Copper Oxides Nanopowders
Synthesis by S.P.V.D. and Characterization

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The solar physical vapour deposition (s.p.v.d.) is an original process to prepare nanopowders. In this context, the paper presents and discusses the most important results referring to the CuO nano-powders doped with Mn, obtained by S.P.V.D. process. The methods used to characterize the powders after their elaboration were the X-ray diffraction analysis (XRD) and TEM. Also, the ATR-FTIR analysis shows that the number of defects is more in undoped CuO than in Mn-doped copper oxide powders.

Keywords: Nanopowders, Mn-doped, Solar Physical Vapour Deposition, Attenuated Total reflexion

Nanomaterials based on metal oxides with different morphologies have drawn particular attention due to the structural flexibility combined with a variety of properties which have a wide range of potential applications [1-7]. Such metal oxides nanostructures can not only receive the properties from their bulk form such as piezoelectricity, chemical sensing, and photodetection, but also possess unique properties associated with their highly anisotropic geometry and size dimension [1-7]. The study of novel metal oxide nanostructures is a very important issue, from fundamental and industrial point of view. An important topic is to directly synthesize nanostructured materials with a particular morphology and desired functionality for specific applications.

In the science and technology of copper oxide nanopowders several key subjects have to be completed: controlling the morphology and chemical composition of the powders; purity and particle size during the synthesis; controlling the level of the dopants. Until now the copper oxide powders with different morphology (prismatic, ellipsoidal, hexagonal, nanowire, nanorod) were obtained by sol-gel, hydrothermal, hydrolysis, microwave etc [1-6].

An original process to prepare copper oxide nanopowders, pure and doped, is the Solar Physical Vapour Deposition (Solar PVD, S.P.V.D.). In this context, the paper presents and discusses the most important results referring to the CuO nano-powders doped with Mn, obtained by solar energy.

Experimental part
Materials and methods

The solar reactor makes possible to implement high temperature material processing. The pure CuO and Mn-doped nanopowders were obtained using the HELIOTRON at Odeillo/Font Romeu, France. The commercial powders were used like precursors, under 50hPa air pressure and the density solar flux from 910 to 933 W/m^2. The initial powders were sublimated inside the evaporation chamber using solar energy, concentrated by means of a parabolic mirror on the sample. The nanopowders were collected by aspiration on a nanoporous ceramic filter or/and by condensation on a cold finger.

The first method used to characterize the powders after elaboration was the X-ray diffraction analysis (XRD) which was done by an X-Pert Pro diffractometer.

Nanopowders morphology (particles shape and size distribution) has been studied by Transmission Electron Microscopy (TEM).

The IR spectra were recorded using a Jasco 6300 FT-IR spectrometer in the region of 4000 – 400 cm^{-1} with detector TGS, software Spectra Manager II. ATR spectra were obtained with an attenuated total reflection attachment Gladi ATR, apodization Cosine. The instrument had a spectral resolution of 4 cm^{-1}, which was used in all spectra determinations.

Results and discussions

Figure 1 shows the XRD patterns of the pure CuO and Mn-doped powders. It can be observed the presence of the copper (II) oxide (the tenorite phase of CuO, identified by ICCD ASTM file no. 01-089-5899) for each synthetized powder [7].

