

Observation on Zn/Cu distribution in a natural tetrahedrite using anomalous X-ray scattering method with synchrotron radiation

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1 Introduction

Tetrahedrite is known as one of the common ore-mineral that contains economically important elements such as Ag, Cu, Zn and so on. The general chemical formula for the tetrahedrite group minerals is expressed as $A_6[B_4, C^{2+}_2]D^{3+}_4Y^{2-}_{12}Z^{2-}$ [1], and the tetrahedrite group minerals are classified into five sub-series; the tetrahedrite series is defined as the case that A and B are Cu, D is Sb, Y and Z are S, and C is Fe, Cu, Zn etc. In natural samples, the chemical composition of tetrahedrite has very wide variations and is complex. In addition, when D changes to As in the tetrahedrite definition, the series is tennantite. Tetrahedrite and tennantite form a perfect solid solution.

The crystal structure of tetrahedrite has cubic symmetry with the space $I\bar{4}3m$, which does not have the symmetry center. Each composed atom in tetrahedrite is accommodated in as following sites; planer triangle M2 site for A, tetrahedral M1 site for B and C, and tetrahedral X site for D. It is considered that the monovalent and divalent metals, which corresponded to B and C, are perfectly disordered arrangement in the tetrahedral M1 site in tetrahedrite. However, the M1 site in tetrahedrite is occupied by Fe, Cu and Zn, making it very difficult to distinguish these atoms by general structural analysis. In this study, we attempted to clarify the Cu/Zn distribution in M sites of natural tetrahedrite by using a single-crystal anomalous X-ray scattering method with synchrotron radiation at energies near the CuK and ZnK absorption edges.

2 Experimental Procedure

A natural tetrahedrite used for this study is from Tetilla mine, Bolivia (#A226 of the Krantz collection in the Tohoku University Museum). The chemical formula of this sample was determined from 20 points average to be $(Cu_{3.74}Ag_{2.26})_{\Sigma=6.00}[Cu_{4.09},(Zn_{1.18}Fe_{0.74})]_{\Sigma=6.01}Sb_{4.05}S_{13}$ by a wave-dispersive type EPMA (JEOL, JXA-8800M).

Single-crystal anomalous X-ray scattering (SC-AXS) experiments were conducted at the beam line BL-10A, PF, KEK, Japan. The energies of the absorption edges of CuK and ZnK in sulfide were calibrated to 8.944 keV and 9.662 keV, respectively, by measuring Cu-foil, chalcopyrite (CuFeS₂) and sphalerite (ZnS). For measurements near

each absorption edge, X-ray diffraction experiments were performed at two positions: near (-10 eV) and far (-150 eV) positions. Intensity data for structure refinements were collected through 1/8 reciprocal spaces. Structure refinements were conducted using SHELXL [2] with WinGX [3]. Absorption correction for the crystal were conducted using ACACA [4]. In making the contrast map, the phase of structural models of near and far positions at each absorption edge was supposed as the same. Structural figures and contrast maps were drawn by VESTA [5].

3 Results and Discussion

The unconstrained lattice constants of this sample showed cubic symmetry and the X-ray intensity data distribution also shows $m\bar{3}m$ of the Laue symmetry within $R_{int} = 7.02\%$.

The symmetrically reduced model is, therefore, needed to investigate the Cu/Zn distribution in M1 site of tetrahedrite structure because twelve M1 sites in the unit cell are equivalent. So, the tetrahedral $I\bar{4}2m$ model were adapted. The M1 site in $I\bar{4}3m$ model is divided into tetrahedral M1A and M2B sites.

In the contrast map for ZnK edge data, no peaks from Zn were observed at the triangle planer M2 site, and Zn occupies only the tetrahedral M1 site. In contrast, in the case of CuK edge data, Cu accommodates both at M1 and M2 sites. Quantitative evaluation at each site occupation is not possible at this studying stage.

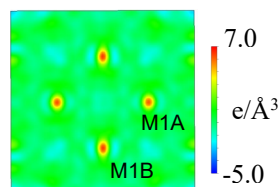


Figure 1 Contrast map of ZnK edge measurements

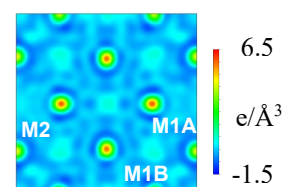


Figure 2 Contrast map of CuK edge measurements

References

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