Determination of the orientation relations between the low- and high-temperature phases of NiS

H. Sowa, H. Klein and R. Nowak[1]

GZG, Dept. of Crystallography, University of Göttingen, Goldschmidtstr.1, 37077 Göttingen, Germany
[1]HASYLAB at DESY, Notkestrasse 85, 22603 Hamburg, Germany

NiS is dimorph. The stable phase at room temperature is millerit β-NiS that crystallizes with the rhombohedral space group *R*3*m* with a = 9.6112(6) Å, c = 3.1508(5) Å [1]. Above 379 °C α-NiS [2] is stable that belongs to the NiAs structure type. This hexagonal phase, space group $P6_3/mmc$, can be quenched to room temperature. The lattice parameters are a = 3.4395(2) Å, c = 5.3514(7) Å [3]. The α- to β-NiS transition is accompanied by an increase of the volume by about 2.8%. This transition often causes the shattering of toughened glass panes since NiS occurs as an impurity in the process of float glass formation [4].

During the phase transition the coordination number of the Ni atoms changes from 5 in millerit to 6 in the NiAs-type structure. The Ni atoms in millerit form clusters of three atoms with very short Ni-Ni distances of $d_{\text{Ni-Ni}}$ = 2.53 Å (Ni metal: $d_{\text{Ni-Ni}}$ = 2.49 Å) while in the high-temperature polymorph chains of Ni atoms are found with $d_{\text{Ni-Ni}}$ = 2.68 Å. Therefore, it is expected that during the transition the crystal structure have to be considerably reorganized and diffusion processes have to be involved.

The kinetics of the phase transition has been extensively studied [2, 5]. Especially α-NiS can show Ni deficiency and the actual transition temperature depends strongly on the stoichiometry of the compounds. Wang et al. [5] showed that the initial composition of α-$Ni_{1-x}S$ influences not only the kinetics but also the path of the α- to β-NiS transition leading to exsolutions of more Ni-deficient α-$Ni_{1-x}S$, whereas β-NiS transforms always to α-NiS with the same composition.

For the present experiments, natural millerite from Wissen/Sieg was used. Single crystals of β-NiS with a length of several millimeters and a diameter of about 350 μm were clamped into a special holder and brought into a vacuum oven that was operated by a Lakeshore 340 controller [6]. This set-up was installed at the beam-line BW5 (fig.1). The beam-energy was 100 keV, the detector was a mar345 area detector. In a first run the pole figures of the millerite were measured at ambient temperature in a range $-27° \le \omega \le 93°$ of the orientation angle ω in steps of 1°. After these measurements the millerit crystal was fast annealed clearly over the point of transition and subsequently slowly cooled down to room temperature. In a second step the pole figures were measured again.

Fig. 1: Vacuum-oven

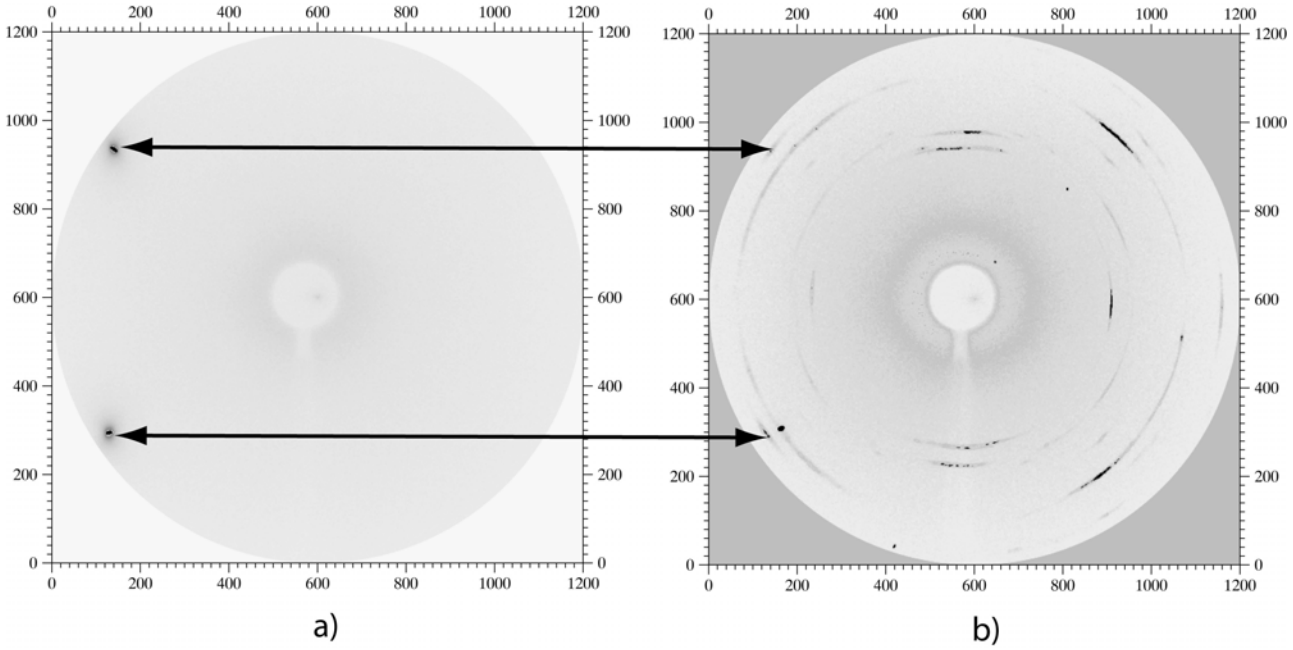

Fig. 2: 2-dimensional diffraction image of a) a β-NiS single crystal, b) the quenched sample of α- and β-NiS

Figure 2a shows a 2-dimensional diffraction image of the millerite single crystal before annealing at ω = 23°. In figure 2b the diffraction image at the same orientation angle after annealing and cooling is shown. In contrast to figure 2a Debye-rings with knots can now be observed coming from the metastable high-temperature polycrystalline α-NiS phase. Beside these rings broad peaks of the low-temperature β-NiS modification occur at the same positions as the reflections of the original single crystal. From the transition to the high-temperature phase a strong texture results (fig.2b) and an orientation correlation between both phases can be noticed.

References

[1] H. Sowa, H. Ahsbahs, and W. Schmitz, Phys. Chem. Minerals 31, 321 (2004).
[2] G. Kullerud and R. A. Yund, J. Petrol. 3, 126 (1962).
[3] J. Trahan, R. G. Goodrich and S. F. Watkins, Phys. Rev. B2, 2859 (1970).
[4] J. C. Barry and S. Ford, J. Mater. Sci. 36, 3721 (2001).
[5] H. Wang, A. Pring, Y. Ngothai and B. O'Neill, Am. Mineral. 91, 171 (2006).
[6] H. Klein, A. Preusser, L. Raue and H. J. Bunge, Mat. Sci. Forum, 495-497, 137 (2005)