## Dependence of the magnetic properties $Gd_{2-x}Ce_xCuO_4$ , $0 \le x \le 0.15$ , on their particle size

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 $Gd_{2-x}Ce_xCuO_4$ ,  $0 \le x \le 0.15$ , have been synthesized by the solid state reaction, the sol-gel technique and the water-in-oil microemulsion, in order to vary the particle size. The samples have been characterized by x-ray diffraction, photon correlation spectroscopy and transmission electron microscopy. Magnetization and ac susceptibility measurements were performed between 4 and 300 K. The extrapolated linear part of the inverse magnetization shifts to lower temperatures as the particle size decreases. The internal field associated to the WF of the Cu moments diminishes with the particle diameter. Differences between the zero-field-cooling and the field-cooling magnetization curves were observed for  $T < T_N$ . These differences depend on the particle size.

Since the discovery of the new family of electron doped superconductors R<sub>1.85</sub>M<sub>0.15</sub>CuO<sub>4</sub> (with R=Pr, Nd, Sm, Eu, and M=Ce, Th)<sup>1</sup> much attention has been focused on the study of the properties of these materials.<sup>2</sup> Gd<sub>2</sub>CuO<sub>4</sub> has been found not to be superconducting when doped with Ce or Th,<sup>3</sup> as contrary to the lighter rare earths compounds. This family crystallizes in the tetragonal Nd<sub>2</sub>CuO<sub>4</sub>-type structure with the Cu(II) ions ordered antiferromagnetically (AF) at  $T_N \approx 270$  K. The interest in Gd<sub>2</sub>CuO<sub>4</sub> lies on the possible relationship between its magnetic properties and its nosuperconducting behavior. The magnetic properties of this compound have been studied in detail for single crystals and powders.<sup>4</sup> This compound shows a WF component below  $T_N \approx 270$  K, possibly due to a distortion of the oxygens surrounding the Cu moment in the T' phase, which occurs for rare earths lighter than Eu(III).

In the present work, we describe the synthesis of  $Gd_{2-x}Ce_xCuO_4$  (with x=0.00, 0.05, 0.10, and 0.15) using a sol-gel technique and water-in-oil (W/O) microemulsions. Both techniques allow us to obtain polycrystalline powders of controlled size. We performed magnetization measurements in order to study the influence of particle size on the magnetic properties of these materials.

We used three different techniques to obtain particles of different sizes:

(1) Solid state reaction, using a stoichiometric mixture of  $Gd_2O_3$  and CuO as starting materials. The mixture was ground in a ball mill and then annealed first at 800 °C for 24 h with several intermediate grindings followed by a second annealing at 850 °C for 48 h. The resulting powder was used as a reference.

(2) Sol-gel technique, using urea as gelificant agent. As starting materials stoichiometric amounts of nitrate salts were used, due to their high solubility in water. The solvent was evaporated directly on a hot plate with continuous stirring. When cooling a gel is formed, which is decomposed in an oven at 250 °C, yielding the precursor of these samples. After grinding the precursor, it was submitted to several annealings at different temperatures in order to obtain particles of different sizes. More details of this process had been previously reported.<sup>5</sup>

(3) Synthesis of  $Gd_2CuO_4$  was done by means of a W/O microemulsion. We used *n*-heptane as organic phase, Aerosol-OT (bis-2-ethyl hexyl sodium sulfosuccinate) as surfactant and a solution of citric acid and nitrate salts as an aqueous phase. The microemulsion was heated on a hot plate to evaporate part of the organic phase. This gel was washed with *n*-heptane and acctone. The resulting powder was dried yielding to the precursor of these samples. After grinding the precursor, it was subjected to different annealings.

The polycrystalline powders were structurely characterized by x rays. The size distribution was measured by photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM). The magnetic measurements were made between 4 K $\leq T \leq 300$  K using SQUID and VSM magnetometers in fields up to 5 kOe.

