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Sol–Gel Synthesis of Fine Gd_2CuO_4 Particles: Influence of Synthesis Variables

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Fine particles of Gd_2CuO_4 were prepared by a sol–gel reaction of an aqueous solution of metal nitrates in the presence of urea, which leads to high-homogeneity polycrystalline powders of Gd_2CuO_4. We have studied the synthesis conditions, demonstrating the existence of a relationship between the calcination temperature and the heating time needed to attain the pure phase. Gd_2CuO_4 was obtained at temperatures of the order of 650°C, lower than temperatures employed in the conventional ceramic technique. The influence of the [urea]/[salts] ratio and an excess of Cu(II) in the starting solution was also studied and discussed. X-ray powder diffraction, inductively coupled plasma atomic emission spectroscopy (ICPAES), photon correlation spectroscopy (PCS), and transmission electron microscopy (TEM) were used to characterize the Gd_2CuO_4 samples obtained.

I. Introduction

Since 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] interest in the study of physicochemical properties and, especially, the magnetic properties of the undoped materials R_2CuO_4 has increased considerably.[3–5] The reason for this interest is the possible relationship between magnetism and superconductivity. Gd_2CuO_4 has not been found to be superconducting when it is doped with Ce or Th,[6] contrary to doping other members of the R_2CuO_4 family (R = Pr, Nd, Sm, Eu). This compound crystallizes in the tetragonal Nd_2CuO_4-type structure[7] and shows a rich and complex magnetic behavior, different from that of the other members of the family.

Until now, all studies of these compounds were performed on single crystals and powders obtained by solid-state reaction. This technique[8] uses metal oxides as starting materials and it needs several calcination steps at high temperatures, during long periods of time, with frequent intermediate grinding. The samples so obtained have several problems (e.g., poor homogeneity, high porosity, no control on the particle size). To avoid these problems, which are common to the synthesis of other types of high-temperature superconductors, several sol–gel techniques have been developed, showing different advantages when compared to the conventional ceramic fabrication techniques. For example, with sol–gel techniques[9–11] high purity and good homogeneity can be achieved. These methods require lower processing temperatures and shorter heating times than conventional techniques. They show a high reproducibility and good control of stoichiometry and the size and shape of the particles obtained. Other advantages include quantitative yield due to complete recovery of solids; versatility to produce new noncrystalline solids, outside the compositional range of normal glass formation, by avoiding crystallization and amorphous phase separation; and the possibility, using their gel properties, to produce special products, such as films, fibers, or porous solids.

In the present work, we describe the synthesis of Gd_2CuO_4 using a sol–gel technique, which leads to high-purity polycrystalline powders at temperatures lower than those used in solid-state reactions. We have also studied the influence of urea concentration in the process. It is noticed that the particle size can have a great influence on the magnetic properties of the material,[12] so we report here the optimum synthesis conditions at the lowest temperatures and shortest calcination times obtained to date, in order to have small particles of Gd_2CuO_4 without any magnetic impurity (e.g., Gd_2O_3) which would disturb the magnetic properties of the Gd_2CuO_4 phase. This procedure represents an easy method of improving conventional ceramic techniques.

II. Experimental Procedure

All reagent-grade chemicals (Aldrich, Steinheim, Germany) employed in the procedure were used without further purification. $Gd(NO_3)_3{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}2.5H_2O$ were dried in a vacuum desiccator and stored in an inert glove box before use, because they are highly hygroscopic. Gd_2CuO_4 was synthesized by solid-state reaction[13] and used as a polycrystalline reference pattern. For this purpose, Gd_2O_3 and CuO were used as starting materials. A stoichiometric mixture of these reagents was ground dry in a ball mill for 2 h and then heated at 850°C with intermediate grindings each 48 h. Almost 400 h was needed to obtain pure Gd_2CuO_4. The calcination time is reduced substantially if grindings between calcinations are more frequent, because grindings allow better chemical homogeneity in the sample, promoting the formation of the phase.

