

Influence of Calcination Temperature on Lattice Parameters and Particle Size of $R_2\text{CuO}_4$ Compounds ($R = \text{Gd}, \text{Nd}$) Prepared by a Sol–Gel Method

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Cuprates $R_2\text{CuO}_4$ ($R = \text{Gd}, \text{Nd}$) were prepared by a sol–gel method that allowed control of the mean particle size by calcining at different temperatures. The samples were characterized using X-ray diffractometry (XRD) and transmission electron microscopy. The results show that the structure of these cuprates is sensitive to the preparation method, particularly the calcination temperature, T_{cal} . The refined lattice parameters a and c , and unit-cell volume V , obtained from the XRD data by the Rietveld method, are found to decrease with increasing T_{cal} , while their mean particle size increased. Between 650 and 950°C, the relative decreases in the lattice parameters were found to be larger for Gd_2CuO_4 than for Nd_2CuO_4 (e.g., 0.07 and 0.03%, respectively, for c). Furthermore, samples prepared by a standard solid state reaction had smaller lattice parameters than the samples prepared by the sol–gel method calcined at lower T_{cal} , while the values for the sol–gel samples calcined at higher T_{cal} approximate those for the solid state reaction samples. © 1996 Academic Press, Inc.

INTRODUCTION

Since the discovery of the family of electron-doped superconductors $R_{1.85}M_{0.15}\text{CuO}_4$ (with $R = \text{Pr}, \text{Nd}, \text{Sm}$, or Eu ; $M = \text{Ce}, \text{Th}$) (1, 2), there has been increasing interest in the properties of the undoped materials, $R_2\text{CuO}_4$ (3). These cuprates all crystallize in the tetragonal space group $I4/mmm$ (No. 139) and have a Nd_2CuO_4 -type structure (T' phase) (4) consisting of a two-dimensional network of edge-linked square-planar network $[\text{CuO}_2]$ groups which are interconnected by planes of R , O , and R atoms (5). The oxygen coordination environment around each $R(\text{III})$ ion is cubic, and the unpaired spins on alternate $\text{Cu}(\text{II})$ ions align antiferromagnetically below a Néel temperature

(T_N) of ca. 270 K (6). The lattice parameters vary according to the rare earth present, decreasing with the ionic radius of $R(\text{III})$ (7).

For $R_2\text{CuO}_4$ that contain rare earths heavier than gadolinium, the T' structure is not stable and these compounds have to be synthesized at high pressure (7). Gd_2CuO_4 does crystallize in the T' phase, but unlike the cuprates of the lighter rare earths, it is not superconducting when doped with Ce or Th (8). Gd_2CuO_4 also shows different magnetic behavior than the cuprates of lighter rare earths (9), possibly because the tetragonal symmetry observed in the latter compounds is slightly distorted in cuprates of rare earths heavier than $\text{Eu}(\text{III})$ (6).

Some of us recently reported (10) that the particle size affects the magnetic properties of Gd_2CuO_4 . Thus, it seems worthwhile to study the structure of this compound as a function of the particle size.

In this work we measured the lattice parameters as a function of particle size for samples of Gd_2CuO_4 and Nd_2CuO_4 prepared by a sol–gel method and compared them with those obtained for ceramic materials prepared by a standard solid state reaction.

EXPERIMENTAL PROCEDURE

The chemicals employed in this work were of reagent grade (Aldrich, Steinheim, Germany) and were used without further purification. An outline of the sol–gel method used to prepare Gd_2CuO_4 particles is shown in Fig. 1. Stoichiometric amounts of $\text{Gd}(\text{III})$ and $\text{Cu}(\text{II})$ nitrates, selected because of their high aqueous solubility, were mixed in water in the presence of urea. The water was evaporated on a hot plate with continuous stirring, and a gel formed

