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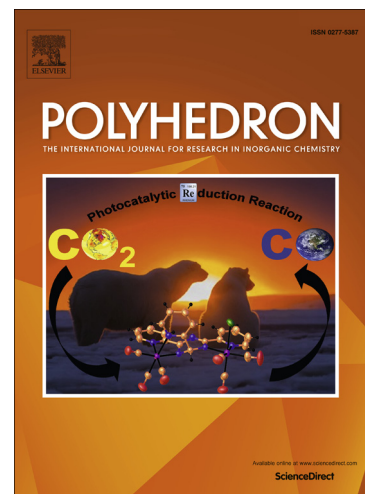
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Polyhedron

A convenient preparation of La_2CuO_4 from molecular precursors

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ABSTRACT

Exhaustive hydrolysis of a mixture of $[La_4(CO_3)(O_2CNBu_2)_{10}]$ and $[Cu(O_2CNBu_2)(py^*)_2]$ (py* = 4-dimethylamino pyridine) in molar ratio 1/2 corresponding to a La/Cu molar ratio 2/1 was carried out in toluene at room temperature. The carbamato derivatives of lanthanum and copper can be easily prepared by extraction of the metal ions from aqueous solution into heptane by the $NHBu_2/CO_2$ system, according to a method previously reported. The copper precursor was selected among a number of derivatives in respect of its easy tractability. The tetragonal modification T' of La_2CuO_4 was obtained by treatment at 600 °C of the intermediate mixed carbonate. The thermal treatment of T'-La_2CuO_4 at 850 °C, followed by cooling down to room temperature, afforded the orthorhombic modification of the mixed oxide.

Introduction

The synthesis of finely divided mono- or multi-metal oxides and the study of their features in dependence of the preparation method is a topical theme [1], in view of the applications of these materials in several fields, as catalysis [2], sensing and electronics [3], to name but a few. In recent years there has been a remarkable interest in the use of molecular species as precursors of these materials, since, with respect to classical solid state methods, this route allows the use of lower temperatures and assures a more homogeneous distribution of the different components of the system when multi-metal oxides are the target. Methods based on progressive hydrolysis of suitable molecular metal complexes, as for instance metal alkoxides or metal carboxylates, have been often exploited [1a,b,e-h]. These processes involve gradual aggregation to oligo- or poly-oxo-derivatives, up to metal hydrated oxides, with final obtainment of the metal oxides by heating.

We have reported in the past some results concerning the partial hydrolysis of metal *N,N*-dialkylcarbamato complexes producing µ-oxo [4] or in some cases carbonato [5] derivatives. Recently, the partial and exhaustive hydrolysis of lanthanides *N,N*-dialkylcarbamato complexes has been described affording the preparation of lanthanide oxides and mixed lanthanide oxides. [6]. The hydrolysis of the hydrocarbon soluble *N,N*-dibutylcarbamato complex of cerium(III), $[Ce(O_2CNBu_2)_3]$, carried out in non polar solvents at room temperature yielded finely divided hydrated cerium(III) carbonate whose treatment at 200 °C in air provided nanostructured ceria [6a]. The synthetic method was extended to the preparation of nanostructured doped ceria affording cerium/lanthanum and cerium/terbium nano-crystalline mixed oxides containing a single crystalline phase with the two metals in the dosed molar ratio [6b]. The similar lability of the metal centers involved in the process reasonably accounted for the success of the preparation of these solid solutions. We reckoned that in principle the method could be extended to the synthesis of multi-metal oxides with a specific stoichiometry. Also in this case the choice of the appropriate precursors is probably crucial. As lanthanides(III) and copper(II) show similar lability, among multi-metal lanthanide oxides the ones related to cuprates, $Ln_xCu_yO_z$, appeared interesting [7]. Several chemical compositions are known and in particular La_2CuO_4 is famous, being the parent of the first family of mixed-metal oxides that were found to show high temperature superconductivity [8].

Here the use of $[La_4(CO_3)(O_2CNBu_2)_{10}]$ [6b] and $[Cu(O_2CNBu_2)_2(py^*)_2]$ (py* = 4-dimethylamino pyridine) as precursors of nanostructured La_2CuO_4 powders is described. The precursors have been chosen on the basis of their preparation, tractability and solubility in scarcely polar solvent. Part of the discussion is devoted to the synthesis of the suitable copper derivative.

2. Experimental

2.1. Materials and instrumentation

All manipulations except extractions were performed under a dinitrogen atmosphere unless otherwise noted. Commercial 4-dimethylamino pyridine (Sigma-Aldrich) was used as received. $[La_4(CO_3)(O_2CNBu_2)_{10}]$ [6b] and $[Cu(O_2CNBu_2)_2(NHBu)_2]$ [9] were prepared according to the literature.

