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

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

La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ was prepared from a cold-pressed pellet of lanthanum filings, ground arsenic, Cu$_2$O 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. La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ crystallizes with a new structure type: $I_4/mmm$, $a = 413.46(7)$, $c = 4144(1)$ pm, $wR^2 = 0.0763$, 328 $F^2$ values, 26 parameters. The new quaternary arsenide oxide La$_3$Cu$_4$As$_4$O$_2$ with La$_3$Cu$_4$P$_4$O$_2$-type structure ($I_4/mmm$) was obtained in polycrystalline form: $a = 413.0(1)$, $c = 2748.6(1)$ pm. The structure of La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ is an intergrowth of structural slabs of LaOCl (PbFCl type), ZrCuSiAs- and La$_3$Cu$_4$P$_4$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 La$_3$Cu$_4$P$_4$O$_2$-related slab form As$_2^{1-}$ dumb-bells at an As–As distance of 249 pm. Electronic band structure calculations reveal La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ as a strongly anisotropic hybride material, composed of covalently bonded metallic CuAs$_4$/4 layers, sandwiched between ionic insulating oxide and chloride blocks.

Key words: Arsenide Oxide, Crystal Chemistry, Electronic Structure

Introduction

First pnictide oxides have been investigated more than 30 years ago [1, 2]. In the very beginning, such pnictide oxides were thought to be binary compounds, most likely because the weakly scattering oxygen atoms had been overlooked in the X-ray experiments. Hadenfeld and coworkers [3, 4] then prepared the compounds $AE_4P_2O$ ($AE = Ca$, Sr, Ba) in quantitative yield and showed that these are valence-precise compounds according to the formula $(4AE^{2+})(2P^{3-})O^{2-}$, whereas the binaries like Sr$_2P$ or Ba$_2P$ do not exist. Later on several quaternary pnictide oxides $AE_2Mn_3Pn_2O_2$ ($AE = Sr$, Ba; $Pn = P$, As, Sb, Bi) [5–9] have been investigated with respect to the magnetic ordering of the manganese substructures. These pnictide oxides are two-dimensional magnetic materials with comparatively high magnetic ordering temperatures [5]. An overview on these materials is given in two review articles [5, 10].

The largest family of pnictide oxides concerns the equiatomic compounds with tetragonal ZrCuSiAs-type structure. The first of the oxidic compounds was UCuPO [11]. Today more than 150 representatives with this structure type are known [12, 13]. These materials have gained a true renaissance in 2008, when superconductivity was discovered in LaFePO [14, 15], LaNiPO [16, 17], and LaFeAsO$_{1-x}$F$_x$ [18]. These structures are built up from layers of condensed $TPn_4/4$ tetrahedra ($T =$ transition metal) which alternate with layers of condensed $ORE_4/4$ tetrahedra ($RE =$ rare earth element). Although diverse stacking and / or substitution variants can be expected, so far only a few examples with other compositions have been found, i. e. the arsenide oxide U$_2$Cu$_2$As$_3$O [19] and the phos-
phide oxides $RE_3Cu_4P_4O_2$ [20, 21] and $La_3Ni_4P_3O_2$ [22, 23].

The recent discovery of the quinary phases $Sr_3Sc_2Fe_2As_2O_5$ [24–26], $Sr_4Sc_2Fe_2As_2O_6$ [27–29], $Sr_4Sc_2Fe_2P_2O_6$ [29, 30], $Sr_4V_2Fe_2As_2O_6$ [31], $Sr_4Sc_2O_2As_2O_6$ [32], $Sr_4Cr_2Fe_2As_2O_6$, and $Ba_4Sc_2Fe_2As_2O_6$ [33] offered the possibility to influence the stacking sequences and thus the distances between the conducting iron arsenide layers. The oxidic slabs of these structures have strong resemblance with the perovskite type. It is thus desirable to systematically search for new stacking variants.