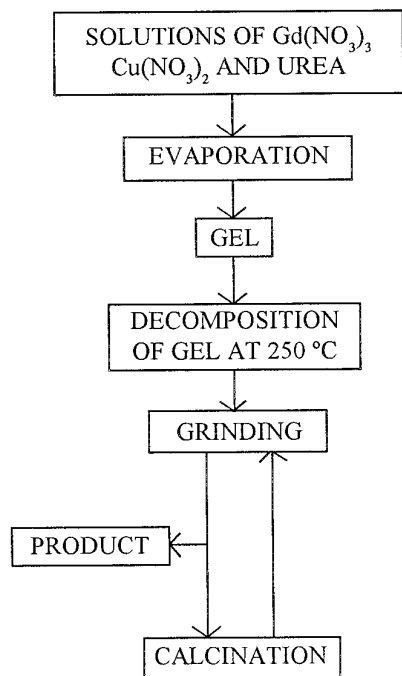


FIG. 1. Scheme showing the steps involved in the sol-gel method used to prepare Gd_2CuO_4 and Nd_2CuO_4 .

upon cooling. This gel was decomposed in an oven at 250°C to yield the sample precursor, which was dry-ground for 30 min in a ball mill, heated at one of seven different temperatures between 650 and 950°C in order to obtain samples with different mean particle sizes, and then further ground for 1 hr. Further details of this method have been reported previously (11). For comparison, samples of Nd_2CuO_4 were also synthesized by the sol-gel method, but were calcined at only three temperatures (950, 750, and 650°C).

Gd_2CuO_4 and Nd_2CuO_4 for use as polycrystalline references in the X-ray diffractometry studies were synthesized by a standard solid state reaction. A stoichiometric mixture of CuO and Gd_2O_3 or Nd_2O_3 was ground dry in a ball mill for 30 min and then calcined successively at 950 and 1000°C for 12 and 20 hr, respectively, in air. The sample was then reground and sintered at 1050°C until single-phase material was achieved.

The polycrystalline powders obtained were structurally characterized at room temperature by X-ray powder diffractometry in a Philips PW-1710 diffractometer fitted with a Cu anode ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54060 \text{ \AA}$ and $\text{CuK}\alpha_2$ radiation, $\lambda = 1.54439 \text{ \AA}$; intensity ratio $[\text{CuK}\alpha_2/\text{CuK}\alpha_1] = 0.5$). Measurements were performed between 20° and 100° (2θ), with a step size of 0.005° and a step time of 2.5 sec.

The Rietveld method (12, 13) was used to derive refined lattice parameters from the X-ray powder diffractograms (XRD), employing the Levenberg-Marquardt least-

squares method to compare the observed and calculated diffractograms and checking the goodness of fit using the chi-square (χ^2) test.

In this work, the instrumental parameters used in the Rietveld method (three parameters for peak width, two for the Gaussianity of pseudo-Voigt function, and two parameters for asymmetry) were derived from the powder diffraction pattern of KCl , and then maintained constant throughout the refinement. For that purpose, commercial KCl powder was annealed at 450°C for 48 hr, and its diffraction pattern was obtained over the range of 2θ values and under the same conditions as described above for the cuprates.

Particle size distributions were determined by TEM in a Philips CM12 microscope. Samples were prepared by dry-grinding the cuprates in a ball mill for 1 hr, in order to separate the particles, dispersing them in water using ultrasound, then immersing a copper grid coated with polyvinyl formal in the dispersion in order to fix the particles to it. At least 20 isolated particles were examined for each sample.

RESULTS AND DISCUSSION

X-ray diffractometry indicated that only 3-hr heating at 950°C is necessary to prepare a pure Gd_2CuO_4 phase using the sol-gel method. Lowering the calcination temperature, T_{cal} , leads to an increase in the calcination time, so that 72 hr at 650°C are necessary to obtain a pure Gd_2CuO_4 phase.

Figure 2 shows the powder diffractogram for Gd_2CuO_4 prepared by the sol-gel reaction and calcined at 800°C . The diffractograms for the sol-gel samples were quite similar, but close examination revealed that the peak resolution was poorer for samples calcined at lower temperatures. Broadening of the peaks is shown in Fig. 3 for the (1 0 1)

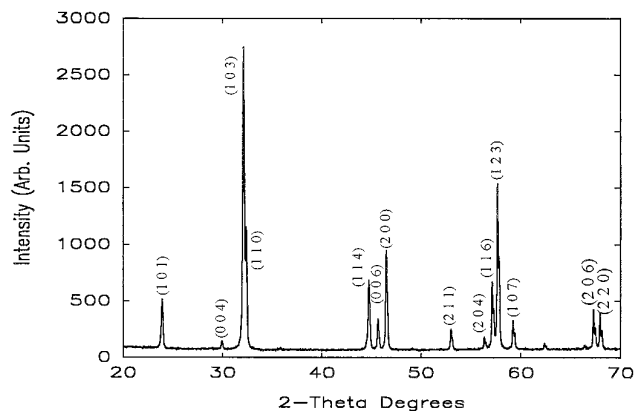


FIG. 2. Indexed X-ray diffraction pattern of the Gd_2CuO_4 sample prepared by the sol-gel method and calcining at 800°C .

