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The Reversible α → β Phase Transition of $Cu_2As_2O_7$

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ABSTRACT: Single crystals of copper(II) pyroarsenate(V), $Cu_2As_2O_7$, were prepared by chemical transport reactions in sealed and evacuated silica ampules starting from stoichiometric mixtures of the component oxides and chlorine as transport agent (temperature gradient 880 → 800 °C, 5 days). $Cu_2As_2O_7$ is dimorphous and shows a reversible α (low-temperature) ↔ β (high-temperature) phase transition at 356(2) °C detected by differential scanning calorimetry (DSC) and high-temperature X-ray powder diffraction (XRPD) measurements. The crystal structure of α-$Cu_2As_2O_7$ ($C2/c$, $Z = 4$, $a = 7.237(3)$, $b = 8.2557(17)$, $c = 9.780(3)$ Å, $\beta = 111.03(2)°$, $R[F^2 > 2\sigma(F^2)] = 0.028$) was determined from single-crystal data at room temperature. It crystallizes isotypically with α-$Cu_2P_2O_7$ and β-$Cu_2V_2O_7$. The thortveitite-type crystal structure of β-$Cu_2As_2O_7$ ($C2/m$, $Z = 2$, $a = 7.0987(3)$, $b = 8.2777(4)$, $c = 4.8666(2)$ Å, $\beta = 110.206(4)°$, R(Bragg) = 0.1056) was determined by means of high-temperature XRPD recorded at 400 °C. The crystal structures of both polymorphs are closely related and consist of infinite sheets of [CuO_x] polyhedra (α: $x = 5$; β: $x = 6$) and interjacent As_2O_7 anions that occur either in a bent (As−O−As) configuration (α-$Cu_2As_2O_7$, bridging angle 145.9(2)°) or in a linear (As−O−As) configuration (β-$Cu_2As_2O_7$). α-$Cu_2As_2O_7$ was further characterized by vibrational spectroscopy. Its IR and Raman spectra are discussed on the basis of a factor group analysis.