

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 FeCl_2 , and FeBr_3 precursors and small amount of CuCl_2 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 cubo-octahedral morphology with a porous core and an unusual homoepitaxial overgrowth on cubic and octahedral faces. In addition to pyrite, secondary crystalliza-

tion 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 $\text{Fe}:\text{S} = 47:53$, 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 (PÓSFAL & 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.
 PÓSFAL, M. & BUSECK, P.R. (1997): EMU Notes in Mineralogy, 1: 193–235.

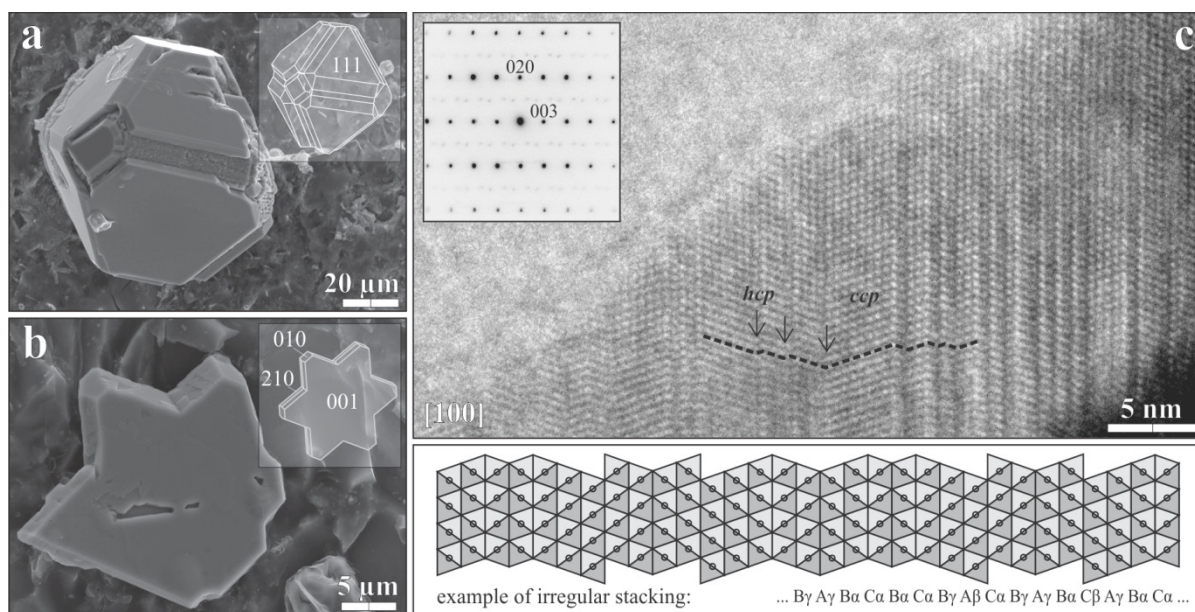


Fig. 1. CVT synthesized Cu-doped Fe-sulphides. (a) SEM image of cubo-octahedral pyrite with epitaxial overgrowth of secondary generation of pyrite; (b) SEM image of interpenetration twinned pyrrhotite, grown in sulphur deficient environment at 600K ; (c) HRTEM image of pyrrhotite in $[100]$ projection. 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 $[0kl]$, $k = 2n + 1$, $l \neq 3n$.