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Solving an unknown phase in a HP/HT Sr-Cu-Ge-O sample

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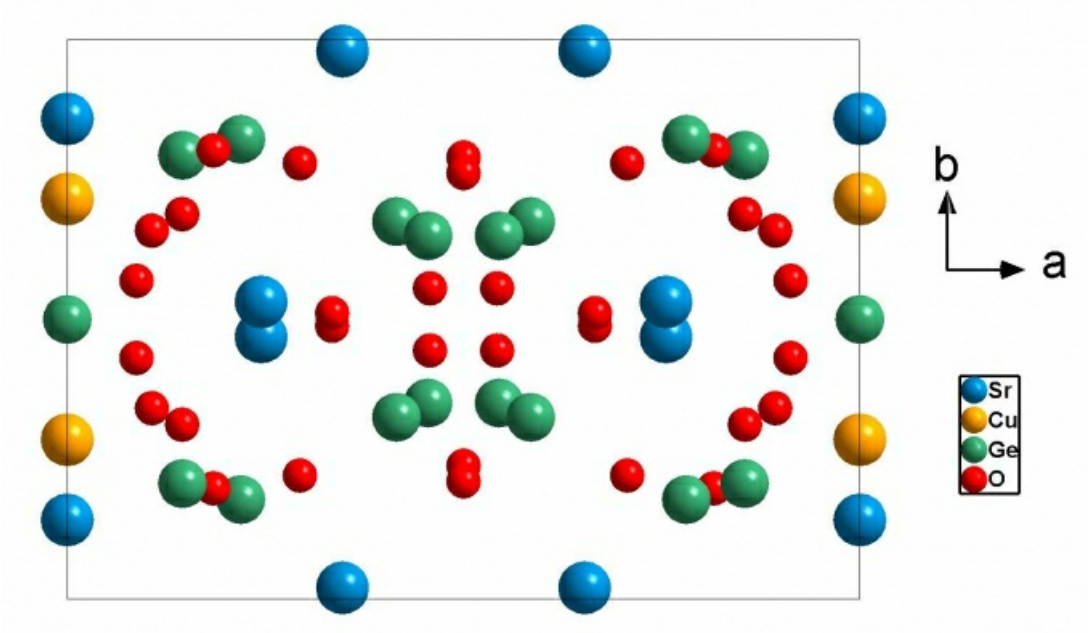
Compounds of the pyroxene family have recently reached a scientific interest thanks to their potential magnetic properties such as the magneto-electric effect or a quasi-one-dimensional magnetic behavior. These physical properties stem directly from their unique crystal structure. It is with this aim that we started investigations on pyroxene compounds with chemical formulas MM'T2O6 (M' = di or trivalent transition metal, M = mono or divalent metal, T = Si or Ge). A sample of global composition SrCuGe2O6, potentially interesting for the ½ spin of Cu2+ which could enhance quantum effects such as magnetic frustration, was synthesized at high pressure (4 GPa) and high temperature (900 °C). It did however not yield a pyroxene phase. X-ray Powder Diffraction (XRPD) showed a great number of diffraction peaks, but which could not be indexed by any known phase, indicating the synthesis of at least one unknown phase. We have therefore undertaken an electron crystallographic analysis of the sample.
In this work we present the transmission electron microscopy (TEM) study of an unknown phase in the Sr-Cu-Ge-O system using precession zone axis electron diffraction (ZA-PED) and electron diffraction tomography (EDT).
The TEM investigation showed that the powder is a mixture of two minority phases, SrO and CuO, and a major phase containing a cation proportion of 7% of Cu, 35% of Sr and 58% of Ge, according to EDS analysis. Supposing Cu2+, Sr2+ and Ge4+ ions in this compound this could correspond to a chemical composition of either Sr5CuGe8O22 or Sr5CuGe9O24.
Selected area electron diffraction (SAED) yielded the cell parameters of the unknown phase as a = 11.6 Å, b = 8.1 Å, c = 10.4 Å and β = 101°. The extinction conditions (h0l: h = 2n) as observed in ZA-PED are compatible with two space groups P2/c or Pc.
Structure solutions were obtained by direct methods in SIR. Several parameters were varied in order to obtain the best structural model: the possible space groups, resolution limits, chemical compositions, kinematical or dynamical approximations for the determination of the structure factor amplitudes. These parameter sets were tested with the ZA-PED and EDT data sets. The best solution was obtained for the composition Sr5CuGe9O24 with space group P2/c.
In this work we applied electron crystallography methods to a powder sample obtained by a high pressure – high temperature synthesis. We solved an unknown monoclinic structure of composition Sr5CuGe9O24 where X-ray powder diffraction was not able to solve the structure. The structure model we propose contains all 9 independent cation positions and almost all oxygen positions.



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