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Synthesis of p-Type Transparent LaOCuS Nanoparticles via Soft Chemistry

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We report here for the first time on the synthesis of nanoparticles of the p-type transparent conductor LaOCuS. Nanoparticles were obtained via a solvothermal route in ethylenediamine with dehydrated lanthanum chloride ($LaCl_3 \cdot 7H_2O$), copper monooxide, and elemental sulfur as precursors. Powder X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray photoelectron spectroscopy ascertained our sample to be of high purity, while laser diffractometry evidenced a monodisperse particle size distribution centered on 126 nm. The absorption spectrum and the current−potential curves recorded under chopped illumination asserted the optical transparency and the p-type electronic conductivity of our LaOCuS nanoparticles.

The oxysulfide LaOCuS is a layered compound built upon PbO-like $^{2}_{\infty}[LnO]^+$ and anti-PbO-like $^{2}_{\infty}[CuS]^-$ slabs, which condense to form a tridimensional edifice.[1] Very interesting properties ensue from this stacking such as a high p-type conductivity coupled with an absorption threshold at 3.14 eV[2] and an intense room temperature exciton emission at 378.2 nm.[3] As a result, LaOCuS may be viewed as a potential candidate for "invisible electronics" in transparent displays and the next generation of short-wavelength light-emitting devices. So far, this material has been prepared as thin films or as micronic polycrystalline samples[2−4] but never as nanoparticles.

The purpose of this paper is to report for the first time on the synthesis of nanoparticles of the p-type transparent conductor LaOCuS. Concomitantly, we investigated the physical properties of these nanoparticles prepared by a soft chemistry route (sample 1) and compared them to those of micronic LaOCuS particles prepared by a ceramic route (sample 2).

Low-temperature hydrothermal synthesis is probably one of the easiest ways to produce nanoparticles. This technique turns out to be very efficient in the particular case of p-type Delafossite materials.[5] Recently, Sheets et al. ended at the synthesis of BiOCuS,[6] a compound isostructural with LaOCuS, via this technique. As expected, attempts to extrapolate the synthetic conditions of BiOCuS to LaOCuS systematically led to the formation of a $La(OH)_3{-}Cu_xS$ mixture. Thus, we embarked on the preparation of the lanthanum copper oxysulfide in ethylenediamine (en) in mild conditions, that is, under autogenous pressure at low temperature with cupric or cuprous oxide, hydrated lanthanide chloride dried in an oven at 100 °C, and elemental sulfur flakes as precursors. Our choice of en as the solvent was dictated by the request for using a nonaqueous solvent with the concomitant ability for dissolving elemental sulfur and favoring the stabilization of Cu^+ cations at the expense of copper metal and Cu^{2+} ions. Namely, for the preparation of sample 1, a 0.715 mg blend of the precursors weighed in stoichiometric amounts was added to 21 mL of en. The mixture was sealed in a Teflon-lined autoclave and heated at 200 °C for 36 h. Then, the product was filtered under a hood, washed with distilled water and ethanol, and dried at ambient temperature. For indication, sample 2, used as benchmark, was prepared in a more trivial way from a mixture of La_2O_3, La_2S_3, Cu, and S in a 2:1:6:3 molar ratio, heated for 120 h at 700 °C (see the Supporting Information).

Figure 1 presents the room-temperature X-ray diffraction (XRD) pattern of sample 1. No crystalline impurity phase is detected, and the whole pattern is consistent with the LaOCuS structure. The structure refinement, carried out on the basis of the model reported by Palazzi,[1] ended at satisfactory reliability factors [$R_p = 8.95\%$, $R_{wp} = 12.05\%$, $R(\text{obs}) = 2.39\%$, $R_w(\text{obs}) = 2.59\%$, $R(\text{all}) = 2.68\%$, $R_w(\text{all}) = 2.62\%$] with a full occupancy of the La, Cu, S, and O sites and reasonable isotropic atomic displacement parameters [0.0115(10), 0.031(2), 0.004(2), and 0.011(6) $Å^{-2}$ for La, Cu, S, and O, respectively]. Release of the constraints on the occupancy rates let the reliability factors unchanged. The modeling of the broadening of the powder XRD peaks on the basis of a

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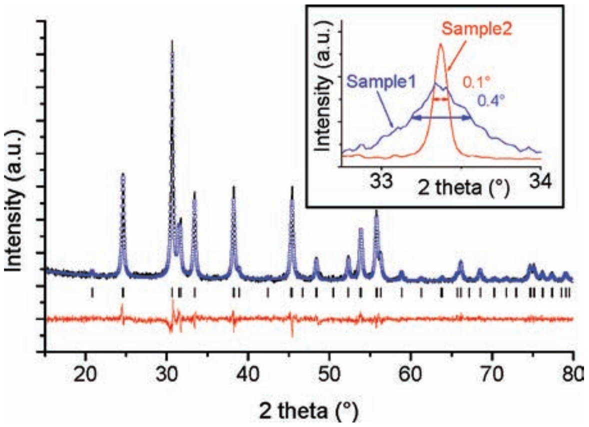