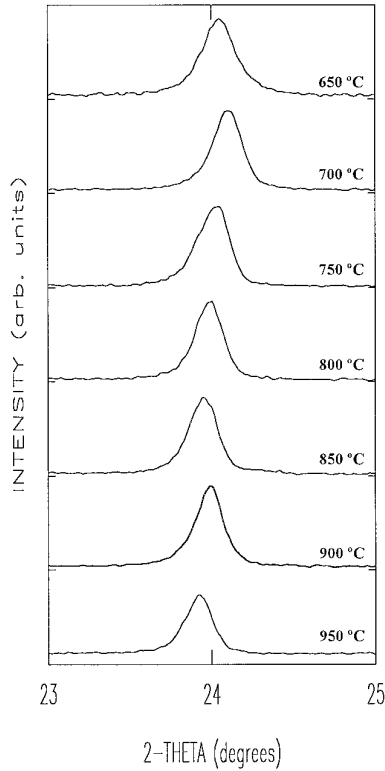


FIG. 3. Evolution of the (1 0 1) peak with the T_{cal} for the Gd_2CuO_4 samples obtained via sol-gel.

peak and may be due to the smaller grain size of the samples prepared at lower T_{cal} .

Tables 1 and 2 give the atomic coordinates (tetragonal $I4/mmm$ space group; group No. 139) and lattice parameters, respectively, for samples prepared by the sol-gel method obtained by the Rietveld refinement. The goodness of the fit (1.1–1.2) indicates an optimum fit of all the samples studied. Figure 4 shows the variation with T_{cal} of the lattice parameters a and c and the unit cell volume V . The lattice parameters decrease as T_{cal} increases; the

TABLE 1

Refined Atomic Coordinates for Gd_2CuO_4 and Nd_2CuO_4 (Space Group $I4/mmm$, Group No. 139); the Estimated Standard Deviation in the Last Digit Is Given in Parentheses

| | x | y | z | Type of atom ($I4/mmm$) |
|------------------|-----|-----|------------------------|------------------------------|
| R : {Gd Nd} | 0 | 0 | 0.3487(2) 0.3515(3) | $4e$ |
| Cu | 0 | 0 | 0 | $2a$ |
| O(1) | 0 | 0.5 | 0.25 | $4d$ |
| O(2) | 0 | 0.5 | 0 | $4c$ |

TABLE 2
Lattice Parameters a and c and Unit-Cell Volume V , for the Gd_2CuO_4 Samples

| Calcination temperature (°C) | a (Å) | c (Å) | V (Å ³) |
|---------------------------------|-----------|------------|-----------------------|
| 950 | 3.8938(4) | 11.8826(5) | 180.16(5) |
| 900 | 3.8940(5) | 11.8841(3) | 180.20(5) |
| 850 | 3.8941(4) | 11.8845(4) | 180.22(5) |
| 800 | 3.8945(5) | 11.8854(4) | 180.27(5) |
| 750 | 3.8946(6) | 11.8860(4) | 180.29(7) |
| 700 | 3.8960(6) | 11.8898(7) | 180.47(6) |
| 600 | 3.8961(5) | 11.8904(4) | 180.49(5) |
| Solid state reaction | 3.8936(4) | 11.8791(2) | 180.14(4) |

absolute effect is larger for c , while the relative effect is similar for a and c (0.06 and 0.07%, respectively). These variations in the lattice parameters are reflected in the value of the unit-cell volume V , which is $\approx 0.2\%$ larger at 650°C than it is at 950°C.

The lattice parameters for the sample prepared by solid state reaction at 1050°C (Table 2) are smaller than those for the samples prepared by the sol-gel method calcined at lower T_{cal} , while the values for the sol-gel samples calcined at higher T_{cal} approximate those for the solid state reaction samples.

