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On the Formation of $FeSe_2$ Single Crystals by Chemical Transport Reactions

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The formation of synthetic ferroselite single crystals, $FeSe_2$, during chemical transport experiments in the system Fe–Cr–Se was observed. The crystals are orthorhombic, $a = 4.804(2)$, $b = 5.784(3)$, and $c = 3.586(2)$ Å. They were characterized by X-ray structure analysis, and refined atom parameters are reported.

Introduction

In the course of experiments in growing single crystals in the series $FeCr_2(S_{1-x}Se_x)_4$ by chemical transport reactions, we investigated the transporting properties of several anhydrous aluminium halides, $AlCl_3$, $AlBr_3$, as well as of mixtures, $AlBr_3 + I_2$, and $AlCl_3 + I_2$. We had already successfully used the latter for the chemical transport of similar systems, $CdCr_2(S_{1-x}Se_x)_4$ (*1*), $ZnCr_2(S_{1-x}Se_x)_4$ (*2*), $Cu_{1-x}Fe_xCr_2Se_4$ (*3*), and $CuCr_2(S_{1-x}Se_x)_4$ (*3*). With $AlCl_3 + I_2$, the end members of the series, $FeCr_2S_4$ and $FeCr_2Se_4$, as well as mixed crystals (within a certain range) could be obtained; details of the preparation and the properties of these crystals will be reported elsewhere. However, when trying to grow crystals of $FeCr_2Se_4$, starting from mixtures of Fe, Cr and Se and using $AlBr_3 + I_2$ as transporting agents, we did not obtain the ternary selenide, but instead observed the formation of well-formed black needles a few tenths of a mm in diameter and up to 15 mm in length that later proved to be $FeSe_2$. The formation of $FeSe_2$ single crystals by chemical transport seems interesting to us because to our knowledge this compound has not yet been synthesized by this easy-to-handle method but only by the far more sophisticated technique of hydrothermal synthesis (*4*).

Experimental

The transport experiments were performed similarly to those already reported for the systems above (*1*, *2*). As starting material a stoichiometric mixture of Fe, Cr and Se, corresponding to a total amount of 0.02 formula weights of $FeCr_2Se_4$ was used. The starting concentrations of the transporting agents were about 10 mg/ml $AlBr_3$ and 8 mg/ml I_2; the temperature gradient was 800 → 700°C. The experiments were carried out over periods of about 100 hr.

Characterization of the Crystals

The crystals were identified by X-ray methods. Preliminary Weissenberg photographs showed the crystals to possess orthorhombic symmetry. Lattice parameters were obtained with the aid of a Nova automated single-crystal diffractometer Syntex $P2_1$ and a least-squares program provided for this instrument, from 15, carefully centered reflections.

The lattice parameters thus obtained are $a = 4.804(2)$, $b = 5.784(3)$, and $c = 2.586(2)$ Å. These values agree well with cell constants measured on samples of naturally occurring $FeSe_2$ (ferroselite) by several authors: Granger (*5*), $a = 4.800$, $b = 5.776$, $c = 3.585$ Å; Kullerud

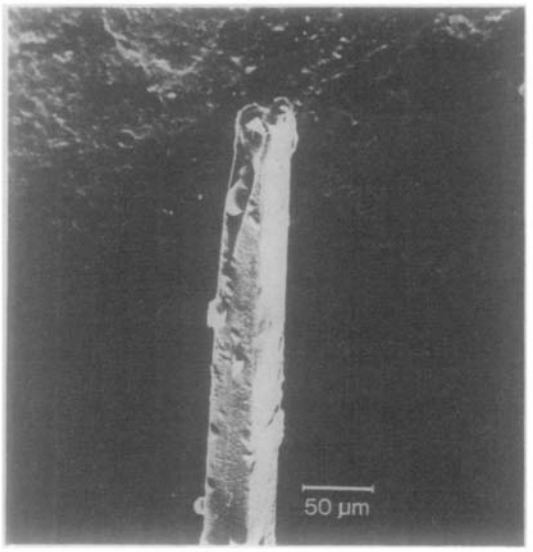

FIG. 1. Scanning electron microscope picture of an as-grown $FeSe_2$ single crystal.