For the synthesis of Gd_2CuO_4 in aqueous solution, a sol–gel reaction with urea was used. An outline of the process is shown in Fig. 1. Stoichiometric amounts of nitrate salts were used as starting materials, due to their high solubility in water. The initial concentrations were 0.2*M* in Gd(III), 0.1*M* in Cu(II), and the urea concentration was varied in the range 1–7.5*M*. The volume of the initial solution was 100 mL and it had blue color. The solvent was directly evaporated on a hot plate at 75°C with continuous stirring. When cooled, a dark blue gel formed, which decomposed in an aerated furnace at 250°C, yielding a precursor of these samples. After dry grinding for half an hour, the precursor was subjected to different heat treatments in order

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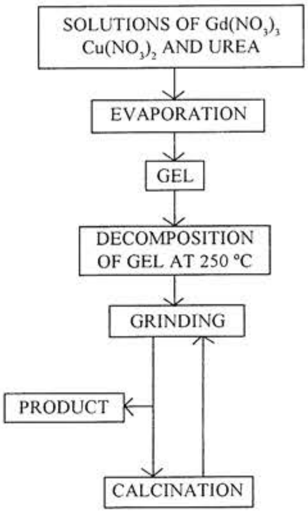

Fig. 1. Scheme of the steps involved in the sol–gel process used for the synthesis of Gd_2CuO_4.

to study the influence of the calcination temperature and the time necessary to obtain the desired phase. The calcination of the samples was carried out in a Quastar HEM·L·1 furnace in a static air atmosphere with a heating rate of 10°C/min. All the samples were cooled to room temperature in the furnace after calcination. A summary of the sol–gel reaction conditions employed is shown in Table I.

The polycrystalline powders were characterized analytically by inductively coupled plasma atomic emission spectroscopy (ICP-AES), using an ICP Perkin-Elmer 5000 with Ar plasma. Samples were prepared by dissolving ≈10 mg of each sample in 5 mL of HCl:HNO_3 (1:1), adding water until 100 mL. The concentration of each element was obtained as an average of three measurements. By means of combustion analysis the proportion of C, H, and N in all the final samples was determined, using a Fisons EA 1108 CHNS-O. The structural characterization was carried out by X-ray powder diffraction, using a Philips diffractometer (PW-1710 with Cu anode radiation Cu$K\alpha$ of λ = 1.54186 Å). The measurements were performed in air at room temperature. In order to determine the size distribution, measurements of photon correlation spectroscopy (PCS) and transmission electron microscopy (TEM) were carried out. The PCS measurements were made with an Ar laser Liconix series 5000 of 5 W operating at λ = 488 nm, with a goniometer ALV-SP80 controlled automatically by means of an ALV-LSE unit. Correlation functions were fitted by the inverse Laplace transform method. For these measurements the particles were ground dry for 1 h and dispersed in ethylene glycol using Triton X-100 as a dispersing agent. TEM measurements were performed in a 120 kV Philips CM12 microscope on all the synthesized samples. In this case, after the dry milling, particles were dispersed in water with an ultrasonic bath. A copper grid coated with polyvinyl-formal was dipped into the dispersion in order to affix the particles to it. At least 20 isolated particles were examined for each sample.

III. Results

The results obtained by X-ray diffraction for the samples synthesized using the solid-state reaction indicate that about 400 h is necessary to obtain the pure Gd_2CuO_4 phase. X-ray patterns of samples heated for shorter periods of time still show peaks of Gd_2O_3 and CuO that have not reacted.

It was observed that with the urea sol–gel route it is possible to obtain the Gd_2CuO_4 phase practically pure, as shown in the X-ray pattern in Fig. 2(d). Figure 3 shows the calcination time needed to obtain the Gd_2CuO_4 phase as a function of the calcination temperature. The time necessary to obtain the pure phase decreases considerably when the calcination temperature increases. Thus, while more than 72 h is needed at 650°C, 36 h at 700°C, 12 h at 750°C, 6 h at 800°C, 3 h or less time at higher temperatures (850°, 900°, and 950°C) is required to obtain phase-pure Gd_2CuO_4. Above 950°C the samples melt. In Fig. 2 we display the time dependence of the Gd_2CuO_4 phase formation for samples heated at 650°C. Other samples, heated at 550° and 600°C, were also prepared, but the desired phase was not obtained even after 120 h. However, in the sample heated at 600°C, peaks of Gd_2CuO_4 appear with low relative intensity, observing a slow evolution to this phase when the calcination time increases. The pure Gd_2CuO_4 phase could probably be obtained at 600°C with calcination times longer than 120 h.