For comparison, XRD data for samples of Nd_2CuO_4 were obtained and refined as described above. As was observed for Gd_2CuO_4 , the neodymium cuprates prepared by the sol-gel method and calcined at different T_{cal} were similar apart from small differences in peak resolution. The calcination time necessary for obtaining a pure Nd_2CuO_4 phase was less than that for Gd_2CuO_4 , with only 6 hr being required at 650°C versus 72 hr for Gd_2CuO_4 at this temperature. One possible reason for such a difference may be in the stability of the T' phase in these compounds. The crystalline cuprates of the rare earths heavier than Pr are isostructural with Nd_2CuO_4 , but the stability of the T' phase decreases with the ionic radius of $R(\text{III})$. Gd_2CuO_4 is the heaviest rare-earth cuprate that can be synthesized at atmospheric pressure, so its preparation by the sol-gel method may be expected to require a longer calcination time.

Table 3 lists the refined lattice parameters obtained for Nd_2CuO_4 . As was observed for the Gd_2CuO_4 samples prepared by the sol-gel method, the lattice parameters for Nd_2CuO_4 all decrease with increasing T_{cal} (Fig. 5) and are larger than those for the sample prepared by the solid state reaction. However, for Nd_2CuO_4 the relative decreases in the lattice parameters with temperature are smaller; c , for example, decreases by only $\approx 0.03\%$ between 650 and 950°C, instead of $\approx 0.07\%$ for Gd_2CuO_4 over the same

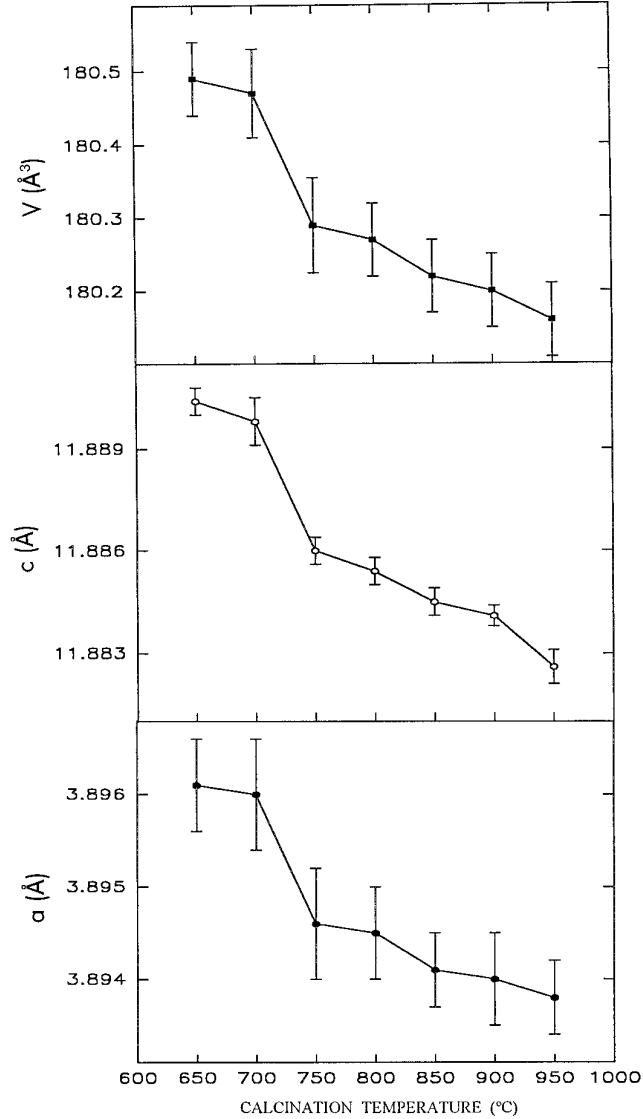


FIG. 4. Variation of the lattice parameters a and c , and the unit-cell volume V with T_{cal} for the Gd_2CuO_4 samples prepared by the sol-gel method.