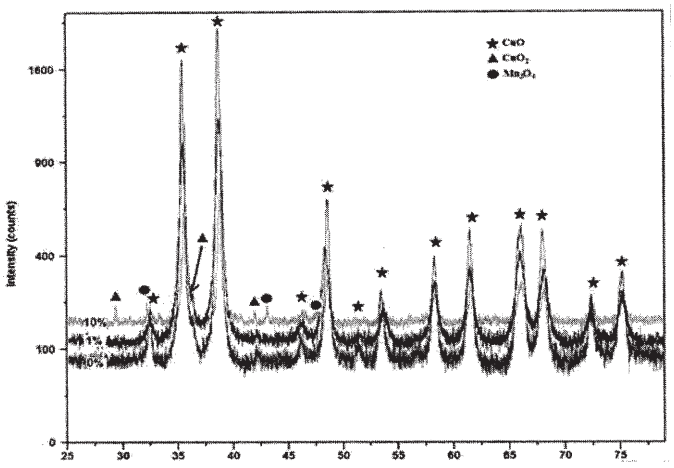

Fig.1. X-ray diagrams of the CuO nanopowders synthesized with solar energy

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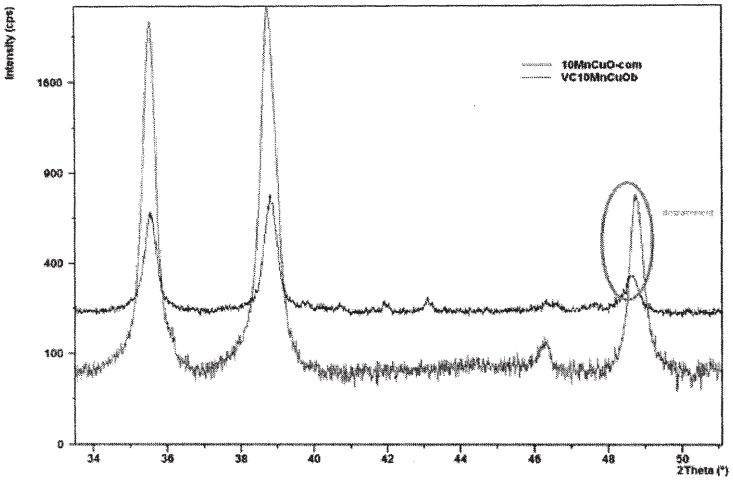

Fig.2.The displacement and enlargement of peaks for CuO obtained nanopowders

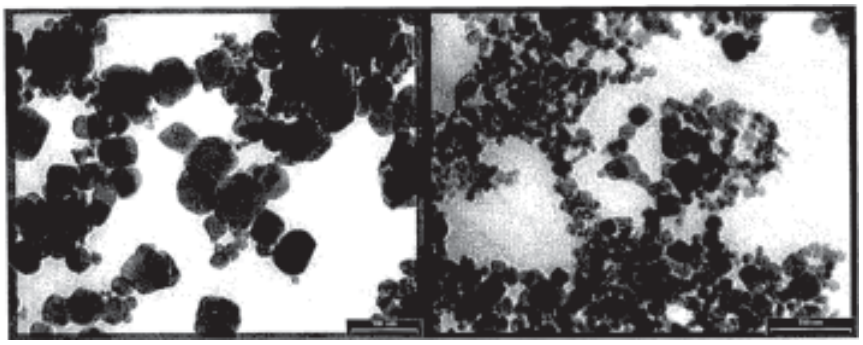

Fig. 3. TEM image of 1 % mol Mn doped CuO and 10% mol Mn doped CuO powders synthesized by S.P.V.D

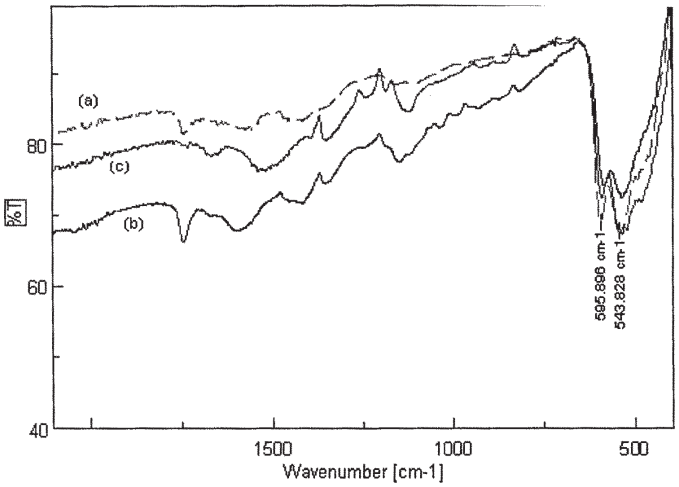

Fig.4. FTIR spectra of (a) undoped, (b) 1% and (c) 10% Mn-doped CuO

Also, it was observed that for small concentration of dopant (1%) all peaks in the XRD patterns can be indexed by the tenorite phase of CuO with a monoclinic structure; however in the case of 10%mol Mn doping, a Mn_3O_4 tetragonal phase appear (identified by ICCD ASTM file no. 01-075-1560) and a peak corresponding to Cu_2O phase (identified by ICCD ASTM file no. 04-016-6875). The presence of Mn like dopant in the crystal structure of CuO is demonstrated by the slight shift to the left of the peaks. It was found, nevertheless, that the displacement increases when the Mn content increases like, as shown in the figure 2 due probably to interstitial or substitution of Cu into the lattice (atomic radius of manganese is bigger than copper) [6].

