

Quaternary Phosphide Oxides $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ and $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ with Ordered $\text{Zr}_3\text{Cu}_4\text{Si}_6$ -Type Structure

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The compounds $\text{Ln}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$ ($\text{Ln} = \text{Pr}, \text{Sm}$) were prepared by annealing the elemental components in a NaCl/KCl flux. They crystallize with an ordered $\text{Zr}_3\text{Cu}_4\text{Si}_6$ -type structure (space group $I4/mmm$, $Z = 2$), which was refined from single-crystal X-ray data for both compounds; $\text{Pr}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$: $a = 397.8(1)$, $c = 2658.7(3)$ pm, $R = 0.046$ for 235 structure factors and 19 variable parameters; $\text{Sm}_3\text{Cu}_4\text{P}_4\text{O}_{2-x}$: $a = 392.8(1)$, $c = 2643.6(3)$ pm, $R = 0.057$ for 145 F values and 19 variables. The refinements showed partial occupancy for the oxygen positions resulting in approximately 1.5 oxygen atoms per formula unit. Half of the phosphorus atoms form pairs with typical two-electron bond distances of 222.8(4) and 221.7(8) pm, respectively. Using oxidation numbers chemical bonding in these phosphide oxides can be rationalized with the formula $(\text{Ln}^{+3})_3(\text{Cu}^{+1})_4(\text{P-P})^{-4}(\text{P}^{-3})_2(\text{O}^{-2})_{1.5}$. Hence, the empirical formula may also be doubled ($\text{Ln}_6\text{Cu}_8\text{P}_8\text{O}_3$), and the compounds are expected to be semiconducting.