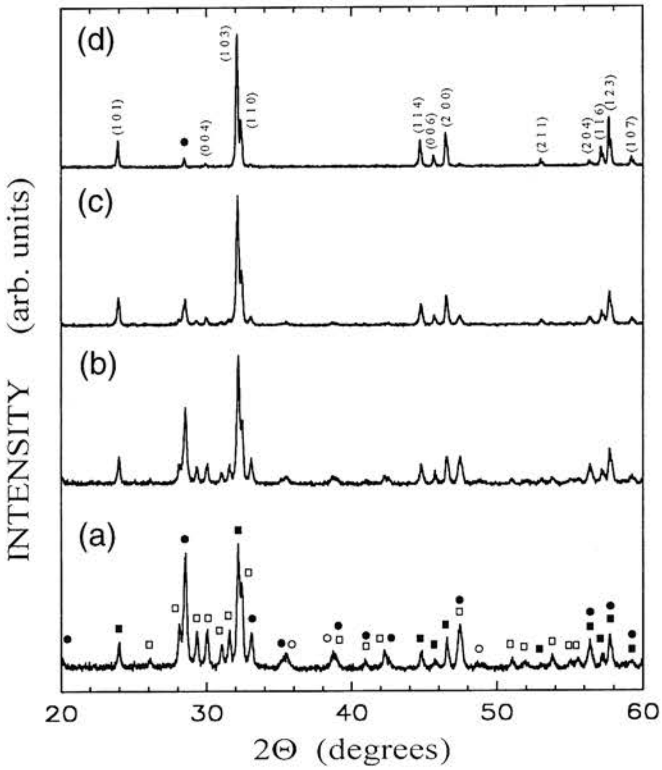

Fig. 2. X-ray diffraction patterns of sol–gel-processed samples heated at 650°C for (a) 12 h, (b) 24 h, (c) 48 h, and (d) 72 h. (■, Gd_2CuO_4, ●, Gd_2O_3 cubic; □, Gd_2O_3 monoclinic; ○, CuO). The indexed peaks correspond to the Gd_2CuO_4 phase.

Table I. Summary of Sol–Gel Reaction Conditions Employed in This Study

Sample	Solvent evaporation temp (°C)	Gel decomposition temp (°C)	Precursor grinding time (h)	Calcination temp (°C)	Calcination time (h)	Sample grinding time (h)
A	75	250	0.5	650	>72	1
B	75	250	0.5	700	36	1
C	75	250	0.5	750	12	1
D	75	250	0.5	800	6	1
E	75	250	0.5	850	3	1
F	75	250	0.5	900	3	1
G	75	250	0.5	950	3	1

The influence of the molar [urea]/[salts] ratio (Ψ) was studied for values of Ψ in the range 3–25 for the calcination temperature of 700°C (see Table II). It was observed that an increase of Ψ increases the relative intensity of the main peak of Gd_2O_3 with respect to that of the Gd_2CuO_4 phase. The best results (absence of Gd_2O_3 peaks) are obtained for values of $\Psi \approx 5$, since for $\Psi \geq 10$, although the formation process of Gd_2CuO_4 is faster, the main peak of Gd_2O_3 remains even after very prolonged heatings, never reaching the pure Gd_2CuO_4 phase. With $\Psi \approx 5$, this peak disappears after a calcination of 36 h at 700°C.