FTIR spectra in the solid state were recorded with a Perkin-Elmer "Spectrum One" spectrometer, with ATR technique. The lanthanum content in the reagent was determined according to this procedure: the sample was treated in a platinum crucible with diluted HNO_3 and the mixture gently warmed; the resulting solution was then evaporated to dryness. After calcination, the weight of the

solid residue (corresponding to the lanthanum oxide) was determined. The copper content in the precursor was determined by EDTA titration.

BET analysis were performed using N_2 adsorption at 77 K (ASAP 2020, Micrometitics).

The La/Cu ratio determination in the lanthanum cuprate was performed by inductively coupled plasma optical emission spectrometry (ICP-OES Thermo Scientific ICAP6300 Duo) with external calibration at λ 324.754 nm (Cu) and λ 412.323 nm (La). Samples were acid digested with *aqua regia* solution in a ceramic crucible on a hot plate till complete dissolution and properly diluted with distilled water.

Transmission electron microscopy (TEM) measurements and selected area electron diffraction (SAED) were collected by using a LIBRA 200FE ZEISS at 200 kV. TEM data analysis were performed with iTEM Software (Olympus Soft Imaging Solutions).

2.1.1. Preparation of [Cu₂(O₂CNBu₂)₄(py)₂] (py = pyridine)

Pyridine (4.9 g, 62.0 mmol) was added to a solution of $[Cu(O_2CNBu_2)_2(NHBu_2)_2]$ (3.9 mmol) in toluene (70 mL). The mixture was stirred under CO_2 at room temperature. The solution was cooled at –30 °C. A turquoise crystalline solid separated from the solution and after 12 h the suspension was filtered. After filtration the solid was dried under vacuum (1.3 g; 68.5 % yield). Anal. Calcd for $[Cu_2(O_2CNBu_2)_4py_2]$, $C_{46}H_{82}Cu_2N_6O_8$: CO_2, 18.1; Cu, 13.0. Found: CO_2, 17.6; Cu: 12.9. IR (nujol) (cm^{-1}, range 1700-600 cm^{-1}): 1592 s, 1465 s, 1377 s, 1313 s, 1267 m, 1215 m, 1113 m, 1070 m, 1033 m, 792 m, 751 m, 733 m, 696 m, 670 m, 623 m. Some crystals were selected to carry out X-Ray diffraction studies.

2.1.2. Preparation of [Cu(O₂CNBu₂)₂(py*)₂] (py* = 4-dimethylamino pyridine)

A solution of $[Cu(O_2CNBu_2)_2(NHBu_2)_2]$ (23.5 mmol) in toluene (70 mL) was treated with 4-dimethylamino pyridine (5.74 g, 47.0 mmol). The mixture was stirred under CO_2 at room temperature. The precipitation of a violet solid was observed. The suspension was filtered and the solid was washed with heptane and dried under vacuum (58.1 % yield). Anal. Calcd for $[Cu(O_2CNBu_2)_2py*_2]$, $C_{32}H_{56}CuN_6O_4$: CO_2, 13.5; Cu, 9.7. Found: CO_2, 13.5; Cu: 9.7. IR ATR (cm^{-1}): 2955 w, 2928 w, 2872 mw, 2859 mw, 1614 s, 1552 s, 1540 s, 1467 m, 1450 m, 1414 m, 1391 m, 1349 w, 1312 m, 1294 m, 1231 s, 1203 w, 1113 mw, 1079 w, 1020 m, 950 w, 933 mw, 902 mw, 876 mw, 862 mw, 816 s, 762 mw, 748 mw, 731 w, 674 w. The solubility of the compound in toluene at room temperature is about 7 g/L.

2.1.3. Preparation of La₂CuO₄ by hydrolysis of [Cu(O₂CNBu₂)₂(py*)₂] and [La₄(CO₃)(O₂CNBu₂)₁₀] (La/Cu molar ratio 2)

$[Cu(O_2CNBu_2)_2(py^*)_2]$ (2.035 mmol) were added to $[La_4(CO_3)(O_2CNBu_2)_{10}]$ (1.023 mmol) in anhydrous toluene (100 mL). A solution of H_2O (5.5 mL, 0.307 mmol) in THF (25 mL) was slowly added under stirring. The evolved CO_2 was frequently removed by vacuum/N_2 cycles. A suspension of a finely divided pale blue solid was obtained. The slurry was warmed at 40 °C under stirring for 4 h. After decantation, the waxy residue was washed for three times with a mixture of THF/toluene (volume ratio 1:2; 75 mL). Every time the mother liquor was evaporated to dryness without formation of any solid residue. The light blue powder was finally dried under vacuum at room temperature for 2 h, sealed in vials under N_2 and labelled as **La2Cu-Car** (1.20 g; 87.8% yield as $La_2(CO_3)_3 \cdot Cu(CO_3) \cdot 5\ H_2O$). FTIR-ATR (AD-6) (cm^{-1}): 3316 broad, 1471 s, 1379 s, 1263 w, 1097 w, 1055 w, 1019 w, 847 m, 747 m, 678 m. The amount of the volatile components in the mixed lanthanum/copper carbonate was determined through a simultaneous thermal analyser Netzsch 449 Jupiter, which combines a sensitive balance for use in thermogravimetric analysis (TG) with a heat-flux differential scanning calorimetry (DSC) for simultaneous TG–DSC analysis. TG and DSC analyses were obtained in the following instrumental conditions: open alumina crucibles, heating rate of 10°C/min under 30 ml/min nitrogen gas flow, 25 mg of sample dried at 40°C for six hours.

