

C. Vázquez-Vázquez  
J. Mahía  
M.A. López-Quintela  
J. Mira  
J. Rivas

## Preparation of $Gd_2CuO_4$ via sol-gel in microemulsions

C. Vázquez-Vázquez · J. Mahía  
Prof. M.A. López-Quintela (✉)  
Department of Physical Chemistry  
University of Santiago de Compostela  
15706 Santiago de Compostela, Spain

J. Mira · J. Rivas  
Department of Applied Physics  
University of Santiago de Compostela  
15706 Santiago de Compostela, Spain

**Abstract** We have synthesized microparticles of  $Gd_2CuO_4$  via sol-gel technology in microemulsions, carrying out the sol-gel process inside the microdroplets of the microemulsion. The microemulsion was a mixture of cyclohexane/brij 96/ aqueous phase (70:20:10% weight). Urea was used as gelificant agent. The method is based on removing solvents from the mixture applying vacuum in order to obtain a gel when cooling

down. By calcinating the gel at low temperatures, we have attained the crystallization of  $Gd_2CuO_4$  microparticles. Samples were characterized by x-ray diffraction (XRD), photon correlation spectroscopy (PCS), and dc-magnetization (vibrating sample magnetometer (VSM)).

**Key words** Sol-gel – microemulsions – microparticles –  $Gd_2CuO_4$  – magnetic properties

### Introduction

The discovery of the new family of electron-doped superconductors  $R_{1.85}M_{0.15}CuO_{4-y}$  (with  $R$  = rare earth, and  $M$  = Ce, Th) [1, 2] has pointed out the great importance of the undoped  $R_2CuO_4$  [3–5] because of the possible relation between magnetism and superconductivity.  $Gd_2CuO_4$ , a perovskite-like compound with  $Nd_2CuO_4$ -type structure (T'-phase) [6], does not become superconductor when doped with Ce or Th [7], contrary to the lighter rare earths ( $R$  = Pr, Nd, Sm, Eu), and shows a complex magnetic behavior different from the other members of the family.

Until now, all the studies of these compounds have been performed on single crystals and powders obtained by solid state reaction [8]. This technique, which uses metal oxides as starting materials and needs several annealings at high temperatures during long time with frequent intermediary grindings, has however several problems, like, for example, poor homogeneity and high porosity of the samples, no control on the particle size, etc. To avoid these problems, which are common to the

synthesis of other type of high temperature superconductors, several sol-gel techniques have been developed, showing different advantages compared with the conventional ceramic fabrication techniques. For example, with sol-gel techniques [9–12] high purity and good homogeneous materials are achieved, they require lower processing temperatures and shorter annealing times than conventional techniques, they present high reproducibility, and they offer good control of the stoichiometry, size and shape of the particles obtained.

The study of fine and ultrafine particles has prompted increasing interest due to the new properties the materials present when grain size is reduced and, as a consequence, the new applications which can appear. The microemulsion method is a suitable way to synthesize monodisperse and nanosize particles.

A microemulsion is a thermodynamically stable system composed of (at least) three components: two immiscible and a surfactant. Taking advantage of the different solubility of salts between an aqueous and an organic phase, we can use water-in-oil (W/O) microemulsions as reaction

medium. W/O microemulsions are made up by nanodroplets of water dispersed in a continuous oily phase with the surfactant at the interface [13]. Surfactant molecules control nanodroplets size, and these can be used as microreactors [14–18].

In the present work we describe the synthesis of Gd<sub>2</sub>CuO<sub>4</sub> microparticles via sol–gel technology in microemulsions, which allow to obtain polycrystalline powders at lower temperatures than those used by solid state reaction.

