because is the only optically active (non-cubic) phase [1].

Larger $BaGe_5$ crystallites were now obtained by heating quenched Ba_8Ge_{43} at 460 °C for 88 days. Germanium coalescences to rounded particles and the minority Ba_6Ge_{25} phase form large equiaxial grains. The XRPD pattern of $BaGe_5$ can be indexed on the basis of an orthorhombic unit cell (a = 10.723(2) Å, b = 9.283(1) Å and c = 14.784(2) Å). The microstructure shows groups of elongated $BaGe_5$ crystallites oriented almost parallel to each other, being perpendicular to their short [010] axis (see Fig. 1a). Planar defects parallel to the b axis are observed. As shown in Fig. 1b, they are antiphase (010) boundaries. It seems that the quasi-parallel $BaGe_5$ crystals were created from the same Ba_8Ge_{43} grain, becoming larger by re-crystallization during annealing and continuing parallel during growing.

The electron diffraction results (no superlattice reflections were observed) confirm the orthorhombic unit cell found by XRPD. Several SAED zone patterns were recorded; six of them are illustrated in Fig. 2 (precession angle 1°). The [031] and [211] patterns show reflections of higher Laue zones. The reflection condition for $hk0$ reflections is $h = 2n$, for $h0l$ reflections is $h + l = 2n$, for $h00$ reflection is $h = 2n$ and for $00l$ reflections is $l = 2n$. Some reflection conditions fail by tilting to some zones due to dynamical effects on thick lamellas. No extinctions conditions were observed for $0kl$ or $0k0$ reflections. The possible space group of $BaGe_5$ is *Pmna* (probable number of formula units Z = 10 and Pearson Symbol *oP*60). The crystal structure determination in the space group *Pmna* using PED intensity data (22 different zones) was attempted so far without success.

1. W. Carrillo-Cabrera, S. Budnyk, Yu. Prots, Yu. Grin, Z. Anorg. Allg. Chem. 2004, **630**, 2267.
2. We thank Prof. H. Lichte (Triebenberg Lab, TU Dresden) for measuring time on the Philips CM20 microscope.

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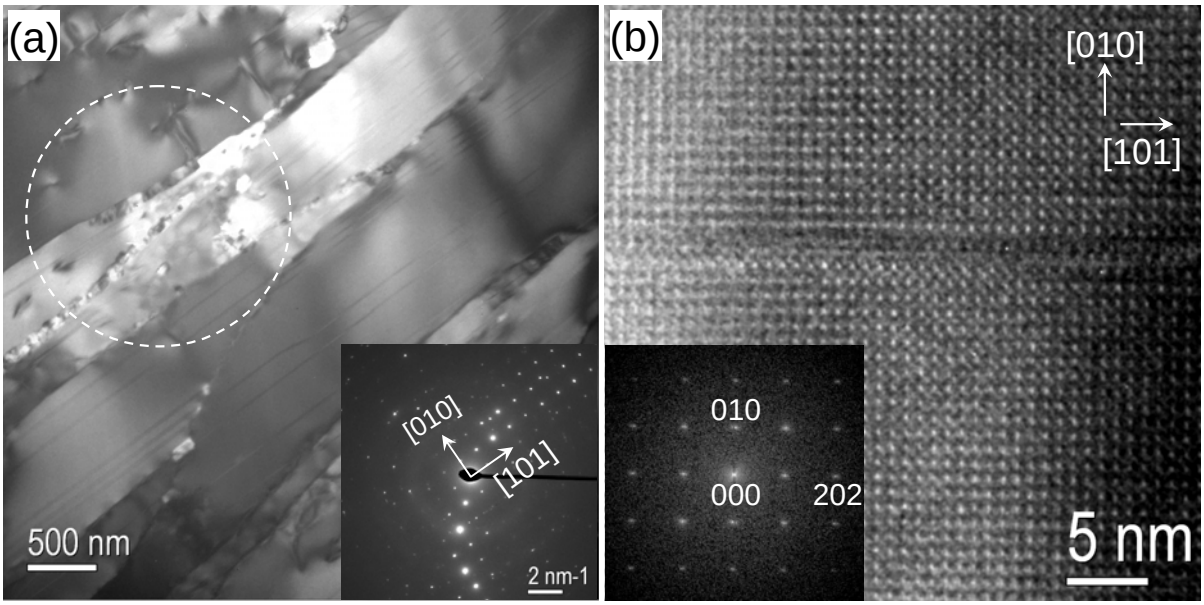