A sample of **La2Cu-Car** was heated in air in a furnace at 600 °C for 12 h and a black solid formed that was labelled **La2Cu-Ox600**. Its XRD powder diagram showed the presence of a tetragonal crystalline phase of La_2CuO_4. For ICP analysis, a sample of **La2Cu-Ox600** (19 mg) was heated over a heating plate in a porcelain crucible in the presence of aqua regia (2 mL) for four times, dissolving the solid residue in 2 % aqueous HNO_3 (50 mL). A portion of the solution (100 μL) was further diluted 10 mL and then measured by ICP analysis which revealed a metal content of 2.15 ppm (La) and 0.48 ppm (Cu) corresponding to a La/Cu molar ratio of 2.05.

A portion of **La2Cu-Ox600** was heated at 850 °C for 6 h and labelled **La2Cu-Ox850**. Its XRD powder diagram showed a single crystalline phase corresponding to an orthorhombic phase of La_2CuO_4. TEM studies confirmed the presence of the La_2CuO_4 tetragonal phase in **La2Cu-Ox600** and of the orthorhombic one in **La2Cu-Ox850** as evidenced by the XRD diffraction measurements.

2.2. *Crystallographic Determinations.*

The X-ray diffraction study was carried out at room temperature by means of a Bruker Smart Breeze CCD diffractometer operating with graphite-monochromated Mo-K_α radiation. The sample was glued to a glass fibre and its lattice parameters were evaluated as a preliminary step to the crystallographic study. On the basis of those results the intensity data collection was done up to the

limits mentioned in Table 1. The intensities were corrected for Lorentz and polarisation effects and for absorption by means of a multi-scan method [10]. The structure solution was obtained by the automatic direct methods contained in SHELX97 programme [11]. After the completion of the molecular model, the first refinement cycles led to unrealistic C–C bond distances in one of the butyl branches of the carbamato ligand and to abnormally prolate displacement ellipsoids for the atoms in this residue and the pyridine ligand. Based on these results, we treated these groups as statically disordered over two positions; the sum of the alternative positions was constrained to unity. Hydrogen atoms were treated as riding in idealized geometry, and all non-hydrogen atoms were assigned anisotropic displacement parameters. Convergence was reached for the reliability factors listed in Table 1. The programs contained in the suite WINGX [12] were also used for other control calculations and preparation of publication material.

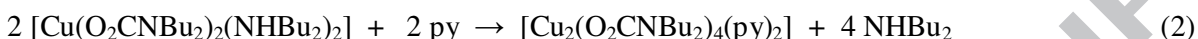**Table 1.** Crystal data and structure refinements

	$[Cu_2(O_2CNBu_2)_4(py)_2]$
Formula	$C_{46}H_{82}N_6O_8Cu_2$
Fw $(g \cdot mol^{-1})$	974.25
λ (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.7841(2)
b (Å)	9.1438(2)
c (Å)	28.1425(6)
β (°)	99.8520(10)
V (Å^3)	2734.14(10)
Z	2
ρ_{calc} $(Mg \cdot m^{-3})$	1.183
μ (mm^{-1})	0.828
θ range (°)	2.345 - 26.993
Data collected	20236
Independent reflections	5955
R_{int}	0.0277
Restraints/Parameters	221 / 335
Goodness-of-fit (GOF) on F^2	1.141
R_1; wR_2 $[I > 2\sigma(I)]$	0.0792; 0.2141
R_1; wR_2 [all data]	0.1062; 0.2311
Res. dens. $(e \cdot Å^{-3})$	0.538; −0.466

Results and discussion

Solid state methods of preparation of La_2CuO_4 starting from mixtures of metal oxides and/or carbonates require several cycles of grinding and heating at high temperature and often afford mixed phases. Some syntheses that avoid these problems have been recently reported in the literature: they describe the use of intimately dosed precursors, like oligo-hetero-nuclear molecular species with the right molar ratio between the two metals [13] or, alternatively, sol-gel routes [14]. The strategy here adopted starts from solution of the molecular precursors of the single metals. Its success depends on the observance of some rules: 1) the molar ratio between the two precursors has to be the right one, to avoid the formation of solid mixtures, difficult to purify; 2) in the course of the aggregation of the particles to form the solid precursor of the final oxide (in our case the mixed carbonate) this molar ratio must be maintained. The former point can be easily respected is the precursors have a well-defined composition and are treatable without particular difficulties. The fulfilment of the latter point assumes that both metal centres are involved with a similar rate in the aggregation process in such a way that, even if the initial solid material is not a single specific product or a defined solid solution, nevertheless an intimate blended precipitate is obtained where the preset molar ratio is preserved. If this is the case, a subsequent relatively mild thermal treatment can favour the formation of the desired product.