### Experimental procedure

In all synthesis procedures carried out in this work the chemicals employed were Aldrich h.p. In order to obtain a polycrystalline reference pattern, Gd<sub>2</sub>CuO<sub>4</sub> was synthesized by solid state reaction. For this purpose, Gd<sub>2</sub>O<sub>3</sub> and CuO were used as starting materials. Gd<sub>2</sub>O<sub>3</sub> was previously dried 3 h at 650 °C. A stoichiometric mixture of these reagents was ground in a ball mill during several hours and then annealed in several steps with intermediary grindings: 12 h at 950 °C, 20 h at 1000 °C and, finally, 24 h at 1080 °C with a slow cooling rate of 2 °C/min.

For the synthesis of the microparticles we started with a microemulsion which contained 70% in weight of cyclohexane (organic phase), 20% of Brij 96, or decyl ethyleneglycol oleyl ether (surfactant), and 10% of an aqueous solution containing the metallic nitrates and urea, used as gelificant agent ([urea]/[salts] = 10). The sol–gel method with urea is explained elsewhere [12]. This system is not a single phase microemulsion at room temperature, but it becomes a single phase above 40 °C. Solvents were removed applying vacuum at 45 °C yielding to the formation of gels inside the droplets when cooling down. Vacuum periods range from 6 to 48 h. When the microemulsion was cooled down the mixture became a gel below 20 °C. Gels were calcinated at several temperatures (600°, 700° and 800 °C) during various periods of time (3, 15 and 39 h) in order to remove organic compounds and to get the crystallization of Gd<sub>2</sub>CuO<sub>4</sub>.

The structural characterization of the polycrystalline powders was carried out by x-ray powder diffraction, using a diffractometer Philips PW-1710 with Cu anode (radiation CuK<sub>α1</sub> of  $\lambda = 1.54060 \text{ \AA}$ ). The measurements were performed in air at room temperature. In order to determine the size distribution, measurements of photon correlation spectroscopy (PCS) were carried out. These measurements were performed with an Ar laser Liconix series 5000 of 5 W operating at  $\lambda = 488 \text{ nm}$  and a goniometer ALV-SP80 controlled automatically by means of an ALV-LSE unit. For these measurements, particles were dispersed in water. Magnetization of the samples was measured with a vibrating sample magnetometer (VSM).

### Results and discussion

By x-ray diffraction the ceramic sample was identified as pure and well crystallized Gd<sub>2</sub>CuO<sub>4</sub>. For the sol–gel in microemulsion method it was observed that at low temperatures cubic Gd<sub>2</sub>O<sub>3</sub> and CuO were the predominant phases but longer calcination periods, or higher temperatures, resulted in more proportion of Gd<sub>2</sub>CuO<sub>4</sub>. In Table 1, we summarize the peak area ratio between the mean peak of Gd<sub>2</sub>O<sub>3</sub> ( $d \approx 3.122 \text{ \AA}$ ) and the mean peak of Gd<sub>2</sub>CuO<sub>4</sub> ( $d \approx 2.770 \text{ \AA}$ ). The best results at 600 °C were obtained for 6 h under vacuum (area ratio approx 1:1). It was observed that, in general, the proportion of Gd<sub>2</sub>CuO<sub>4</sub> increases as the annealing temperature increases and also better crystallizations are obtained annealing for longer periods of time. In Fig. 1 is shown the evolution of the samples with the annealing temperature for 6 h under vacuum and 3 h of thermal treatment. An average crystallite size,  $D_{\text{hkl}}$ , was determined by applying the Debye–Scherrer's formula using the half maximum width,  $\beta$ , of x-ray diffraction peak at  $d \approx 2.770 \text{ \AA}$ :

$$D_{\text{hkl}}(\text{\AA}) = \frac{0.9 \cdot \lambda}{\beta \cdot \sin \Theta}$$

where  $\lambda$  is the x-ray wavelength and  $\Theta$  the Bragg angle. Results are shown in Table 2. We observe, as expected, a tendency to a great increase of crystallite size as the annealing temperature and annealing time increase.

By photon correlation spectroscopy (PCS) we obtained the size of the aggregates. The results show that the average hydrodynamic radius of the aggregates ranges between 250 and 450 nm regardless of annealing temperature and annealing time.

