The composite modulated structure of cupropearceite and cupropolybasite and its behavior toward low temperature

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**ABSTRACT**

Cupropearceite, \([(\text{Cu},\text{Ag})_3\text{Fe}_{0.01}\text{Zn}_{0.02}\text{Pb}_{0.01}]\text{As}_2\text{S}_6\text{Fe}_{0.01}\text{S}_3\text{]}\text{][Ag,\text{CuS}_3]\), and cupropolybasite, \([(\text{Cu},\text{Ag})_3\text{Zn}_{0.02}\text{Pb}_{0.01}]\text{As}_{6.27}\text{Zn}_{0.62}\text{(Cu}_{0.19}\text{As}_{0.77}\text{S}_7\text{]}\text{][Ag,\text{CuS}_3]\) both exhibit fast-ion conduction at very low temperatures. The structural relationship between the various phases is not fully understood as yet and is addressed in this study. Samples of these materials were studied by means of synchrotron radiation at room temperature and transmission electron microscopy at room temperature and low temperature (both liquid N\(_2\) and liquid He) to have a better understanding of the stabilization of the fast-ion conducting form at low and ultra-low temperature in these minerals. The study at room temperature did not evidence any doubling of unit-cell parameters with respect to the basic \text{Tac} unit cell, of the type typically observed for minerals of the pearceite-polybasite group. On the other hand, relatively strong and well-defined satellite reflections relating to the pseudo-hexagonal arrangement of the Ag\(^+\) ions at G ± ~1.39(1) <110>* positions of the reciprocal space, where G represents the average structure Bragg reflections, were clearly observed. Although this seems to suggest that the Ag\(^+\) ion distribution can adequately be described by a two-dimensional displacive modulation of the average \text{P}3\text{m}1 structure (\text{Tac} polytype) with the incommensurate modulation wave vectors of the satellite reflections \(\mathbf{q}_1 = \mathbf{a}_1* + \mathbf{b}_1*\) and \(\mathbf{q}_2 = -0.39(1)\mathbf{a}_1* - \mathbf{b}_1*\), where the subscript F indicates the framework substructure, the structure observed is better described as a composite modulated structure because of the intensity asymmetry of the satellite reflections. Low-temperature TEM investigations show that the satellites are still present at both 90 and 4.2 K, with a remarkable temperature-dependent shift in their positions giving rise to a variation of the coefficient \(\alpha\) of the modulation vectors from 0.39 at room temperature, trough -0.40 at 90 K to -0.5 at 4.2 K. Thus, the incommensurate modulation, strengthened by the very low temperature, approaches almost the \(\alpha\) ~ -0.5 value, indicative of a commensurate modulation. The 4.2 K structure could thus be a low-temperature commensurate superstructure (“lock-in phase”), observed for the first time in the minerals of the pearceite-polybasite group.

**Keywords:** Cupropearceite, cupropolybasite, structure modulation, TEM, synchrotron radiation, incommensurate-to-commensurate phase transition.

**INTRODUCTION**

Cupropearceite and cupropolybasite (Bindi et al. 2007a) are members of the pearceite-polybasite group of minerals. They exhibit the general formula \([(\text{Cu},\text{Ag})_M\text{S}_4\text{]}\text{][Ag,\text{CuS}_3]\), with \(M\) dominated by As (in the case of cupropearceite) or by Sb (in the case of cupropolybasite), and have been recently structurally characterized (Bindi et al. 2006a, 2007a). On the whole, their structure (Fig. 1) can be described as a regular succession of two layer modules stacked along the \(\mathbf{c}\) axis: a first layer module \(A\) with composition \([(\text{Cu},\text{Ag})_M\text{(As,Sb)}_2\text{S}_4\text{]}\), and a layer module \(B\) with composition \([\text{Ag,\text{CuS}_3}\text{]}\). In the structure, (As,Sb) forms isolated (As,Sb)\(_2\)S\(_4\) pyramids typically occurring in sulfosalts, copper links two sulfur atoms in a linear coordination, and silver occupies sites with coordination ranging from quasi-linear to almost tetrahedral. In the \(B\) layer, the silver cations are found in various sites corresponding to the most pronounced probability density function locations of diffusion-like paths (Bindi et al. 2006a).

The complex crystal-chemical features observed in these minerals were initially studied by Frondel (1963) who considered that this group of minerals could be divided into two series based on their unit-cell dimensions: (1) pearceite-antimonpearceite, characterized by a relatively high-Cu content and a “small” unit cell (\(a\sim 7.4–7.5, c\sim 11.9 \text{\AA}\)) initially labeled “111” but more recently referred to using the more explicit polytype suffix “\text{Tac}” (Bindi et al. 2007b), consistent with the notation of Guinier et al. (1984), and (2) polybasite-arsenpolybasite, characterized by a lower Cu content and doubled unit-cell parameters, initially labeled “222” but, more recently “\text{M}2\text{a}2\text{h}2\text{c}” (Bindi et al. 2007b). Moreover, an additional unit cell of intermediate dimensions, initially labeled “221” or “\text{T}2\text{ac}” (Bindi et al. 2007b), was independently discovered by Harris et al. (1965), Hall (1967), Edenharer et al. (1971), and Minčeva-Stefanova et al. (1979).

By means of an integrated SCXREF, DSC, CIS, and EPMA study, Bindi et al. (2006a) showed that all members of the pear-