The influence of an excess of $Cu(NO_3)_2$ (10–100 mol%) with respect to the stoichiometric metal ion concentration in the starting solution was also studied, observing that this excess leads to larger percentages of the Gd_2CuO_4 phase until this excess reaches a critical value of ≈50 mol%, as can be seen in Table III. If the excess concentration increases above this critical value, then the formation of simple oxides begins to be promoted. X-ray patterns of the samples prepared with an excess of $Cu(NO_3)_2$ show CuO as secondary phase, indicating that this excess leads to the formation of this oxide after the treatment of the samples. The CuO is not magnetic, so it does not disturb the magnetic properties of the Gd_2CuO_4 phase, contrary to Gd_2O_3. Therefore, its presence is not important for the magnetic study of the samples. It was also observed that the quenching of the samples (in air) does not change the proportion of the Gd_2CuO_4 phase obtained.

The proportion of C, H, and N in the final samples determined by combustion analysis is lower than the detection limit of this technique, about 0.3 wt%. The average molar ratio Gd/Cu obtained by ICP for all the synthesized samples is 2.1 ± 0.1, demonstrating that the stoichiometry of the starting solutions is maintained in the final samples.

Two TEM photographs are presented in Fig. 4, one (a) for a sample obtained using solid-state reaction and the other (b) for a sample prepared via sol–gel calcined at 800°C. It was observed that the ceramic sample has a high polydispersity with a relatively large average size (≈1–2 μm). For the sample prepared via sol–gel it can be observed that the average size is smaller (≈300 nm). These sizes agree well with those obtained by PCS, as can be seen in Fig. 5. Also observed was a change in the average size for the sol–gel samples heated at different calcination temperatures.[12]

IV. Discussion

It was observed that the molar relationship Ψ = [urea]/[salts] has an important influence on the formation of the pure Gd_2CuO_4 phase. These results can be explained taking into account the role played by urea in the synthesis reaction. In aqueous solution, metallic ions are coordinated by water molecules. When the urea aqueous solution is heated at 75°C, urea begins to decompose to CO_3^{2-} and NH_3, releasing hydroxide ions.[4] The rate of urea decomposition depends on the temperature and on urea concentration, but is slow in our reaction conditions.[15] Some new ligands which can substitute for water in the coordination positions as new species (NH_4^+, OH^-, CO_3^{2-}) appear in solution. The substitution degree of water by other ligands depends on the nature and on the concentration of metallic ions and ligands. The elimination of water by evaporation promotes the substitution of water ligands, according to the following scheme:

$$[M\cdot(H_2O)_m]^{n+} + xL^{q-} \xrightarrow{k} [M\cdot(H_2O)_{m-x}\cdot L_x]^{p+} + xH_2O\uparrow \quad (1)$$

where M = Cu, Gd and L = NH_3, OH^-, CO_3^{2-}, urea.

The initial aqueous solution has an acidic pH (≈4.5). The pH remains acid during most of the evaporation process and, when urea begins to decompose, a precipitate appears. An X-ray pattern of the precipitate indicates that $Cu_2(OH)_3NO_3$ is formed, due to the acidic medium. When the solution volume has reduced to ≈15–20 mL, the pH changes to ≈8.0, accompanied by a dark-blue color for the solution. At this moment, the precipitate is completely redissolved. While the mixture cools, a gel is formed, due to the condensation of monomers through the hydroxide ligands, forming long chains.[16] Metallic ions will then be located in the gel network. Hence, the final stoichiometry of the product obtained will be determined by the relationship between the complexation rates of Gd(III) and Cu(II), which will be a function of the rate constants and the metallic ion and urea concentrations, so the complexation process in the gel determines the final composition of the sample. Complexation rates should be balanced so that various metal species can mix and copolymerize uniformly. Then, for specific concentrations of metallic ions, there will be an optimum value of Ψ for which the complexation of Gd(III) and Cu(II) will occur in an appropriate proportion so the distribution of the ions in the gel results only in the Gd_2CuO_4 phase, after the decomposition of the gel and calcination. For values of Ψ different from the optimum, the complexation is larger for one of the ions than for