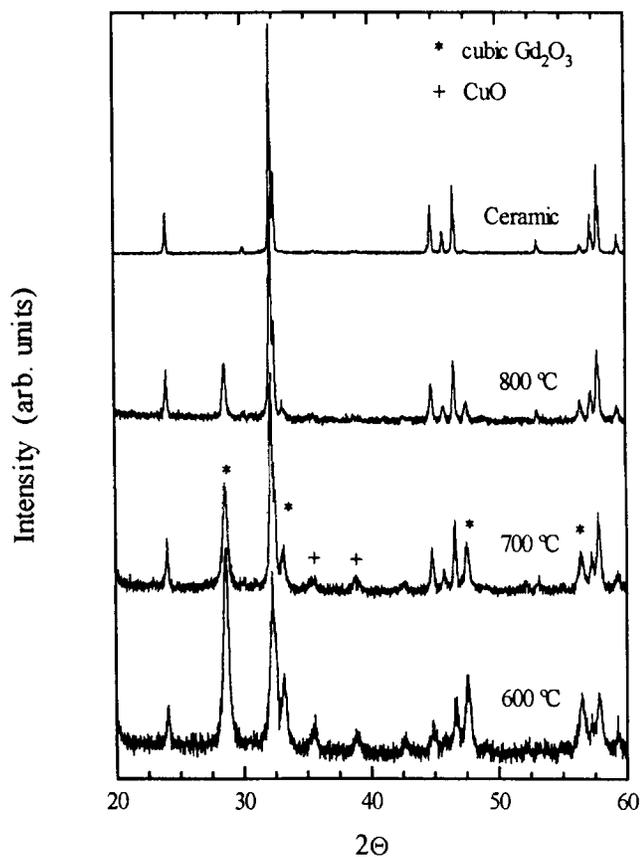
Initial magnetization of the samples was measured at different temperatures. The measurements of magnetization as a function of the applied magnetic field show a linear dependence but this linearity presents some deviations near zero magnetic fields. Extrapolating the linear part to zero magnetization we obtain a magnetic field which has been reported before in monocrystals [3–5] and ceramic samples [7] as an internal magnetic field intrinsic of the sample and related to the canting of the antiferromagnetic order of the copper ions. In Fig. 2 the internal field of the samples of 48 h under vacuum and the ceramic sample are represented as a function of the temperature. The internal fields for the ceramic sample agree well with those reported in the literature: maximum  $H_{\text{int}} = 815 \text{ Oe}$ . However, for the microemulsion samples this  $H_{\text{int}}$  strongly diminishes as the annealing temperature decreases, becoming nearly zero for samples annealed at 600 °C. The same phenomenon had been reported before by Chevalier and Mathieu for  $\alpha\text{-Fe}_2\text{O}_3$  [19] and was related with a decrease

**Table 1** Peak area ratio between the mean peak of cubic  $Gd_2O_3$  ( $d \approx 3.122 \text{ \AA}$ ) and the mean peak of tetragonal  $Gd_2CuO_4$  ( $d \approx 2.770 \text{ \AA}$ ) as a function of evaporation time (in %)

	45 °C 6 h	45 °C 12 h	45 °C 24 h	45 °C 48 h
600 °C 3 h	110	130	201	135
600 °C 15 h	82	100	153	150
600 °C 39 h	98	108	153	164
700 °C 3 h	83	89	56	111
700 °C 15 h	72	82	36.7	100
700 °C 39 h	48	59	21.4	79
800 °C 3 h	34.0	28.6	23.4	50
800 °C 15 h	23.4	25.6	16.4	33.5
800 °C 39 h	17.6	22.6	07.9	16.6

**Table 2** Crystallite sizes of  $Gd_2CuO_4$  particles obtained by the Debye-Scherrer's formula using the mean peak of  $Gd_2CuO_4$  (in nm)