The molecular precursors here selected can be easily prepared and have a well defined composition. Well defined lanthanide *N,N*-dibutylcarbamato complexes can be promptly prepared starting from aqueous solution of the metal chloride by extraction in hydrocarbons containing $NHBu_2$ saturated with CO_2.[15] For instance, the lanthanum species, $[La_4(CO_3)(O_2CNBu_2)_{10}]$, prepared according to this procedure, has been previously used [6b] for the preparation of a lanthanum cerium mixed oxide. About copper, the derivative $[Cu(O_2CNBu_2)_2(NHBu_2)_2]$ would have the advantage of a simple and rapid preparation, also in this case by extraction from aqueous solution of copper(II) salts (chloride or sulphate) [9], nevertheless the product is not easily treatable since it liquefies at about 30 °C. Although it was not structurally characterized, it is reasonable to suppose that it has an arrangement similar to that of the *N,N*-dibenzylderivative $[Cu(O_2CNBz_2)_2(NHBz_2)_2]$ (Bz = CH_2Ph) that is a mononuclear species where the copper centre shows coordination number 4 and planar geometry, with two monodentate carbamato ligands in *trans* position and the other sites occupied by the amines which are involved in hydrogen bonds with the non-coordinated oxygen atom of the carbamato groups [9]. With the purpose of obtaining a more convenient copper precursor, $[Cu(O_2CNBu_2)_2(NHBu_2)_2]$ was treated with pyridine to substitute the coordinated amine. No reaction was observed under N_2, presumably for the higher basicity of $NHBu_2$ with respect to

the heteroaromatic nitrogen base. Nevertheless, by operating in the presence of CO_2, the substitution proceeded smoothly. Carbon dioxide is able to subtract $NHBu_2$ according to equilibrium 1, so forcing the substitution reaction 2.

$$2\ NHBu_2 + CO_2 \rightarrow [NH_2Bu_2][O_2CNBu_2] \tag{1}$$

$$2\ [Cu(O_2CNBu_2)_2(NHBu_2)_2]\ +\ 2\ py\ \rightarrow\ [Cu_2(O_2CNBu_2)_4(py)_2]\ +\ 4\ NHBu_2 \tag{2}$$

In the product, according to the elemental analysis, the py/Cu molar ratio was 1, and its crystal structure, obtained by single crystal X-ray diffraction methods, showed that the species was formed by dinuclear molecules as reported in Figure 1. The formation of mononuclear or dinuclear derivatives, $[Cu(O_2CNR_2)_2(NHR_2)_2]$ or $[\{Cu(O_2CNR_2)_2\}_2(NHR_2)_2]$, respectively, probably is related to the nature of the amine, to the conditions used in the course of the crystallization and, in addition, to the relative solubility of the two species. For instance, in the case of R = Et, both species were separated in different conditions [16].
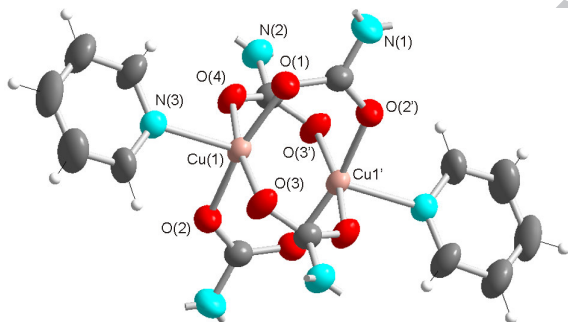

Figure 1 View of the molecular structure of $[Cu_2(O_2CNBu_2)_4(py)_2]$. Butyl groups bonded to the nitrogen atoms have been omitted for clarity. $' = 1 - x, 2 - y, 1 - z$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu_2(O_2CNBu_2)_4(py)_2]$