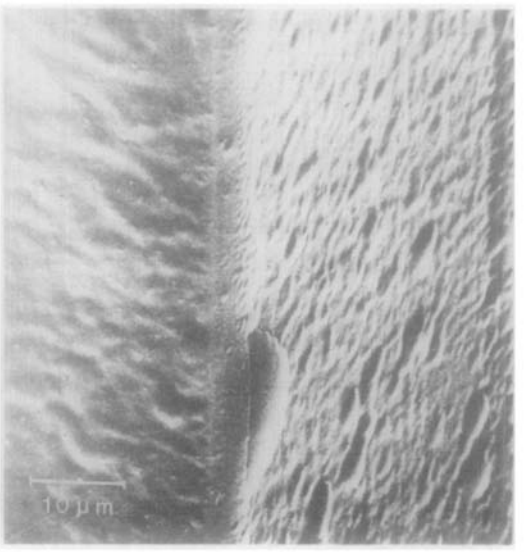

FIG. 2. The same crystal at higher magnification showing the surface structure.

(6), $a = 4.814$, $b = 5.798$, $c = 3.600$ Å; and Buryanova and Komkov (7), $a = 4.79$ (2), $b = 5.74(2)$, and $c = 3.58(2)$ Å.

As the starting material contained chromium, a crystal was analyzed by electron microprobe analysis, but no traces of chromium nor traces of halogen could be detected.

The same crystal was submitted to a scanning electron microscope examination. Fig. 1 shows a fragment of the crystal (the tip has broken off) at relatively low magnification and Fig. 2 the same fragment at a higher magnification; ripples and pits, similar to etch pits, can be seen, the nature of which is not clear. These are probably etch pits caused by the transporting agent in the course of the short back transport that occurred when, at the end of transport experiment, the temperature gradient was reversed in order to remove volatile compounds from the tip of the ampoule.

In order to verify the identity of our sample with ferroselite and possibly get some information on the degree of disorder of the crystal, an X-ray structure analysis was performed on the same crystal. The intensities of 330 independent reflections with $2\theta \leqslant 80°$ were measured on the Syntex diffractometer using Mo K_α radiation (graphite monochromator) and ω-scan. 315 reflections were observed ($I \geqslant 1.96\sigma$), these reflections were corrected for absorption and used for the structure analysis.

Ferroselite possesses the Marcasite structure, the space group is *Pnnm* (6); the unit cell

TABLE I

FRACTIONAL ATOMIC COORDINATES AND THERMAL PARAMETERS[a]

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}[b]	B_{23}[b]
Fe	0	0	0	0.575 (41)	0.413 (41)	0.949 (46)	0.003 (36)	0	0
Se	0.2134 (2)	0.3690 (1)	0	0.618 (26)	0.533 (27)	1.004 (30)	−0.041 (18)	0	0

[a] The anisotropic temperature factor is of the form $\exp -[\frac{1}{4}(B_{11}h^2a^{*2} + \ldots 2B_{12}hka^*b^* + \ldots)]$.

[b] B_{13} and B_{23} are required by symmetry to be zero.

contains two formula species. The iron atoms lie on species positions, 0, 0, 0, and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$.

The four selenium atoms have the positions $\pm(u, v, 0; \frac{1}{2}-u, v+\frac{1}{2}, \frac{1}{2})$ with $u = 0.21$, and $v = 0.37$. Series of isotropic and anisotropic least-squares refinements converged to final discrepancy factors $R_1 = 6.4\%$ and $R_2 = 6.6\%$. The discrepancy factors are defined as

$$R_1 = [\sum ||F_0| - |F_c||/\sum |F_0|] \cdot 100$$

$$R_2 = [\sum w_i||F_0| - |F_c||^2/\sum w_i|F_0|^2]^{1/2} \cdot 100.$$

The final atomic parameters and the anisotropic temperature factors are listed in Table I. Attempts to refine the occupational parameters for the selenium atoms did not give significant deviations from the stoichiometric composition $FeSe_2$; we therefore conclude that the degree of disorder in the crystal is rather low.

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