During our systematic phase analytical studies and crystal growth experiments on quaternary $ZrCuSiAs$-type pnictide oxides [34–37] we repeatedly used salt fluxes. In contrast to the many syntheses on $RE$ type pnictide oxides [34–37] we repeatedly used salt flux medium. In the system $La$-$Cu$-$As$-$O$ we observed (fluxes. In contrast to the many syntheses on $RE$ type pnictide oxides [34–37] we repeatedly used salt flux medium. The glass ampoule was heated in a tube furnace to 773 K, held there for 24 h, then heated to 1123 K as flux medium. The glass ampoule was heated in a tube furnace to 773 K, held there for 24 h, then heated to 1123 K, kept at that temperature for 3 d and then cooled down to r.t. by shutting off the furnace. At this point no formation of the target compound was observed. Therefore the resulting powder was ground and pressed to a pellet again. The sample was heated up to 1473 K in an evacuated quartz ampoule, kept there for 2 d and then cooled down to r.t. by shutting off the furnace. This resulted in the formation of polycrystalline $La_5Cu_4As_4O_2$ with $LaOCl$ impurities as confirmed by Guinier powder patterns. Further regrinding and heating of the sample led to no further decrease of the by-product.

**EDX data**

Several selected single crystals were analyzed using a LEICA 420 I scanning electron microscope with LaB$_6$, Cu, InAs and KCl as standards. No impurity elements heavier than sodium (detection limit of the instrument) were observed. The compositions (excluding the oxygen content) as determined semiquantitatively by EDX of all examined crystals were in good agreement with the composition refined from the single crystal X-ray data.

**X-Ray powder and single crystal diffraction**

The polycrystalline samples were characterized by Guinier patterns (imaging plate detector, Fujifilm BAS-1800) with Cu$_{K\alpha}$ radiation and $\alpha$-quartz ($\alpha = 491.30$, $c = 540.46$ pm) as an internal standard after each reaction step. Correct indexing of the diffraction lines was ensured through intensity calculations [39] using the atomic positions of $La_3Cu_4As_4O_2$ and $LaOCl$ [38]. The tetragonal lattice parameters of both phases were refined by least-squares calculations yielding $a = 413.46(7)$, $c = 444.4(1)$ pm for $La_3Cu_4As_4O_2$ and $a = 414.7(1)$, $c = 687.7(1)$ pm for $LaOCl$. For the latter compound we find good agreement with the literature data (a = 412.09(2), $c = 688.40(7)$ pm) [38]. The new quaternary arsenide oxide $La_5Cu_4As_4Cl_2$ with $La_3Cu_4As_4O_2$-type structure ($I4/mmm$) was obtained in polycrystalline form: $a = 413.0(1)$, $c = 2748.6(1)$ pm.
Platelet-shaped single crystals were isolated from the initial sample for the preparation of La$_5$Cu$_4$As$_4$O$_4$Cl$_2$. They were first investigated on a Buerger precession camera (white Mo radiation, Fujifilm imaging plate) in order to check the first investigated on a Buerger precession camera (white Mo radiation, Fujifilm imaging plate) in order to check the quality for intensity data collection. A suitable crystal was then used for the intensity data collection with graphite-monochromatized Mo$K\alpha$ radiation on an IPDS-II diffractometer (oscillation mode). All relevant crystallographic data for the data collection and evaluation are listed in Table 1.

**Structure refinement**

Careful examination of the data set revealed a body-centered tetragonal lattice with high Laue symmetry and no further restrictions, leading to the possible space groups $I4/mmm$, $I4/amn$, $I42/m$, $I4m2$, and $I422$, the centrosymmetric group of which was found to be correct during the structure refinements. The starting atomic positions were deduced by Direct Methods with SHELXLS-97 [40], and the structure was refined using SHELXL-97 [41] (full-matrix least-squares on $F^2$) with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within two standard deviations, and in the final cycles the ideal occupancy parameters were assumed again. The final difference Fourier synthesis was flat. Table 1 contains the crystal data and parameters pertinent to data collection and refinement. The positional parameters and interatomic distances are listed in Tables 2 and 3.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/ids/depos/anforderung.html) on quoting the deposition number CSD-421137.