Cu(1)–O(1)	1.968(4)	Cu(1)–O(3)	1.961(3)
Cu(1)–O (2)	1.971(4)	Cu(1)–O(4)	1.968(3)
Cu(1)–N(3)	2.1826(17)	Cu(1)···Cu(1')	2.6263(9)
O(1)–Cu(1)–O(2)	169.02(14)	O(1)–Cu(1)–O(3)	89.86(18)
O(1)–Cu(1)–O(4)	87.62(16)	O(2)–Cu(1)–O(3)	89.44(18)
O(2)–Cu(1)–O(4)	91.01(18)	O(3)–Cu(1)–O(4)	169.06(14)
O(1)–Cu(1)–N(3)	95.90(17)	O(2)–Cu(1)–N(3)	95.07(17)
O(3)–Cu(1)–N(3)	95.7 (2)	O(4)–Cu(1)–N(3)	95.2(2)

The structure of $[Cu_2(O_2CNBu_2)_4(py)_2]$ consists of centrosymmetric dinuclear molecules with paddle-wheel cage, as shown in Fig. 1. Four dibutylcarbamato ligands bridge the Cu(II) centers and the coordination is completed by two apical pyridines. The butyl legs of the carbamato ligands and the pyridine are disordered at room temperature. The former have been omitted from the figure for clarity, while the pyridine was drawn in its most populated position. This type of structure is very common in Cu(II) carboxylates and the Cambridge Crystallographic Data Base contains several examples. For paddle-wheel molecules CuO_4N type Cu···Cu distance ranges between 2.575 and 3.261 Å with a mean value 2.67(5) Å. Our compound shows a Cu···Cu distance very close to this value: 2.626 Å.

Despite its crystalline nature, the compound was rather sticky and deliquescent in such a way that its quantitative transfer from a container to another was difficult.

Another complex was then prepared by reacting $[Cu(O_2CNBu_2)_2(NHBu_2)_2]$ with 4-dimethylamino pyridine (py*). The reaction carried out under CO_2 proceeded with formation of $[Cu(O_2CNBu_2)_2(py^*)_2]$. Unfortunately, several attempts of crystallization afforded twinned crystals unsuitable for X-ray diffraction studies. However, the solid was well formed and easily treatable, so it was used to try the preparation of the lanthanum cuprate La_2CuO_4.

Both $[Cu(O_2CNBu_2)_2(py^*)_2]$ and $[La_4(CO_3)(O_2CNBu_2)_{10}]$ show a good solubility in hydrocarbons. They were dissolved in toluene in the right molar ratio (La/Cu = 2.0) and their hydrolysis was carried out by addition of a solution of an excess of H_2O in THF. From the suspension a pale-blue solid was recovered, **La2Cu-Car**. The filtrate did not contain detectable amounts of copper and lanthanum, thus supporting the complete precipitation of both metals presumably in the form of carbonates or oxo-carbonates. An X-ray powder diagram revealed that the material was amorphous. The infrared spectrum was characterized by a broad absorption at about 3350 cm^{-1} attributable to H–O stretching vibrations of H_2O and by intense bands centred at 1470 and 1380 cm^{-1} attributable to the C–O stretching vibrations of the carbonato ions corresponding to the absorptions reported in the literature for $La_2(CO_3)_2 \cdot 5H_2O$ [17]. As the bands are a bit broad it is possible that the bands due to the copper carbonate, the most intense at 1503 and 1393 cm^{-1} [18] are overlapped to the ones of the lanthanum derivative. Alternatively the solid could be a mixed carbonate instead of a mixture of hydrate $La_2(CO_3)_3$ and $Cu(CO_3)$.

TG-DSC analysis in the range 20-1000°C of **La2Cu-Car** (Fig. 2) shows complex curves with mass changes of 13.05% and 26.38% in the ranges 20-245°C and 245-1000°C, respectively. The collected data is in agreement with the hypothesis that we are in the presence of a species having formula $La_2Cu(CO_3)_4 \cdot 5H_2O$. In fact, the first mass change is close to stoichiometric value due to the dehydration (13.4%) of $La_2Cu(CO_3)_4 \cdot 5H_2O$, while the second one to the decarbonation