X-ray diffraction of the samples synthesized by the solid state reaction indicates a pure Gd<sub>2</sub>CuO<sub>4</sub> phase. Similar data for Gd<sub>2</sub>CuO<sub>4</sub>, obtained via sol-gel, show almost a pure phase for samples annealed at temperatures as low as 650 °C. The time necessary to obtain this phase decreases considerably when the calcination temperature increases. For example, 72 h are needed at 650 °C but only 3 h at 950 °C. Seven samples temperatures were obtained. between these two  $Gd_{2-x}Ce_xCuO_4$  (with x=0.05, 0.10, and 0.15) was also prepared via sol-gel. It was observed that when the annealing temperature decreases so does the solubility of Ce in the compound. When x = 0.05, 0.10, and 0.15 the pure phase is obtained only for temperatures above 700, 750, and 900 °C, respectively. For samples synthesized in W/O microemulsions, the Gd<sub>2</sub>CuO<sub>4</sub> phase is obtained at 700 °C. X-ray diffraction shows the presence of  $\approx 10\%$  of Gd<sub>2</sub>O<sub>3</sub> as a secondary phase. The amount of this secondary phase is almost independent of the annealing temperature. Five samples were



FIG. 1. Average diameter of  $Gd_2CuO_4$  particles as a function of the annealing temperature for samples obtained via sol-gel.

prepared between 700 and 950  $^{\circ}\mathrm{C}$  using W/O microemulsions.

The particle size of the different samples was measured by PCS. Figure 1 shows the average diameter of the particles as a function of the annealing temperature for samples obtained via sol-gel. As it can be seen the particle size increases with annealing temperature. The particles synthesized by ordinary solid state reaction present high polydispersity, contrary to the obtained by the wet methods, with sizes in the range  $0.2-4 \mu m$ .

Figure 2 shows two TEM photographs, one for a sample prepared by the solid state reaction [Fig. 2(a)], and the other for a sol-gel sample annealed at 750  $^{\circ}$ C [Fig. 2(b)]. As it can







FIG. 2. TEM photographs (a) for a sample prepared by solid state reaction and (b) for a sol-gel sample annealed at 750  $^{\circ}$ C.



FIG. 4. Inverse of dc susceptibility curves vs temperature for sol-gel and ceramic  $Gd_2CuO_4$  samples.



FIG. 5. Extrapolated temperatures from dc and ac susceptibilities for sol-gel  $Gd_2CuO_4$  samples.

be seen, ceramic samples are relatively large ( $\approx 1 \mu m$ ), while the sol-gel particles are of the order of  $\approx 100$  nm. The sizes measured by PCS and TEM agree well.

dc magnetization data show that the WF component found in single crystals and in polycrystalline samples of  $Gd_2CuO_4$  below  $\approx 270$  K<sup>4</sup> as shown in Fig. 3(a) for a ceramic sample, is depressed in a sample annealed at 800 °C, as seen in Fig. 3(b). The WF peak in single crystals occurs at the ordering temperature of Cu(II) moments and is due to a distortion from a perfect square of the CuO<sub>2</sub> plane, because of the displacement of oxygen atoms along the normal to the Cu-O bond. Such a distortion results in spin-canted antiferromagnetic domains ("canted" AF ordering of the Cu moments). This property is better appreciated when plotting the  $\chi^{-1}$  vs T, as done for sol-gel Gd<sub>2</sub>CuO<sub>4</sub> samples in Fig. 4. If we associate the extrapolated temperature of the linear part of  $\chi^{-1}$  with the onset of WF, we observe that the transition temperature seems to be reduced with the particle size. ac susceptibility measurements done in the same samples held



FIG. 6. Internal fields obtained from M vs H measurements for sol-gel, ceramic and single crystal Gd<sub>2</sub>CuO<sub>4</sub> samples.



FIG. 7. Internal fields obtained from M vs H measurements for sol-gel  $Gd_{2-x}Ce_xCuO_4$  samples.

similar results. In Fig. 5 it is shown the extrapolated temperature,  $T_{\rm extr}$ , obtained by ac and dc measurements. The disappearance of the internal field could be explained if the size of the particles becomes comparable with the correlation length of the Cu(II) antiferromagnetic order. Another explanation could be due to the surface effects which become more important for smaller particles and such effects could slightly modify the lattice parameters, which are determinant in the onset of WF.<sup>2</sup> It is worth mentioning that besides the effects on this peak, other features observed are the decrease of the absolute magnetization values and differences between field cooling (FC) and zero field cooling (ZFC) magnetization curves.

In Fig. 6 the evolution of the internal field,  $H_i$ , extrapolated from the paramagnetic part of M vs H measurements at high field as a function of the temperature for sol-gel is presented. Values for ceramic and single crystal samples are also included. It is clear that the internal field diminishes with the particle size.

For the sol-gel  $Gd_{2-x}Ce_xCuO_4$  samples,  $H_i$  decreases with the annealing temperature and cerium doping as seen in Fig. 7. The internal field is more sensitive to the thermal annealing than to cerium doping.

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