MS27-2-15 Pressure as switch for ionic conductivity in minerals of the pearceite-polybasite group #MS27-2-15

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Abstract
Pearceite-polybasite group minerals (PPGM), $[(Ag,Cu)_6(As,Sb)_2S_7][Ag_9CuS_4]$, are intriguing materials with Ag^+ fast ion conduction character that have attracted a lot of interest in the recent years. The notation of the chemical formula reflects the fact, that PPGM are composed of two different layers: layer A with general composition $[(Ag,Cu)_6(As,Sb)_2S_7]^{2-}$ and layer B with general composition $[Ag_9CuS_4]^{2+}$, whereat layer B is the place where the ionic conductivity takes places (BINDI et al. 2007). The root-name pearceite is given to minerals where As is dominant over Sb and the root-name polybasite for Sb-dominant phases. In addition, a suffix is attached to the root-name to give crystallographic information on the superstructure variant. Trigonal polytypes with lattice parameters a ~ 7.5, c ~ 12.0 Å are given the hyphenated italic suffix -*Tac*, trigonal polytypes with lattice parameters a ~ 15.0, c ~ 12.0 Å have -*T2ac* and monoclinic polytypes with a ~26.0, b ~» 15.0 c ~ 24.0 Å, β ~ 90° have -*M2a2b2c* as suffix. Depending on the exact chemical composition and disorder of the Ag and Cu atoms within the crystal structure a number of different crystal structures and their temperature-induced phase transitions are known (e.g. BINDI et al. 2006).

In order to test the possibility to use pressure as a switch for superconductivity, i.e. to induce phase transitions from the ionic conduction form to an ordered or partially ordered superstructure form with Ag ions “frozen-up” into fixed atomic positions, in situ single-crystal diffraction experiments of PPGM have been performed in the diamond anvil cell.

A crystal fragment of pearceite-*Tac*, $Ag_{13.3}Cu_{3.8}As_{1.5}Sb_{0.4}S_{11}$, *a* = 7.3510(6), *c* = 11.892(1) Å, *V* = 556.5(1) Å^3, *P*-3*m*1, from the Clara Mine, Oberwolfbach, Schwarzwald, Germany, shows strong diffuse diffraction features parallel to *c** at ambient conditions that are characteristic for the high temperature fast ion conduction form. On pressure increase the appearance of additional reflections at *h*/2 and *k*/2 reveals a phase transition to the *T2ac* superstructure between 0.1 and 1.2 GPa (1.2GPa: *a* = 7.3137(5), *c* = 11.723(4) Å, *V* = 542.8(2) Å^3). Furthermore, diffuse maxima condense within the originally uniform diffuse diffraction features and a number of sharp satellite reflections appear at 1.2 GPa and move their position with increasing pressure. These features are in accordance with the explanation of a composite modulated structure model for the PPGM superstructures (WITHERS et al. 2008). A crystal of polybasite-*T2ac*, $Ag_{15.0}Cu_{1.7}Sb_{1.8}As_{0.2}S_{11}$, *a* = 15.1006(5), *c* = 11.9329(4) Å, *V* = 2356.5(1) Å^3, *P*321, from the Husky Mine, Elsa, Yukon Territory, Canada, transforms to the *M2a2b2* superstructure variant, *a* = 14.785(5), *b* = 22.643(9), *c* = 25.48(2) Å, α = 89.94(5), β = 90.69(5), γ = 89.98(3), V = 8531(9) Å3 between 3.5 and 5.4 GPa.

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