The Reversible $\alpha \rightarrow \beta$ Phase Transition of Cu$_2$As$_2$O$_7$

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ABSTRACT: Single crystals of copper(II) pyroarsenate(V), Cu$_2$As$_2$O$_7$, 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$_2$As$_2$O$_7$ is dimorphous and shows a reversible $\alpha$ (low-temperature) → $\beta$ (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 $\alpha$-Cu$_2$As$_2$O$_7$ (C$2/c$, $Z = 4$, $\alpha = 7.237(3)$ Å, $\beta = 8.2557(17)$ Å, $c = 9.780(3)$ Å, $\rho = 111.03(2)^\circ$, $R(F^2) = 2.15(F^2) = 0.028$) was determined from single-crystal data at room temperature. It crystallizes isotypically with $\alpha$-Cu$_2$P$_2$O$_7$ and $\beta$-Cu$_3$V$_2$O$_7$. The thortveitite-type crystal structure of $\beta$-Cu$_2$As$_2$O$_7$ (C$2/m$, $Z = 2$, $\alpha = 7.0987(3)$ Å, $\beta = 8.2777(4)$ Å, $c = 4.8666(2)$ Å, $\beta = 110.206(4)^\circ$, 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$_2$] polyhedra ($\alpha$: $x = 5$; $\beta$: $x = 6$) and interajacent As$_2$O$_7$ anions that occur either in a bent (As–O–As) configuration ($\alpha$-Cu$_2$As$_2$O$_7$, bridging angle 145.9(2)°) or in a linear (As–O–As) configuration ($\beta$-Cu$_2$As$_2$O$_7$). $\alpha$-Cu$_2$As$_2$O$_7$ was further characterized by vibrational spectroscopy. Its IR and Raman spectra are discussed on the basis of a factor group analysis.