SYNTHESIS OF Fe-SULPHIDES BY CHEMICAL VAPOUR TRANSPORT METHOD

ZAVAŠNIK, J.*, ŠOBAK, M., PODLOGAR, M. & REČNIK, A.

Department for Nanostructured Materials, Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia * E-mail: janez.zavasnik@ijs.si

In natural pyrite, a small amount of copper was shown to induce twinning (DANEU et al., 2005). In order to verify this hypothesis we prepared iron sulphides by chemical vapour transport (CVT) method using halides as transporting agents (BUTLER & BOUCHARD, 1971). Equimolar parts of FeCl₂, and FeBr₃ precursors and small amount of CuCl₂ were heated to 600°C in an evacuated quartz tube in a horizontal single-zone furnace. Vapour phase migrated through a sulphur trap within a temperature gradient from 600 to 550°C for 72 hours. Nucleation of iron sulphides occurred in two temperature zones. As soon as the temperature reaches 600°C, iron immediately reacts with sulphur in the main temperature zone to form up to 3 mm large simple hexagonal plate-like crystals of pyrrhotite. During this reaction some of the iron halides are transported to the lower temperature zone at 550°C where they react with sulphur to produce pyrite and pyrrhotite, both nucleating from the vapour phase. Pyrite crystals in this second zone have a cubooctahedral morphology with a porous core and an unusual homoepitaxial overgrowth on cubic and octahedral faces. In addition to pyrite, secondary crystallization of pyrrhotite in form of star-like twins is observed. A six-fold symmetry of twins suggests either an interpenetration twinning in basal $\{001\}$ planes or 120° rotational twinning with the [001] twin axis and $\{110\}$ prism planes as twin contact planes. EDS analysis of pyrrhotite, normalised to pyrite composition, indicates a slightly substoichiometric composition of Fe:S = 47:53, which suggests that pyrrhotite formed after pyrite as a result of sulphur deficiency. Corresponding electron diffraction pattern indicates that pyrrhotite is incommensurable. TEM study of twinned pyrrhotite revealed alternation of ccp and hcp sequences, coherently intergrown on a unit-cell scale (PÓSFAI & BUSECK 1997); ccp sequences are prevailing in the structure and may be the main cause of apparent twinning.

References

BUTLER, S.R. & BOUCHARD, R.J. (1971): Journal of Crystal Growth, 10: 163–169.

DANEU, N., REČNIK, A. & DOLENEC, T. (2005): 7th Multinational Congress on Microscopy: 197–198.

PÓSFAI, M. & BUSECK, P.R. (1997): EMU Notes in Mineralogy, 1: 193–235.

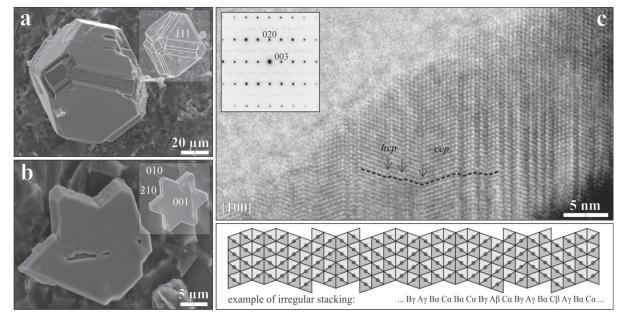


Fig. 1. CVT synthesized Cu-doped Fe-sulphides. (a) SEM image of cubo-octahedral pyrite with epitaxial overgrowth of secondary generation of pyrite; (b) SEM image of interpenetration twinned pyrrhotite, grown in sulphur deficient environment at 600K; (c) HRTEM image of pyrrhotite in [100] projection. Irregular alternation of ccp and hcp stacking is visible near the thin edge of the crystal. The electron diffraction pattern (inset) shows weak incommensurable reflection pairs along [0kl], k = 2n + 1, $l \neq 3n$.