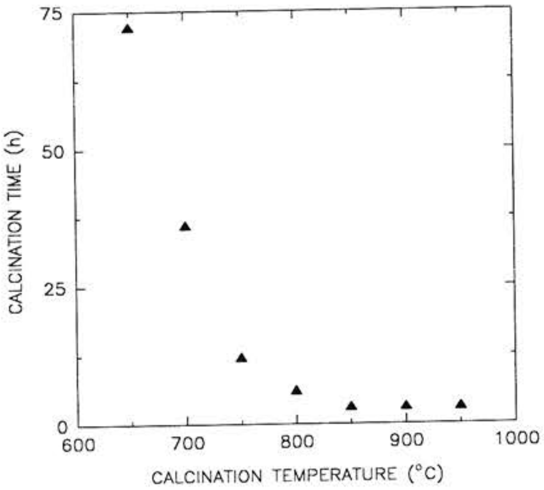

Fig. 3. Calcination time necessary to obtain the Gd_2CuO_4 phase as a function of the calcination temperature.

Table II. Relative Intensity of the (2 2 2) X-ray Diffraction Peak of Gd_2O_3 with Respect to the (1 0 3) X-ray Diffraction Peak of Gd_2CuO_4, for Different [urea]/[salts] Ratios (Ψ), as a Function of Calcination Time for a Sol–Gel Sample Treated at 700°C

Ψ	6 h	12 h	24 h	36 h
5	62	33	7	0
10	12	9	8	5
15	45	33	26	22
20	54	55	43	35
25	82	64	54	49

Table III. Relative Intensity of the (2 2 2) X-ray Diffraction Peak of Gd_2O_3 with Respect to the (1 0 3) X-ray Diffraction Peak of Gd_2CuO_4, for Different Molar Excess of $Cu(NO_3)_2$ as a Function of the Calcination Time for a Sample Treated at 700°C and Ψ = 10

Excess	6 h	12 h	24 h	48 h	72 h
Stoichiometric	12	9	8	4	2
10%	14	11	8	7	6
20%	3	3	2	1	0
30%	2	0	0	0	0
40%	1	0	0	0	0
50%	0	0	0	0	0
70%	5	4	3		
100%	71	29	12		

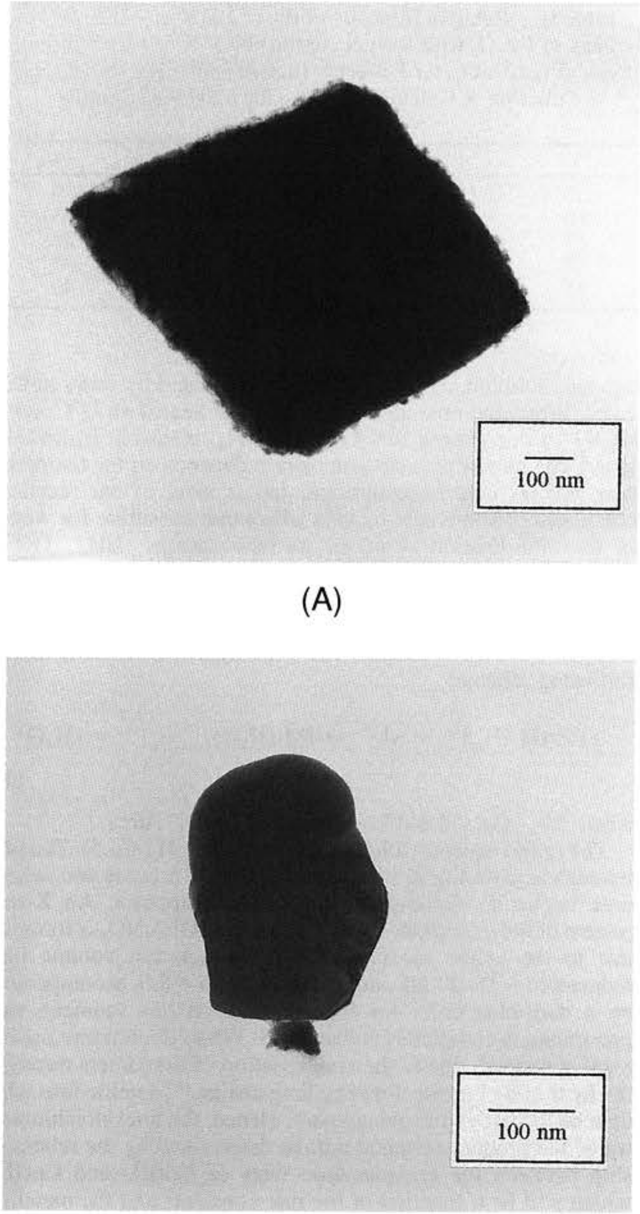

Fig. 4. TEM photographs (A) for a sample prepared using solid-state reaction and (B) for a sample prepared via sol–gel calcined at 800°C.