### Computational details

Self-consistent DFT band structure calculations were carried out using the LMTO-method (program Tb-Lmto-Asa) [42]. Detailed descriptions are given elsewhere [43]. The reciprocal space integrations were done with the tetrahedron method [44] using 550 irreducible $k$-points out of 6859 (grid of $19 \times 19 \times 19$) in the tetragonal body centered Brillouin zone. The basis set consisted of La:6$s$/$\{6p\}$/5$d$,$4$f$, Cu:4$s$/$4p$/3$d$, As:4$s$/$4p$/4$d$, O:3$s$/$2p$/3$d$ and Cl:4$s$/$3p$/3$d$. Orbital given in parenthesis were downfolded [45], and the O:2$s$ and Cl:3$s$ orbitals were treated as core states. In order to achieve space filling within the atomic sphere approximation, interstitial spheres are introduced to avoid too large overlap of the atom-centered spheres. The empty spheres positions and radii were calcu-
Fig. 1. View of the LaOCl (PbFCl type), LaFeAsO (ZrCuSiAs type), U$_2$Cu$_2$As$_3$O$_7$ (U$_2$Cu$_2$P$_3$O$_7$ type), La$_3$Cu$_4$P$_4$O$_2$ (own type), and La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ structures along the short unit cell axis. The layers of condensed FeAs$_4$/4, CuAs$_4$/4, CuP$_4$/4, OLa$_4$/4, and OU$_4$/4 tetrahedra are emphasized. Lanthanum (uranium), transition metal, arsenic, chlorine, and oxygen atoms are drawn as light grey, black filled, medium grey, open, and dark grey circles, respectively. For details see text.

Discussion

Crystal chemistry

The pnictide oxide La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ crystallizes with a new structure type with a comparatively long tetragonal c axis of 4144 pm. However, the structure is built up from simple slabs that are known from other binary and ternary structures. In Fig. 1 we present views on the LaOCl [38], LaFeAsO [46], U$_2$Cu$_2$As$_3$O$_7$ [19], La$_3$Cu$_4$P$_4$O$_2$ [20], and La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ structures. All the transition metal (T)-containing compounds show tetrahedral pnictogen (Pn) coordination of the transition metal atoms. These TPr$_4$/4 tetrahedra share four common edges, leading to layers perpendicular to the c axis. The oxygen atoms show tetrahedral lanthanum or uranium coordination and again, these OLa$_4$/4 and OU$_4$/4 tetrahedra share common edges. The stacking sequences of these layers are different in the four structures. The new structural motif in the crystal chemistry of pnictide oxides is the insertion of a chloride-containing slab which is located always between two layers of condensed OLa$_4$/4 tetrahedra. This arrangement is well known from LaOCl [38] with PbFCl-type structure.

The lanthanum atoms are the most electropositive component of the La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ structure, and they will have largely lost their valence electrons. The oxygen and chlorine atoms are both isolated, and one can safely ascribe the formal oxidation numbers $-2$ and $-1$ to these. Two crystallographically independent arsenic sites occur. The As1 atoms form dumb-
bells at an As1–As1 distance of 249 pm, close to the As–As distance of 252 pm within the layers of gray arsenic [47]. Here we can assume single-bond character and a formal oxidation number $\text{As}^{2-}$. In contrast, the As2 atoms are isolated, leading to $\text{As}^{2-}$. Similar to Pr$_3$Cu$_4$P$_4$O$_{2-x}$ and Sm$_3$Cu$_4$P$_4$O$_{2-x}$ [21], to a first approximation, the copper atoms can be counted as monovalent. Then an electron partitioning scheme $(5\text{La}^{3+})(4\text{Cu}^{1+})(2\text{As}^{2-})(\text{As}^{2-})(4\text{O}^{2-})(2\text{Cl}^-)$ is obtained with one surplus negative charge. At first sight one might think of oxygen vacancies like in Pr$_3$Cu$_4$P$_4$O$_{2-x}$ and Sm$_3$Cu$_4$P$_4$O$_{2-x}$ [21]. However, refinement of the oxygen and chlorine occupancy parameters revealed full occupancy within one standard deviation. Also the As1–As1 bond does not allow higher bond order. In view of these restraints and the dark grey color (with metallic luster) of La$_5$Cu$_4$As$_4$O$_4$Cl$_2$, a slightly higher oxidation state of 1.25$^+$ for the copper atoms might be probable. Also for the structurally closely related silicide Zr$_3$Cu$_4$Si$_6$ [21, 48] an uneven oxidation number of +1.5 was proposed for the copper atoms, and a similar situation occurs for the phosphides CaCu$_{1.75}$P$_2$ and SrCu$_{1.75}$P$_2$ [49] and the arsenide CaCu$_{1.75}$As$_2$ [50]. The slightly higher oxidation state of the copper atoms in La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ was also proven by magnetic susceptibility measurements. Although the sample contained LaOCl as a by-product, we measured the temperature dependence of the magnetic susceptibility. The 100 Oe data gave no hint for superconductivity and showed weak paramagnetism.