Figure 1. (a) TEM image (FIB thin cut) of long annealed sample (450 °C / 88 d), showing elongated crystals from $BaGe_5$ with defects (dark lines parallel to [101]) and Ge precipitates at grain boundaries or inside the grains. The inset is a SAED pattern of the area marked by a circle. (b) HRTEM image taken along $[10\bar{1}]$ illustrating a planar defect, a (101) antiphase boundary. In this $[10\bar{1}]$ projection, the upper part is shifted by a half period along the [101] direction. The inset is the FFT of the lower part.

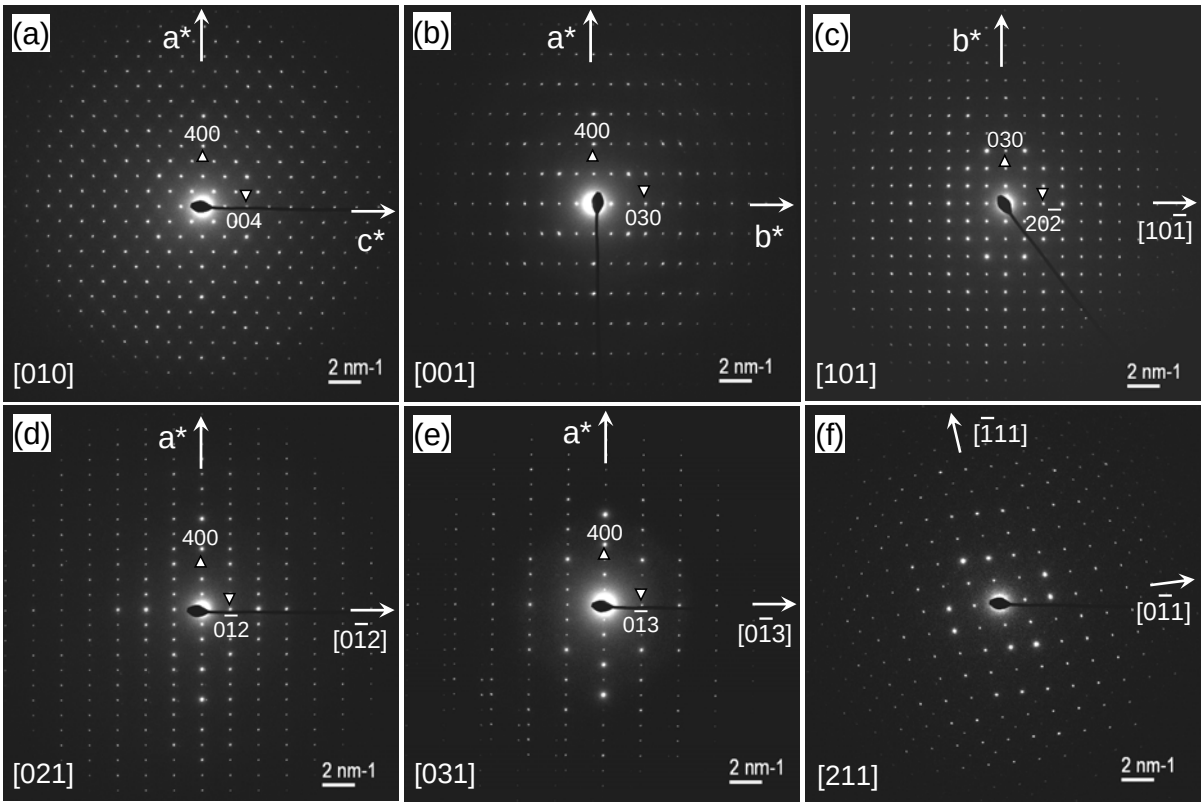

Figure 2. (a) [010], (b) [001], (c) [101], (d) [021], (e) [031] and (f) [211] SAED patterns of $BaGe_5$ recorded using a precession angle of 1° (powdered TEM samples).

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