the other, producing ion segregations in certain areas of the gel. These areas yield other phases from the Gd_2CuO_4 phase when the precursor is calcined. As we have indicated above, the optimum Ψ value experimentally found is $\Psi \approx 5$. Once Gd_2O_3 and CuO are formed for $\Psi \neq 5$, they do not interact when the samples are heated at temperatures lower than 850°C, as experimentally observed for the solid-state reaction (see above).

The influence of an excess of $Cu(NO_3)_2$ in the starting solution was studied in order to obtain Gd_2CuO_4 particles with the shortest calcination times (and, therefore, the smallest particle size) and without magnetic impurities (Gd_2O_3), which would interfere in the magnetic properties of the desired phase. The results can be explained through the different complexation rates of the two metals for a fixed value of Ψ. The rate constant of the process (1), k, is directly proportional to the ratio z/r,[17–21] where z is the ion charge and r the ion radius. This ratio is larger for Gd(III) than for Cu(II): 3.20 for Gd(III) and 2.78 for Cu(II). Thus, the complexation rate for Gd(III) will be faster than for Cu(II). It is noticed that the complexation rate is also proportional to the metallic ion concentration. Therefore, if the Cu(II) concentration increases by means of an excess of $Cu(NO_3)_2$, the complexation rate for Cu(II) will increase, compensating the larger value of k for Gd(III). Similar complexation rates for the two metallic ions will promote the distribution of the ions in the gel in the stoichiometric ratio, yielding only the Gd_2CuO_4 phase. If the Cu(II) excess is too high, the complexation rate for Cu(II) will be larger than for Gd(III), promoting the formation of other phases in the final sample.

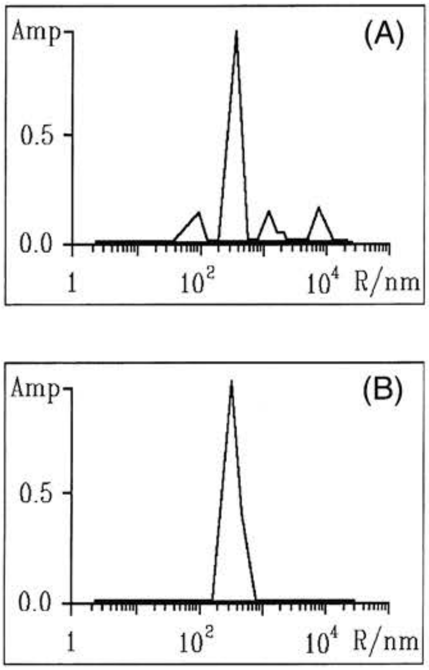

Fig. 5. Size distribution obtained by PCS (A) for a sample synthesized using solid-state reaction and (B) for a sample prepared via sol–gel calcined at 800°C.

V. Conclusions

The formation of Gd_2CuO_4 in aqueous solution was studied. It was observed that the sol–gel reaction in the presence of urea permits obtaining practically pure Gd_2CuO_4. The existence of a relationship between the calcination temperature of the samples and the calcination time was proved. Taking into account this relationship, we were able to obtain the nearly pure phase at temperatures as low as 650°C. The influence of the [urea]/[salts] ratio and an excess of $Cu(NO_3)_2$ in the initial solution on the amount of the Gd_2CuO_4 phase obtained was studied. These results were interpreted taking into account the role played by the urea and the excess of $Cu(NO_3)_2$ in the complexation kinetics. Finally, it was observed that the samples prepared via sol–gel lead to particles smaller than those obtained using solid-state reaction.

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