The uneven formal oxidation state of the copper atoms leads to metallic behavior for the CuAs$_{4/4}$ slab within the La$_5$Cu$_4$As$_4$O$_4$Cl$_2$ structure. These intermetallic slabs are well separated by fully ionic slabs, i.e. the layers of condensed OLa$_{4/4}$ tetrahedra and the LaOCl slab. Summing up, the insertion of chloride slabs leads to an interesting extension of the pnictide oxide crystal chemistry. Further synthetic investigations in this field are in progress.

**Chemical bonding analysis**

The band structure was calculated in order to shed light on the electronic properties of La$_5$Cu$_4$As$_4$O$_4$Cl$_2$. Fig. 2 shows the total electronic density of states (DOS) which reveals the compound as metallic with a rather low DOS at the Fermi level. The filled area in Fig. 2 represents the contribution of the Cu-3$d$ states, which are almost completely occupied. This is suggestive of a state close to a $d^{10}$ configuration in accord with Cu$^{1+}$, which is seemingly not in agreement with the ionic partitioning scheme $(5\text{La}^{3+})(4\text{Cu}^{1+})(2\text{As}^{2-})(\text{As}^{2-})(4\text{O}^{2-})(2\text{Cl}^-)$.
discussed above. However, such charges are rather formal numbers to approximate the electron distribution. Particularly in metallic systems, there is no need to have a charge-balanced formula, even though such situations are often stable. Our calculations give no hint for a partially filled 3d-shell of copper. On the other side, Fig. 2 clearly shows that the s- and p-orbitals of the arsenic atoms are far from being completely filled, thus the assumption of As\textsuperscript{3−} and As\textsuperscript{2−} appears not to be reasonable. This is different from the oxygen and chlorine atoms, where the s- and p-orbitals (not shown in Fig. 2) are almost completely filled basically in agreement with $O^-$ and $Cl^-$ states, respectively. Furthermore, a certain part of the electrons ($\approx 4\%$) occupy states of the interstitial spheres and cannot be assigned to any atom. The latter reflects the metallic character of the compound, which is nevertheless mainly confined to the CuAs\textsubscript{4}/4 layers. This becomes also clear from the band structure shown in Fig. 3. Several bands cross the Fermi level ($E_F$) sufficiently steep to produce metallic conductivity. The character of these bands is mainly copper-3d, strongly hybridized with arsenic 4s-4p orbitals. Thus, very small parts of the Cu-3d states appear above the Fermi level, but this is certainly not sufficient to justify a higher oxidation state of copper.

Altogether, the electronic structure calculations reveal La\textsubscript{5}Cu\textsubscript{4}As\textsubscript{4}O\textsubscript{4}Cl\textsubscript{2} as a strongly anisotropic hybride material, composed of covalently bonded metallic CuAs\textsubscript{4}/4 layers sandwiched between ionic insulating oxide and chloride blocks.

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[32] Y. L. Xie, R. H. Liu, T. Wu, G. Wu, Y. A. Song, D. Tan,


[42] O. K. Andersen, O. Jepsen, Tight-Binding LMTO (version 4.7c), Max-Planck-Institut für Festkörperforschung, Stuttgart (Germany) 1994.


