ORDER AND DISORDER IN $ZnGeP_2$ CRYSTALS

G. Kimmel[1,2], Y. Shimony[1], O. Raz[2], M.P. Dariel[2]

[1]*NRCN, P.O.Box 9001, Beer-Sheva, Israel*
[2]*Ben-Gurion University of the Negev, P.O. Box 653, Beer-Sheva, Israel*

Abstract

Early studies using differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques have shown that the low temperature stabilized phase of ZGP (α-ZGP) undergoes at 950 °C a phase transformation to β-ZGP, the high temperature allotrope with the cubic zinc-blende structure. In α-ZGP, Zn and Ge atoms occupy different crystallographic sites, while in β-ZGP, Zn and Ge are randomly distributed on the same site. As a result, the unit cell of α-ZGP consists of two adjacent units of β-ZGP, forming a tetragonal chalcopyrite structure.

High quality $ZnGeP_2$ (ZGP) crystals were grown by means of the Horizontal Gradient Freezing technique and characterized by X-ray diffraction (XRD) and optical measurements. Analysis of diffraction patterns taken at room temperature, showed the presence of the tetragonal α-ZGP crystals and of a small amount of coherently oriented cubic phase having the zinc-blende (sphalerite) structure. There was no significant increase in the amount of the cubic phase after quenching of ZGP from above the $\alpha \rightarrow \beta$ transition (950 °C). However, rapid cooling of the melt resulted in the presence of high amount of a cubic phase.

The formation of a disordered cubic phase from the rapidly cooled melt can be attributed to local deviations from stoichiometric concentration and incomplete ordering of the (Zn,Ge) sublattice. The origin of a cubic phase in crystals grown slowly at high temperatures has not been determined yet. It may be associated with antiphase boundary regions generated during the growth of the single crystal.

Crystals were grown under temperature gradient covering the entire liquidus range from the highest solid ZGP down to the ZGP-Ge eutectic point. The products formed at different temperatures, above and below the $\alpha \rightarrow \beta$ transition, were carefully characterized, and an amount of cubic phase was found even in crystal regions that solidified below the $\alpha \rightarrow \beta$ transition. This result strengthens the interpretation of the cubic regions as being due to faults produced during solidification. The results of this study will be given in details.

1. Introduction

Early studies using differential thermal analysis (DTA) and X-ray diffraction (XRD) techniques have shown that the low temperature stabilized phase of ZGP (α-ZGP) undergoes at 950 °C a phase transformation to β-ZGP, the high temperature allotrope with the cubic zinc-blende structure [1-3]. In α-ZGP, Zn and Ge atoms occupy different crystallographic sites, while in β-ZGP, Zn and Ge are randomly distributed on the same site. As a result, the unit cell of α-ZGP consists of two adjacent units of β-ZGP, forming a tetragonal chalcopyrite structure [1, 4].

The existence of disordering cubic in ZGP was expected by several research groups, either by single crystal or by powder diffraction [1, 5, 6]. A comprehensive study of disordering in an isomorphous material $ZnSnP_2$ was reported by Vaipolin et al [7]. Using powder diffraction technique, Vaipolin et al. based their studies on diffraction lines which appear in the chalcopyrite and forbidden in disordered sphalerite. In ZGP it is impossible to use this method because the atomic numbers of Ge and Zn are too close for obtaining extra lines due to ordering of Ge and Zn site occupancies. Hence, in the present work a whole pattern treatment has been used for powders of ZGP, and line profile fitting of oriented single crystals was done, to approve or disapprove the existence of disordered cubic phase.

2. Experimental

Polycrystalline ZGP was prepared by a multi-step direct reaction between Zn,Ge and P (99.9999% pure) in sealed quartz ampoules. Single crystals were grown in the course of the present study using the Horizontal Gradient Freeze (HGF) technique in pyrolytic carbon or boron nitride boats, enclosed in evacuated fused silica tubes. The growth process was performed in three-zone resistance furnace with a low thermal gradient (< 0.05 °C/mm). An extra amount of phosphorus was added to the fused silica container to compensate for the phosphorus deficiency. The crystals that were obtained weighted up to 75 grams and were shiny. Some single crystal boules were obtained from a commercial company.

