

Charge density distribution and its temperature dependence of inorganic sulfides with lone pair electrons

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Introduction

Stibnite, Sb_2S_3 is the most common and widespread of antimony minerals. The room temperature symmetry of stibnite is often described as Pbnm ($a = 11.23$, $b = 11.31$, $c = 3.84 \text{ \AA}$). Actually, Kyono et al. [1] adopted the same symmetry model in their low-temperature study of stibnite and discussed the electron density distribution of the Sb lone pairs. However, dielectric permittivity measurements indicated a first order phase transition at 290.7 K [2]. Thereafter a further first order phase transition was identified, associated with a total loss of spontaneous polarization above 420 K [3]. Lukaszewicz et al. [4] confirmed that stibnite (II) has $\text{P}2_1\text{nm}$ symmetry at 320 K while the high temperature form was predicted to be Pbnm. The structure and symmetry of the low temperature form, stibnite (III), however, remain unresolved. We present here an interim report for elucidation of phase transitions and the role of lone pair electrons of stibnite [5].

Experimental

A horizontal-type four-circle diffractometer at beam line 14A of the Photon Factory, High Energy Accelerator Research Organization was used. Vertically polarised X-rays of 0.75035 \AA wavelength were calibrated using a spherically ground standard Si crystal. Scattered X-rays were detected with an eight-channel avalanche photodiode detector with around 75% detection efficiency [6]. The sample size was approximately $80 \times 50 \times 50 \text{ \mu m}^3$. The diffracted intensity of the strongest reflection 020 marked approximately 120,000 cps. Since the weak reflections in concern had intensities less than 1,000 cps at most, the use of synchrotron X-rays was essential for the study of systematic extinction rules of stibnite.

Results

As shown in the Figures 1 and 2, for example, several changes in extinction rules with temperature were observed. Our interpretations are as follows: Above 420 K stibnite (I) is centrosymmetric Pbnm. Stibnite (II) is stable between 290 and 420 K and is acentric $\text{P}2_1\text{nm}$. Below 290 K stibnite (III) is stable and systematic absences indicate that this phase is monoclinic of symmetry $\text{P}2_1$ or Pm, or triclinic P1, while the cell

dimensions remain geometrically orthorhombic. These findings are in agreement with variations in physical properties reported in the literature.

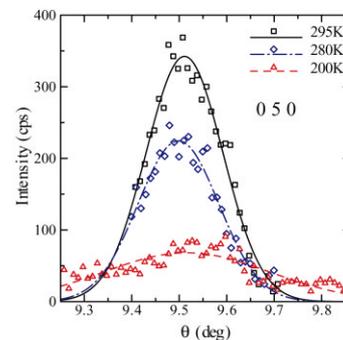


Figure 1. Diffraction profile of 0 5 0.

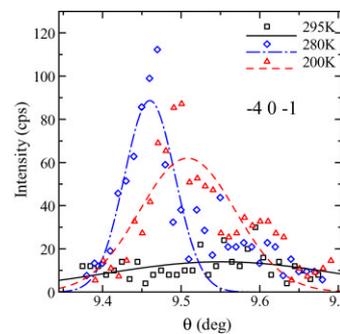


Figure 2. Diffraction profile of -4 0 -1.

References

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