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

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Abstract

Cupropearceite, $[(Cu_{3.51}Ag_{2.50}Fe_{0.01})_{\Sigma 6.02}(As_{1.72}Sb_{0.24})_{\Sigma 1.96}S_7][Ag_9CuS_4]$, and cupropolybasite, $[(Cu_{3.82}Ag_{2.42}Zn_{0.02}Pb_{0.01})_{\Sigma 6.27}(Sb_{1.19}As_{0.73})_{\Sigma 1.92}S_7][Ag_9CuS_4]$, 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 *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 $\mathbf{G} \pm \sim 1.39(1)$ <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 $P\overline{3}m1$ structure (*Tac* polytype) with the incommensurate modulation wave vectors of the satellite reflections $\mathbf{q}_1 = \sim 0.39(1)(\mathbf{a}_F^* + \mathbf{b}_F^*)$ and $\mathbf{q}_2 = \sim 0.39(1)(\mathbf{a}_F^* - \mathbf{b}_F^*)$, 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 α 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 $\alpha \sim 0.5$ 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.