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For the SPVD obtained CuO pure and Mn-doped nanopowders, TEM analysis (fig.3) reveal hexagonal and square particles with nanometric size of 22 to 46 nm. TEM images demonstrate the influence of Mn as dopant, due to the interstitial or substitution position in the crystal at small percentage of Mn and also due to the presence of cubic Mn_3O_4 structures for 10%mol Mn doped nanopowders.

FTIR analysis

The FTIR spectrum of CuO shows three characteristic strong peaks at 493, 543 and 595 cm^{-1} associated with the Cu-O vibrations.The spectra of CuO and doped nanopowders with MnO 1% and 10% as run by ATR are presented in Figure 4 (distorssions were eliminated by the advanced ATR corrections, ATRc).

With the addition of Mn the peaks are shifted at 537 and 587 cm^{-1} for Mn-doped (1 %) and at 536, 592 cm^{-1} for Mn-doped (10%), in the samples obtained by the process with solar energy.

The shifts due to Mn doping may be associated with the decrease in the surface area and surface defects [8].

Since this peaks is sharper in undoped CuO, it is inferred that the defects are more feqvently in the sample than in Mn-doped CuO.

Figures 5 and 6 presents the ATR-FTIR spectra of initial Mn-doped CuO powders and of similar samples Mn-doped CuO nanopowdres synthesized by S.P.V.D.

The information on the surface area and surface defects gained from the FTIR spectra can be used to understand the sensing mechanism of these samples [4].

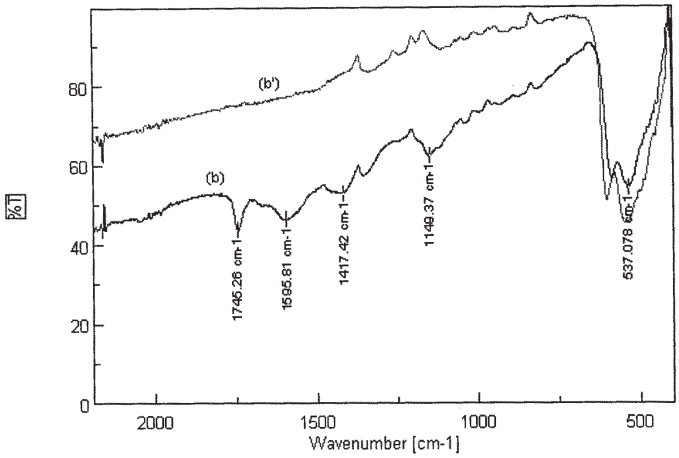

Fig.5. FTIR spectra of initial Mn-doped CuO powders 1% (b) and Mn- doped CuO nanopowdres synthesized by S.P.V.D. 1% (b')

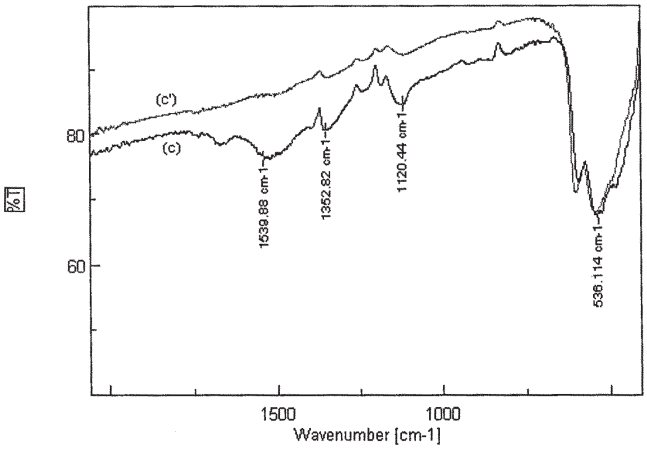

Fig.6. FTIR spectra of intial Mn-doped CuO powders 10% (c) and Mn-doped CuO nanopowders synthesized by S.P.V.D. 10% (c')

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