Oriented samples were prepared from the grown boules by Laue Back Reflection alignment, following by conventional cutting, grinding and polishing procedures.

The XRD equipment was a Bragg-Brentano diffractometer with $\theta/2\theta$ independent axes. Radiation source: Philips PW1730 generator with Cu anode. Power used: 40 kV, 40 mA; Slits: 0.1° - 0.2 mm - 0.1°; Detector: Xe proportional; Monochromator: Graphite attached to the detector.

The (112) and (004) planes where examined by $\theta/2\theta$ XRD scans of oriented crystals cuts. The diffraction peaks were analysed by line profile fitting.

Fine powders were prepared by hand grinding and by ball milling. The samples were put into an insert with the dimensions of $30 \times 15 \times 0.5$ mm^3. The data collected by step scanning; step size: 0.02°; measuring time: at least 1 sec; Scanning range: 16-155 °2θ. Since Ge and Zn have similar atomic scattering factors, the lines which are sensitive for disordering in Ge-Zn atomic occupation are absent or very weak. Therefore, the whole pattern fitting method was applied. The best tool was Rietveld refinement procedure, providing evaluation of phase amount and residual factor (R-Bragg) for two phases, comparing with the residual for a single phase choice. The Rietveld software was DBWS-9411 [8].

Powder samples prepared in the following variety:

(A) normally grown at β-ZGP zone close to the melting point;
(B) grown below the ZGP $\beta \rightarrow \alpha$ transition;
(C) isothermal treatment at β-ZGP (980 °C) for 12h and quench to cold water.
(D) prolong annealed at α-ZGP phase (500 °C).

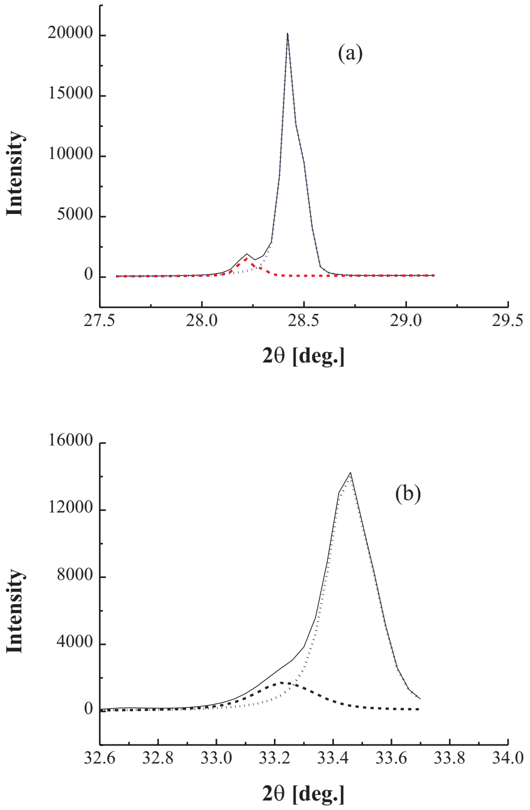

Fig 1.
(a) Expanded view of x-ray diffraction pattern of (112) cut ZGP single crystal. The raw spectrum (solid line) is shown together with the α-phase (112) (dotted) and β-phase (111) (dashed) lines, which were extracted from the raw curve by line profile fitting.
(b) Expanded view of x -ray diffraction pattern of the (004)-plane cut ZGP single crystal. The α-phase (004) (dotted) line and the β-phase (200) (dashed) line obtained by line profile fitting from the raw spectrum (solid line) are shown together with the raw curve. See text for details.

3. Results

The results of single crystal diffraction for samples grown at β-ZGP zone close to the melting point, are displayed in Fig 1a and 1b. After line profile fitting, Figs. 1a and 1b show side-peaks near (112) and (004) lines respectively. The side-peaks shown in the figures are almost disappear after annealing at 500 °C for 200 hours. The intensities of the side-peaks exhibit diffraction from another phase coherent with the chalcopyrite diffraction lines.

Table 1a: Crystal data for $ZnGeP_2$ chalcopyrite type.