Figure 1. Rietveld refinement of the LaOCuS X-ray diagram for sample 1 prepared via the solvothermal technique [observed (blue), calculated (black), and difference (red) lines]. Inset: Comparison of the full-width half-maximum of the (1, 1, 1) diffraction peak of LaOCuS synthesized through the solvothermal (sample 1, blue curve) and ceramic (sample 2, red curve) routes.

fundamental parameters approach led to a mean crystal size of about 50 nm compared with 500 nm for sample 2 (see the inset in Figure 1). Energy-dispersive X-ray spectroscopy microprobe analyses on single crystals of samples 1 and 2 assert the chemical composition of the prepared material [i.e., La/Cu/S molar ratios of 1:0.93:0.93(4) and 1:1.10:1.01(5), respectively], while X-ray photoelectron spectroscopy (XPS) measurements agree with the occurrence of La^{3+} and Cu^{+} cations only in both materials (Cu $2p_{1/2}$/La $3d_{5/2}$ peaks at 933.1/836.5 and 932.9/836.7 eV for samples 1 and 2, respectively; see Figure S1 in the Supporting Information).

Scanning electron microscopy (SEM) images of samples 1 and 2 are given in Figure 2. Sample 1 depicts regular spherical grains with an average diameter of 110 nm (Figure 2a), which may condense in larger conglomerates (Figure 2b). In the opposite fashion, sample 2 evidences well-faceted hexagonal crystals that inherit the layered feature of the LaOCuS crystal structure with basal dimensions larger than 1 μm and a thickness of about 150 nm (Figure 2c).

From laser diffractometry (Figure 2), it appears that sample 1 consists of 480 nm agglomerates, which split into 126 nm-diameter single particles after 15 min of sonification in ethanol. That would correspond to spheres denoted by SEM analysis. In contrast, the sample 2 particles follow a bimodal size distribution centered on 1.1 and 5.4 μm, the relative ratio of which is only slightly impacted by sonification. On the basis of SEM images, it is reasonable to believe that the ceramic sample consists of ~1 μm particles that agglomerate into ~5 μm-diameter blocks. Of course, changes in the morphology and size of the LaOCuS samples go along with a modification of the specific surface area, which decreases from 24.36(7) m^2/g for sample 1 to 6.60(1) m^2/g for sample 2.

Photographs of the LaOCuS samples are gathered in Figure 3. To the naked eye, the color change is striking, going from off-white for sample 1 to brown for sample 2. This trend is corroborated by the Kubelka−Munk transformed diffuse-reflectance spectra of LaOCuS powders. For both samples, a steep absorption threshold is located at about 3.1 eV, as reported in the literature.[2] Nevertheless, while a slight and continuous increase of the absorption with energy is observed for sample 1 in the visible range, sample 2 exhibits a large absorption in the visible range with a marked onset at about 2.25 eV.

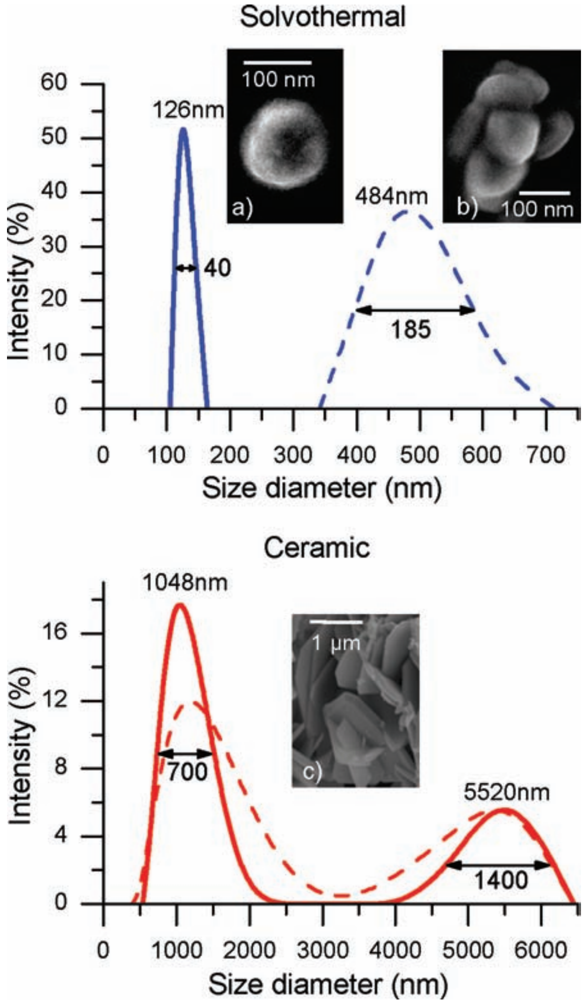

Figure 2. Laser particle size analysis on samples 1 (blue/solvothermal) and 2 (red/ceramic) before (dashed line) and after (solid line) sonification in ethanol for 15 min. The intensities of the signals are represented as a function of the particle size diameter. Inset: SEM photographs of samples 1 [particle (a) and agglomerate (b)] and 2 (c).