(26.2%) of the $La_2Cu(CO_3)_4$ with the formation of the product La_2CuO_4. Therefore, in the DSC graphic the endothermic peak at about 100 °C could be related to the loss of five H_2O molecules, while the other endothermic peaks at 300, 500°C and the two broad peaks in the temperature range 550-800°C to the loss of CO_2. To be noted that a TG-DSC study of hydrated $La_2(CO_3)_3$ reports the ultimate CO_2 release between 525 and 770 °C, assigned to the loss of CO_2 by $La_2O_2(CO_3)$ [19].
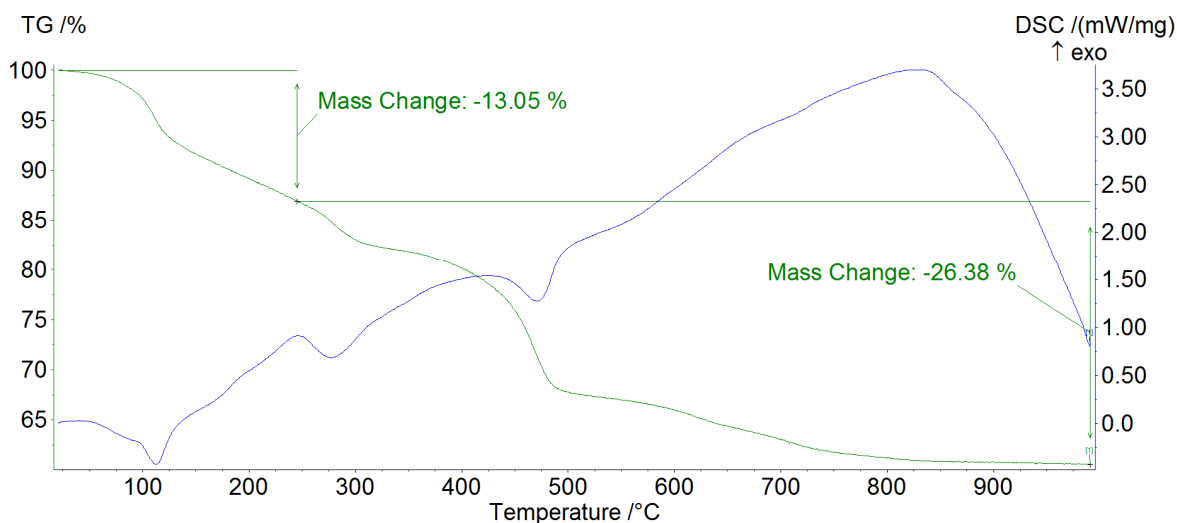

Figure 2 – TG-DSC analysis in the range 20-1000°C of the mixed lanthanide/copper carbonate using 25 mg sample dried at 40°C for six hours, open alumina crucibles and a heating rate of 10°C/min under 30 ml/min nitrogen gas flow.

A sample of **La2Cu-Car** was heated in a furnace in air at 400 °C for 6 h, turning black. XRD diagram of the powder did not reveal the formation of any detectable crystalline phase.

Another sample of the mixed carbonate was heated at 600 °C for 12 h, with formation of **La2Cu-Ox600**. In this case the X-ray powder diffractogram showed the lines due to a tetragonal phase (*I* 4/*mmm*, no. 139) of La_2CuO_4 (Figure 3a). A comparison with the calculated diffraction patterns relative to the tetragonal T and T' modifications of La_2CuO_4 showed that our compound corresponded to the apparently metastable [20] T' phase I4. A full pattern matching fitting refinement [21] of our pattern gave cell parameters a = 4.02, c = 12.58 Å with a unit cell volume of 203 $\mathring{A}^3$, very close to those reported for the T' modification. The average crystallite size was estimated to be about 15 nm by the Scherrer equation [22].
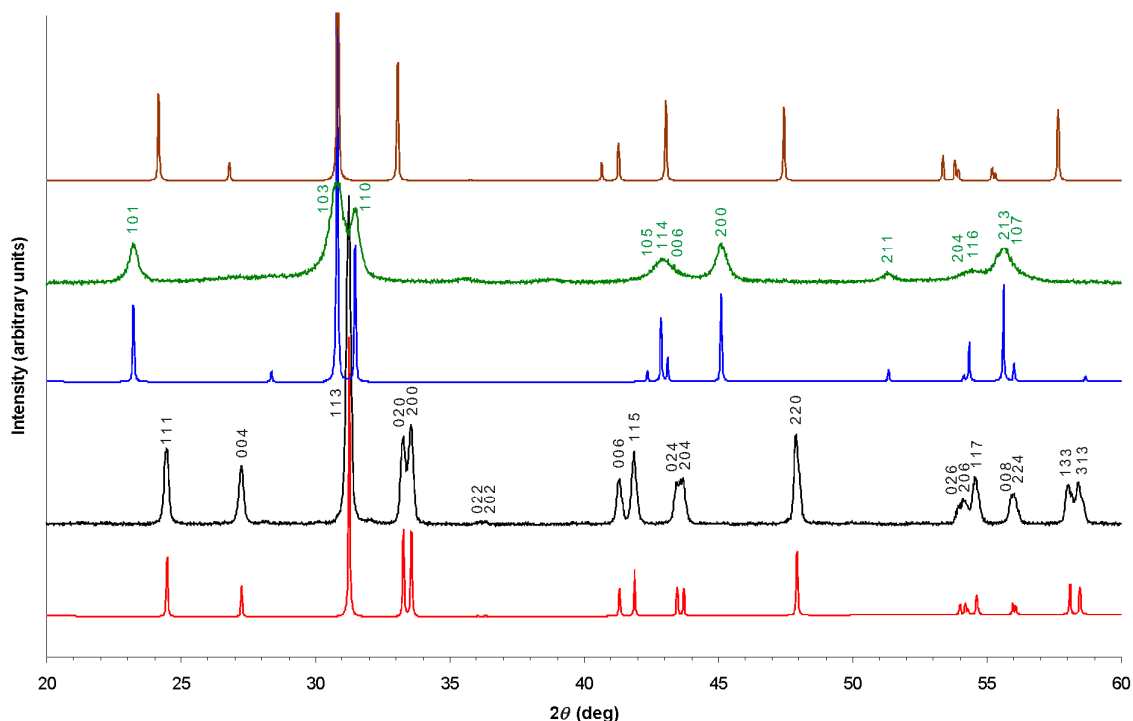
Figure 3. Comparison between experimental XRD pattern of **La2Cu-Ox850** (black) and calculated XRD pattern of O phase (red) and between experimental XRD pattern of **La2Cu-Ox600** (green) and calculated XRD patterns of T' (blue) and T (brown) phases.

