Poster

Temperature dependence of single-crystal diffuse scattering in cupropearceite, $[Cu_6As_2S_7][Ag_9CuS_4]$

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The minerals of the pearceite-polybasite group are well-known for their structural complexity, including the presence of twinning, different polytypes and modulated structures [1]. They have general formula $[M_6T_2X_7][M_{10}X_4]$ with M = Ag and Cu, T = As and Sb, and X =S, Se and Te, giving rise to a wide range of compositions and eight different endmembers [2]. Pearceite and polybasite series are characterised by a different predominant trivalent ion, As or Sb respectively, and their crystal structure is usually described in terms of two different A and B units (A = $[M_6T_2X_7]^{2-}$ and B = $[M_{10}X_4]^{2+}$) alternating along the **c** axis [1]. A characteristic feature of this group of minerals is the presence of highly mobile Cu^+ and Ag^+ cations, which is related to their peculiar physical properties, such as fast-ion conduction. Moreover, three different polytypes were identified in this series: the *Tac* polytype, which is the high-temperature form and shows fast-ion conductivity, the *T*2*ac*, partially ordered, and the *M*2*a*2*b*2*c*, which occurs at low temperature and is fully ordered. The presence of mobile cations in this mineral series has also been related to the occurrence of strong diffuse scattering features, mostly characterised by means of electron diffraction [3].

In this study, we characterised by single-crystal diffuse X-ray scattering a sample of cupropearceite as a function of temperature from 100 to 325 K. The average crystal structure of this mineral has been described in the *Tac* unit-cell type and $P\bar{3}m1$ space group and in a 8-fold unit-cell with monoclinic symmetry at 100 K [1]. Starting from these data, we extended the study of cupropearceite allowing us to follow the evolution of the X-ray total scattering in a wider temperature range and closer to the *Tac*-*M*2*a*2*b*2*c* phase transition occurring below room temperature, at ~240K. A careful analysis of the diffuse scattering features and their variation as a function of temperature allows to assess, as previously hypothesized [4], the presence of disorder in both the A and B units comprising the structure. Interestingly, the diffuse scattering features in the *hk*0 plane decrease approaching the phase transition and continue to do so upon cooling in the whole studied temperature range, leading to a much weaker signal at 100 K and suggesting that its variation is not strictly related to the occurrence of the phase transition. On the other hand, the diffuse signatures in the *hhl* plane reduce at a slower rate and are thus still intense at the lowest temperature reached, suggesting a higher degree of disorder along **c***. Based on the ultra- low-temperature electron diffraction data, the ordering of Cu and Ag in the A module was suggested as the main driver of a further phase transition to a commensurate structure [4]. Analysis of the diffuse scattering along **c*** could help clarify the structural evolution underlying the phase transition by disentangling the progression of ordering in the two different units.

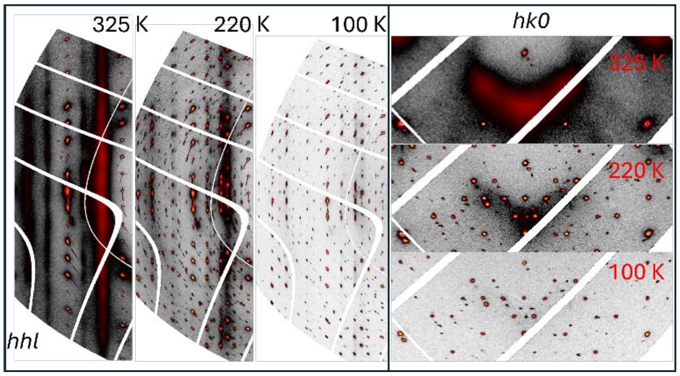

Figure 1. Evolution of the diffuse scattering features in cupropearceite

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