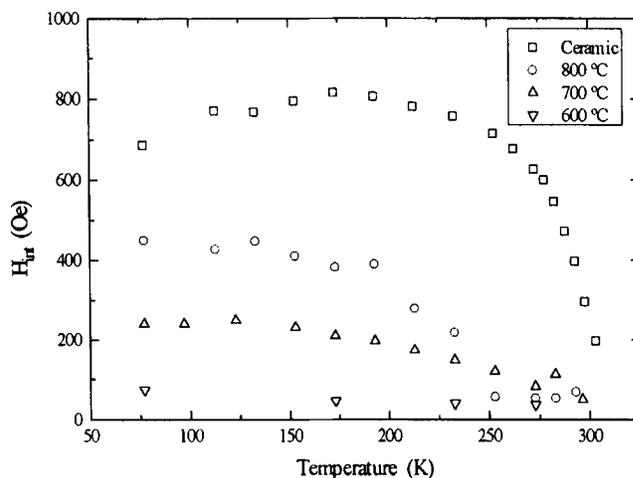
	45 °C 6 h	45 °C 12 h	45 °C 24 h	45 °C 48 h
600 °C 3 h	19.2	14.0	18.0	14.4
600 °C 15 h	20.4	16.9	23.2	19.0
600 °C 39 h	25.8	21.4	27.7	21.4
700 °C 3 h	83	69	42.4	78
700 °C 15 h	118	122	42.8	106
700 °C 39 h	142	109	40.5	125
800 °C 3 h	145	125	93	64
800 °C 15 h	295	276	153	120
800 °C 39 h	1380	413	122	176



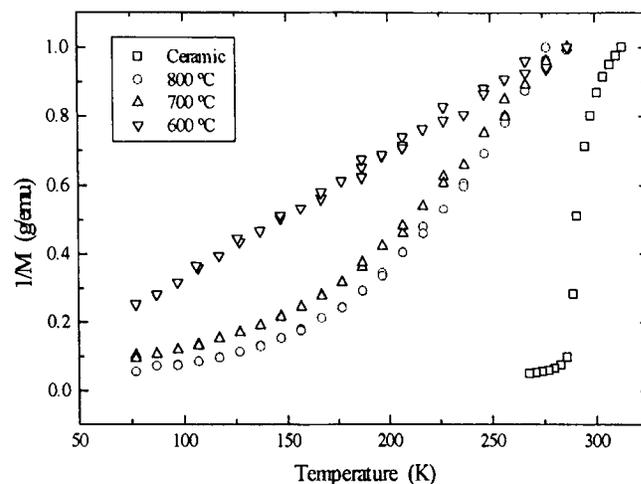
**Fig. 1** Phase evolution as a function of the annealing temperature for the samples at 6 h under vacuum and 3 h of thermal treatment

of particle size. So, as the annealing temperature decreases, particle size also decreases and this reduction of size modifies the magnetic properties of  $Gd_2CuO_4$ .

Magnetization of the samples was measured as a function of the temperature. A plot of  $1/M$  vs temperature is shown in Fig. 3.  $1/M$  was normalized for all calcination temperatures for best comparison. By extrapolating the



**Fig. 2** Internal fields vs. temperature for the samples at 48 h under vacuum at different annealing temperatures



**Fig. 3** Normalized  $1/M$  vs. temperature for the samples at 48 h under vacuum at different annealing temperatures

linear part of  $1/M$  at high temperatures, we have observed a shift of the extrapolated temperature to lower temperatures as the calcination temperature decreases, becoming

almost zero for 600 °C, 140 K for 700 °C, 170 K for 800 °C and 287 K for the ceramic sample. These results can again be explained by the size reduction of the particles because the size constraints lower the long range interaction between the copper magnetic moments, modifying the magnetic properties of the material.

## Conclusions

We have synthesized Gd<sub>2</sub>CuO<sub>4</sub> microparticles by a new method which consists of a sol-gel process carried out

inside the nanodroplets of the microemulsion. This method improves the conventional solid state reaction techniques, lowering considerably the annealing temperature required to obtain well-crystallized materials. Smaller size particles have been obtained than those synthesized by ceramic techniques. Great differences have been observed on the magnetic properties of particles prepared by those techniques.

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