Traces of CuO (tenorite) were observed. According to the preset La/Cu molar ratio, the presence of tenorite should be accompanied by an equivalent amount of lanthanum in the form of oxide or oxo-carbonate [19]. Although no evidence of other crystalline phases was observed, this does not exclude the presence of the lanthanum species, as they could be amorphous. On the other hand, ICP-OES analysis carried out on a **La2Cu-Ox600** sample confirmed a La/Cu molar ratio of 2.05.

BET analysis revealed the presence of a non-porous metal oxide with a surface area of 10.9 m^2/g. Although some sporadic examples of surface areas higher than 15 m^2 g^{-1} are reported for La_2CuO_4 [14b], the usual range is 0.5–11. The value observed for our sample is close to the highest limit in this range.

After treatment of **La2Cu-car** at 850 °C **La2Cu-Ox850** was obtained. Its X-ray powder diffractogram showed the lines due to the *Fmmm* (69) orthorhombic phase (Figure 3b). A full pattern matching fitting refinement [21] of our pattern gave cell parameters *a* = 5.36, *b* = 5.41, *c* = 13.15 Å with a unit cell volume of 381 Å^3. The average crystallite size was estimated to be about 50 nm by the Scherrer equation [22].

TEM analysis of the metal oxides agrees with XRD results. Selected area electron diffraction (SAED) analysis of **La₂Cu-Ox600** and **La₂Cu-Ox850** revealed their high crystallinity (Fig. 4). Their electron-diffraction patterns were successfully indexed based on tetragonal (*I4/mmm space*

group) and orthorhombic (*Fmmm space group*) La$_2$CuO$_4$, respectively. Although the two samples showed a common lamellar structure, a different crystal morphology was observed. La$_2$Cu-Ox600 appeared composed by thin e small lamellae composed of polycrystalline sheets of about 500 nm in size (Fig 4 a). On the other hand, La$_2$Cu-Ox850 showed larger and well shaped crystalline aggregates of micrometer sizes composed by clearly defined hundreds-nanometer crystalline domains (Fig. 4 b). Since the particle sizes observed by TEM refer to crystalline aggregates they are considerably larger then the mean crystallite size obtained by the Scherrer equation.
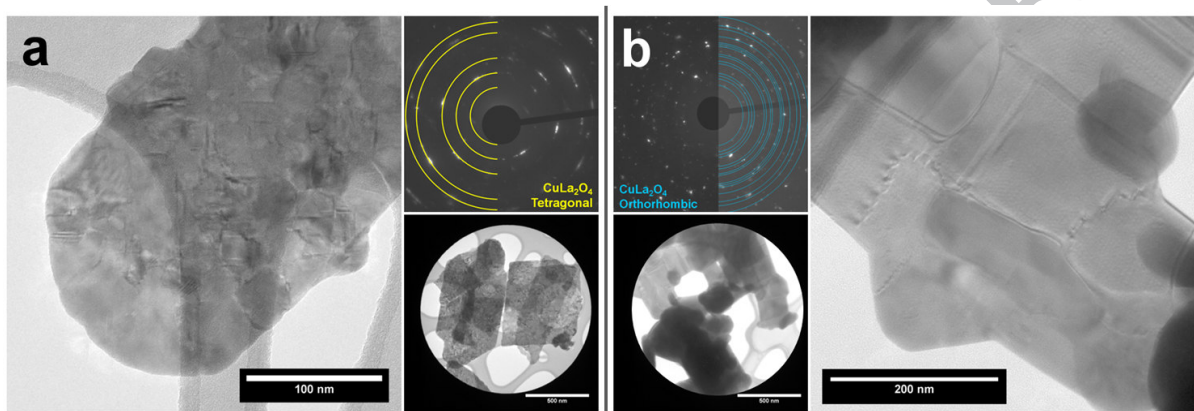

Fig. 4: a) La$_2$Cu-Ox600 sample, representative TEM micrograph (left side) and SAED analysis with the corresponding low-mag TEM micrograph (right side); b) La$_2$Cu-Ox850 sample, representative TEM micrograph (right side) and SAED analysis with the corresponding low-mag TEM micrograph (left side).