TABLE 3
Lattice Parameters a and c and Unit-Cell Volume V , for the Nd_2CuO_4 Samples

| Calcination temperature (°C) | a (Å) | c (Å) | V (Å ³) |
|------------------------------|-----------|------------|-----------------------|
| 950 | 3.9406(6) | 12.1639(2) | 188.89(7) |
| 750 | 3.9410(6) | 12.1676(3) | 188.98(5) |
| 650 | 3.9411(3) | 12.1678(3) | 188.99(3) |
| Solid state reaction | 3.9402(5) | 12.1617(5) | 188.81(5) |

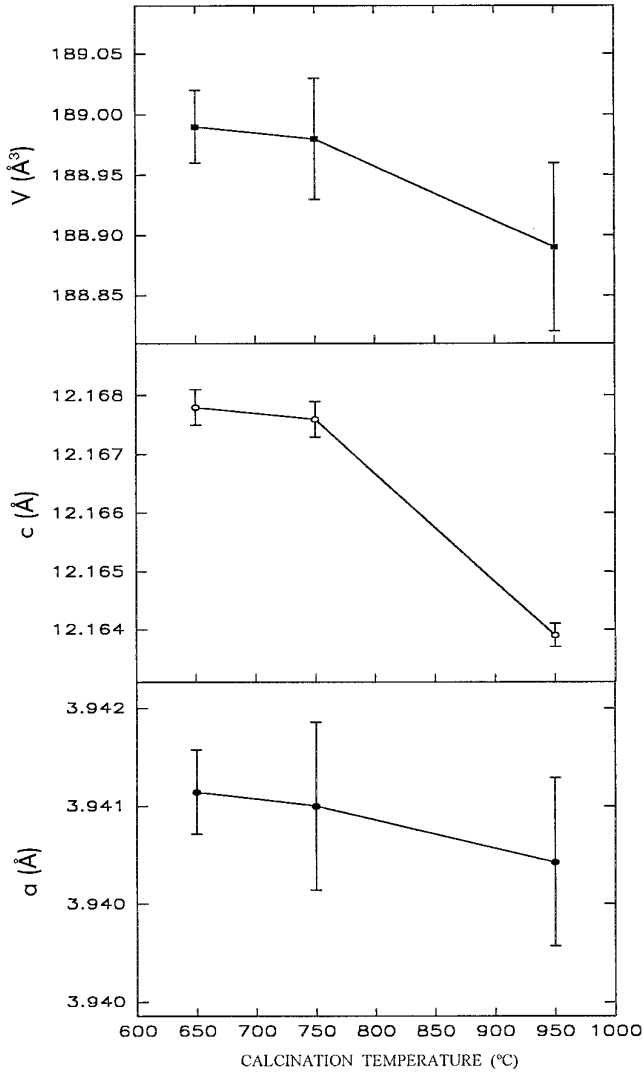


FIG. 5. Variation of lattice parameters a and c , and the unit-cell volume V with T_{cal} for the Nd_2CuO_4 samples prepared by the sol-gel method.

temperature range. Once again, the greater stability of the T' phase in Nd_2CuO_4 may account for this difference.

Notice that the variation with the T_{cal} of the lattice parameters of rare-earth cuprates is less significant than that arising from substitution of the rare earth. For example, when Gd is replaced by Eu in $R_2\text{CuO}_4$ compounds prepared by solid state reaction, the c parameter decreases $\approx 0.17\%$ ($a = 3.9015(5)$ Å and $c = 11.9027(3)$ Å, for Eu_2CuO_4) instead of $\approx 0.07\%$ for the Gd_2CuO_4 samples prepared by the sol-gel method and calcined at different T_{cal} . Nonetheless, these small differences in the lattice parameters of the samples prepared by the sol-gel method may have appreciable effects on the magnetic properties of these compounds (14).