Space group: $I\bar{4}2d$
Lattice parameters: $a = 0.5466(1)$ nm, $c = 1.0709(2)$ nm.
Atomic positions: 4 Ge (b); 8 P (d) x = 0.2586 (20); 4 Zn (a)

Table 1b: Crystal data for disordered ZGP (sphalerite type)

Space group: $F\bar{4}3m$
Lattice parameters: $a = 0.544(1)$ nm
Atomic positions: 2 Ge (a); 4 P (d); 2 Zn (a)

The crystal data for the chalcopyrite and for the sphalerite are given in Table 1. The chalcopyrite data are in agreement with previously reported data [4].

A mixture of chalcopyrite and sphalerite phases was found in powders: (a) normally grown close to the melting point; (b) grown below 950 °C, near the eutectic. c) in the commercial material (Table 2, samples A,B,C). At those cases a significant drop in R-Bragg factor was found when a mixture of chalcopyrite and sphalerite was assumed instead of a pure chalcopyrite structure. At all cases the amount of the sphalerite found to be near 21 mole %. The diffraction lines of the cubic phase were severely broadened, which can be associated with an average crystallite size of 5 nm.

A single chalcopyrite phase found to be a better choice than a mixture of chalcopyrite and sphalerite for Rietveld refinement of powders of: (a) quenched from 980 °C; (b) annealed at 500 °C for 200 h (Table 2, samples D,E). In these cases when a mixture of chalcopyrite and sphalerite is assumed instead of a pure chalcopyrite phase, it was difficult to refine the data. It was necessary to freeze the line shape parameters, otherwise there was no solution. There was no improvement of R-Bragg factors, relatively to a single chalcopyrite phase. The amount of the sphalerite found to be near 11 mole %. However, this is not a real solution, because it was impossible to refine the line profile.

It should be noted that ball milling improves the refinement results.

4. Discussion

Both single crystal and powder diffraction show that the purity of the chalcopyrite can be controlled by thermal annealing. However, in the present study the two diffraction methods provided us different sort of information.

The results from the single crystal cuts tell that the additional phase is coherently locked in the chalcopyrite. It is also clear that this phase almost disappears during prolonged thermal annealing.

Table 2: Refinement results of ZGP powders. R_1 is the R-Bragg while assuming a pure chalcopyrite phase. R_2 is the R-Bragg while assuming a mixture of chalcopyrite and disordered sphalerite. M_C is the amount of the cubic phase while assuming two phases. Q is the relative reduction of the R-Bragg in using two phase instead a pure chalcopyrite. [$Q = (R_2 - R_1)/R_2$]

Sample	R_1 [%]	R_2 [%]	M_C	Q
A	4.3	2.2	21	0.5
B	4.74	1.54	22	0.75
C	17	13	19.5	0.33
D	3.95	3.85	10.2	0.012
E	18.8	20.4	11.8	-0.1

A- commercial product, as received, ball milled.
B- authors' product (specimen 413). Grown close to the melting point, as received, ball milled.
C- authors' product (specimen 413). Grown at the lowest tem perature, near the eutectic, as received, hand grinding.
D- authors' product (specimen 413). Grown close to the melting point, after annealing at 500 °C for 200h, ball milled.
E- authors' product (specimen 413), reheated at 980C and quenched to water. Hand grinding.

The powder diffraction refinement results confirm the existence of disordered cubic phase in normally grown crystals, in amount of 20% wt, regardless of the growing temperature and the pulverizing method. On the other hand, after the annealing at 500 °C for 200 h, or water quenched from 980 °C, the amount of the cubic phase is significantly reduced.

The fact that the stabilization of β-ZGP in room temperature by quenching from 980 °C was failed, do not approve the existence of a disordered structure above 950 °C. It should be noticed that quenching from temperatures above the melting points resulted in a mixture of chalcopyrite with Ge, GeP and Zn_3P_2, showing that the quenching experiment is effective.

5. Conclusions

Crystals of $ZnGeP_2$ are seemingly formed as a mixture of chalcopyrite and sphalerite. This behavior is similar to results of $ZnSnP_2$ structure reported by Vaipolin et al., 1968 [7]. The sphalerite does not associate with a disordered high temperature phase as assumed for $ZnGeP_2$ structure [1-3]. Thermal annealing reduces the amount of the sphalerite.

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