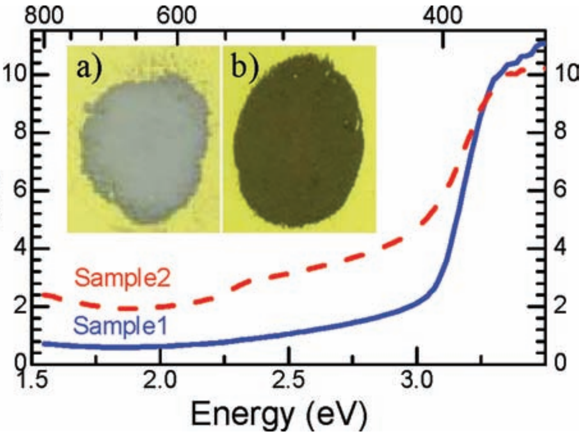

Figure 3. Absorption spectra of the LaOCuS samples prepared via a solvothermal (sample 1, blue solid line) or a ceramic (sample 2 red dash line) route. Inset: Photographs of LaOCuS powder samples (a) 1 and (b) 2.

Contrary to the absorption gap at 3.1 eV associated with a direct transition from the valence band top (built upon Cu 3d

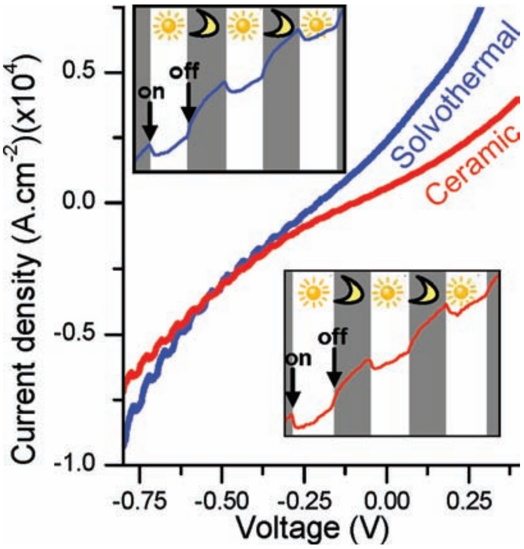

Figure 4. Current−potential curves measured under chopped illumination for samples 1 (solvothermal, blue curve) and 2 (ceramic, red curve). Under illumination (represented by the yellow regions in the insets), the reduction current density is increased, while the oxidation current density remains constant.

and S 3p orbitals) to the conduction band bottom (constructed on Cu 4s orbitals),[7] the origin of this bump in the continuum remains unexplained. Because scattering cannot be involved, we could incriminate the occurrence of nonstoichiometry, requested to account for the p-type conductivity of the materials. The nature of the defects, as well their concentration, could change with the chemical route, which could explain the change in the optical behavior going from sample 1 to sample 2.

The current−potential curves under chopped illumination of samples 1 and 2 are given in Figure 4. These curves are characteristic of a p-type degenerate semiconductor, that is, a semiconductor with a high enough defect concentration to act almost like a metal. Indeed, in the dark, the i(v) curves are characteristic of a quasi-metallic electrode. Namely, the current due to the majority carriers (anodic current for a p-type semiconductor) is analogous to that of a metallic electrode, and the current due to the minority carriers (cathodic currents for a p-type semiconductor) is also very important but to a lesser extent.

Under illumination, the reduction current is strongly enhanced, as witnessed by oscillations in Figure 4, insets. In contrast, the oxidation current remains unchanged under the same conditions. This phenomenon originates in the higher relative increase of the negative charge carriers compared to the positive charge carriers in the material when photoexcited. This is therefore an unambiguous proof of the p-type semiconducting character of LaOCuS nano- and microparticles obtained by a solvothermal and a ceramic route, respectively. The change in the current−potential curves going from sample 1 to sample 2 might be due to a slight modification of the charge carrier concentration with the synthetic route.

We have demonstrated the synthesis of LaOCuS nanoparticles with all characteristics of p-type transparent semiconductors. LaOCuS nanoparticles of about 120 nm were synthesized for the very first time in this work using en under solvothermal conditions. These nanoparticles exhibit a band gap around 3.1 eV, and their p-type character was ascertained by current−potential curves under chopped illumination. These nanoparticles might be used in p-type dye-sensitized solar cells, as well as in photoluminescence devices. Moreover, the new synthetic approach described here opens the door to the preparation of other rare-earth ReOCuS derivatives or doped compounds such as $\mathrm{La}_{1-x}\mathrm{Sr}_x\mathrm{OCuS}$[8−12] and $\mathrm{LaOCuS}_{1-x}\mathrm{Q}_x$ (Q = Se, Te).[2,13−15] Alternatively, this new synthesis route may also be used to prepare nanoparticles of other rare-earth oxysulfides[16−18] or fluorosulfides,[19−21] which may exhibit interesting photocatalytic activity[16,22,23] or p-type conductivity.[24]

Supporting Information Available: Syntheis, characterization, and XPS measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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