

An Extension of Pnictide Oxide Chemistry – Salt Flux Synthesis and Structure of $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

$\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ was prepared from a cold-pressed pellet of lanthanum filings, ground arsenic, Cu_2O and LaOCl in the ideal 3 : 4 : 2 : 2 ratio. The pellet was annealed in an evacuated silica tube at 1473 K for two days and then cooled down to room temperature. LaOCl was always observed as a by-product. $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ crystallizes with a new structure type: $I4/mmm$, $a = 413.46(7)$, $c = 4144(1)$ pm, $wR2 = 0.0763$, 328 F^2 values, 26 parameters. The new quaternary arsenide oxide $\text{La}_3\text{Cu}_4\text{As}_4\text{O}_2$ with $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ -type structure ($I4/mmm$) was obtained in polycrystalline form: $a = 413.0(1)$, $c = 2748.6(1)$ pm. The structure of $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ is an intergrowth of structural slabs of LaOCl (PbFCl type), ZrCuSiAs - and $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ -related slabs. The copper atoms have tetrahedral arsenic coordination, and all oxygen atoms fill lanthanum tetrahedra. In the LaOCl slab we observe a van der Waals gap built up by the chloride anions. Half of the arsenic atoms within the $\text{La}_3\text{Cu}_4\text{P}_4\text{O}_2$ -related slab form As_2^{4-} dumb-bells at an As–As distance of 249 pm. Electronic band structure calculations reveal $\text{La}_5\text{Cu}_4\text{As}_4\text{O}_4\text{Cl}_2$ as a strongly anisotropic hybrid material, composed of covalently bonded metallic $\text{CuAs}_{4/4}$ layers, sandwiched between ionic insulating oxide and chloride blocks.

Key words: Arsenide Oxide, Crystal Chemistry, Electronic Structure