High-temperature phase transitions and thermal expansion of stromeyerite, AgCuS

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Recently, the high ionic conductivity for cations renewed the interest in silver copper sulphide, AgCuS (mineral name stromeyerite). The ionic conductivity in the superionic face-centered cubic (fcc) phase of AgCuS was measured in the temperature range 473-673 K and has a value of 2.38 Ω⁻¹·cm⁻¹ at 573 K [1].

In-situ high-temperature structural studies in the temperature range between room temperature and 693 K were performed at the synchrotron facility Hasylab/DESY (Hamburg, Germany) with the powder diffractometer at beam-line B2 [2]. A 0.3 mm quartz capillary was filled under argon atmosphere with powdered AgCuS and sealed. Subsequently, the capillary was mounted inside a STOE furnace in Debye-Scherrer geometry. The furnace temperature was calibrated using the thermal expansion of NaCl. The wavelength (0.49962 Å) was selected using a Si(111) double flat-crystal monochromator. All diffraction patterns have been collected at fixed temperatures during the heating cycle using an image-plate detector [3] (2θ range 4-45°, step size 0.004°). One additional pattern was taken after the heat treatment and cooling down to RT.

![Figure 1: Examples of Rietveld refinements of the diffraction patterns from stromeyerite. Crosses are experimental data, the line through the crosses is the calculated profile and the lower curve their difference. Tick marks show the calculated positions of AgCuS reflections.](image)

The analysis of the structural behaviour of AgCuS showed the following phase boundaries at elevated temperatures: orthorhombic (β) (Cmc21) $\rightarrow$ hexagonal (α) (P63/mmc) $\rightarrow$ hexagonal (α) (P63/mmc) plus cubic (δ) (Fm3m).

For convenience, the unit cell parameters $a_\text{or}$, $b_\text{or}$, $c_\text{or}$ of the orthorhombic C-centered β-AgCuS were transformed into the primitive pseudo-hexagonal cell with dimensions $a_{\text{phex}}$, $c_{\text{phex}}$, $\gamma_{\text{phex}}$ via...
Figure 2: The unit cell axial ratio \( c/a \), cell dimensions \( a, c, \gamma \) and unit cell volume per formula unit \( V/Z \) of stromeyerite as a function of temperature in the range from RT up to melting point. The lattice parameters of the primitive pseudo-hexagonal and rhombohedral cells of \( \beta \)- and \( \delta \)-AgCuS are illustrated. Inset: unusual thermal expansion along \( c \)-direction of \( \beta \)-AgCuS.

\[
a_{\text{pHex}} = b_{\text{pHex}} = \sqrt{a_{\text{or}}^2 + b_{\text{or}}^2}/2, \quad c_{\text{pHex}} = c_{\text{or}} \quad \text{and} \quad \gamma_{\text{pHex}} = \arccos \left( \frac{(a_{\text{or}}^2 - b_{\text{or}}^2)}{(a_{\text{or}}^2 + b_{\text{or}}^2)} \right).
\]

The unit cell parameter of cubic fcc \( \delta \)-AgCuS was transformed into the primitive rhombohedral one via \( a_{\text{rh}} = \sqrt{2} a_{\text{c}}/2 \), where \( a_{\text{rh}} \) and \( a_{\text{c}} \) are the cell dimensions of the rhombohedral and cubic cells, respectively. Analysis of the thermal behaviour of the lattice parameters (see figure 2) revealed strong anisotropy of the thermal expansion in the \( \beta \)- and \( \alpha \)-AgCuS. Negative thermal expansion in \( c \)-direction was observed in these phases between 316 and 440 K, whereas no anomalies in the thermal expansion in \( a \)-direction were revealed. The discontinuous volume changes of about 2.3\% and 0.6\% at the \( \beta \rightarrow \alpha \) and \( \alpha \rightarrow \delta \) transformations are a very strong indication for a 1st order phase transition. The temperature dependence of the volume thermal expansion within all phases was fitted by linear functions and the volume thermal expansion coefficients are \( 26 \times 10^{-6} \text{ K}^{-1} \), \( 130 \times 10^{-6} \text{ K}^{-1} \) and \( 85 \times 10^{-6} \text{ K}^{-1} \) for the \( \beta \)-, \( \alpha \)- and \( \delta \)-phases, respectively.

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**References**