La$_2$CuO$_4$ crystallizes in three different structures [20], namely a tetragonal one, of the K$_2$NiF$_4$-type (T), an orthorhombic one (O) describable as a distorted K$_2$NiF$_4$ structure and a T' phase (Nd$_2$CuO$_4$-type). The T' modification transforms to the T phase when heated. The O phase was first observed [23] by examining at room temperature the lanthanum cuprate obtained by the solid method procedure. The authors report that it converts to the T modification at 260 °C. Recently the enthalpies of transition among the three phases have been assessed from differential scanning calorimetry studies [24], showing that the T' phase is most likely metastable at all temperatures.

Interest in the different phases of the lanthanum cuprate is related to the studies in the superconductivity field, since La$_2$CuO$_4$ is the only system known so far that can be hole or electron doped in dependence of the used phase, T or T′, respectively. The T phase can be obtained [20] by solid state reaction between the binary metal oxide (temperatures up to about 1000 °C). The T' modification was prepared by flux techniques in fused NaOH, KOH or CsOH at 380 °C [23, 25] or by a two step process in which the T phase is initially reduced with H$_2$ or CaH$_2$ and the reduction product is reoxidized to the T' phase at 300 °C in air [26, 27].

According to the literature [20, 24] the T' phase converts at 450 °C to the T phase that remains unmodified up to 800 °C and by cooling converts to the O phase at about 250 °C. It is reported that the O → T transformation is reversible, while the T' → T one is irreversible [24]. In our case the calcination of the intermediate hydrated mixed carbonate of lanthanum and copper at 600 °C followed by cooling down to room temperature affords the T' modification without evidence of the presence of the O and/or T phases. This result could be explained with a kinetic barrier in our conditions for the T' → T transformation. On the other hand, after heating at 850 °C and then cooling down to room temperature, the O phase is obtained, in agreement with the literature.

4. Conclusions

The hydrocarbon soluble complexes $[La_4(CO_3)(O_2CNBu_2)_{10}]$ and $[Cu(O_2CNBu_2)_2(py^*)_2]$ (py* = 4-dimethylamino pyridine) were found to be good precursors of the lanthanum cuprate La_2CuO_4. Their hydrolysis, carried out in toluene at room temperature, afforded the complete precipitation of the metal ions with formation of $La_2Cu(CO_3)_4 \cdot$ n H_2O, where n depends on the dehydration and storage conditions of the material. The similar lability of the two metal centers lanthanum(III) and copper(II) can account for this outcome, but we cannot exclude that complexes of centers characterized by dissimilar kinetic behavior can interact in the original solution with formation of hetero polynuclear complexes, before or in the course of the hydrolysis, in such a way to favor, also in that case, the evolution towards a multi-metal species.

The mixed lanthanum/copper carbonate produced La_2CuO_4 by thermal treatment. A single crystalline phase corresponding to the T' tetragonal modification of the lanthanum cuprate was obtained at 600 °C. This route to the T' modification of La_2CuO_4 represents an alternative to the few available methods of preparations of this crystalline phase. It is worthy to mention that the here discussed preparation of the lanthanum cuprate from metal dialkylcarbamates could be extended to other systems, becoming a general synthetic low-temperature route to thermolabile mixed oxide phases.

Acknowledgement

Appendix A. Supplementary data

CCDC 1504020 contains the supplementary crystallographic data for complex $[Cu_2(O_2CNBu_2)_4(py)_2]$. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.xxxx/j.poly.xxxxxx.

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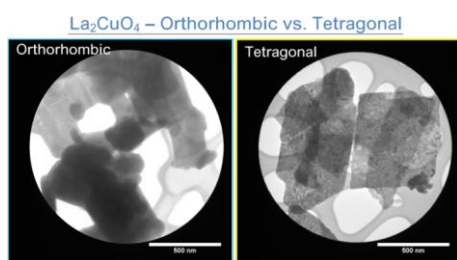
La2CuO4 – Orthorhombic vs. Tetragonal

A convenient preparation of La$_2$CuO$_4$ from molecular precursors

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By exhaustive hydrolysis of a mixture of lanthanum(III) and copper(II) carbamato complexes, La$_2$CuO$_4$ was obtained via the intermediate formation of the mixed carbonate that, by thermal treatment at 600 °C, afforded the tetragonal T' modification of the mixed oxide. The copper complex [Cu$_2$(O$_2$CNBu$_2$)$_4$(py)$_2$] was structurally characterized.