Transmission electron micrographs for samples pre-

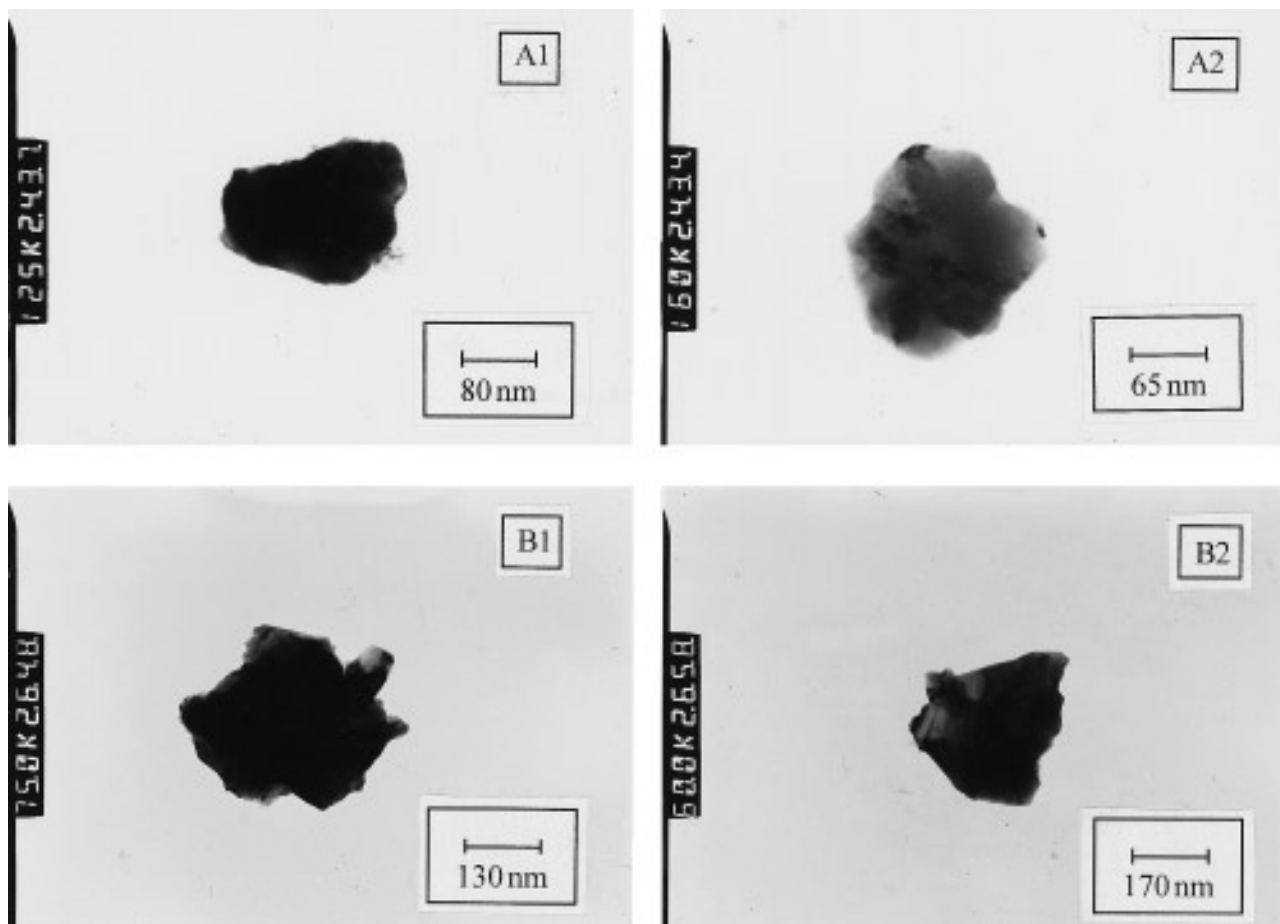


FIG. 6. TEM photographs for two Gd_2CuO_4 samples prepared by the sol-gel method and calcining at 650 (A) and 950°C (B).

pared by the sol-gel method and calcined at 650 and 950°C are shown in Figs. 6a and 6b, respectively. Mean particle sizes were evaluated from these data, and their variation with T_{cal} is shown in Fig. 7 for the Gd_2CuO_4 samples prepared by the sol-gel method. For samples studied here, mean particle size increases with T_{cal} , from 150 ± 25 nm at 650°C to 400 ± 75 nm at 950°C, but was always smaller than the value for Gd_2CuO_4 prepared by solid state reaction at 1050°C ($\approx 1 \mu\text{m}$). A similar increase in mean particle size with T_{cal} was observed for the Nd_2CuO_4 samples. Comparing the variations of lattice parameters and mean particle size with T_{cal} (Figs. 4, 5, and 7), it is seen that the latter decreases as the former increase.

Rietveld refinement also allows one to obtain the particle size. The mean particle sizes obtained by this method (Fig. 8) are smaller than those obtained by TEM, for a determined T_{cal} . However, the same tendency for particle size to increase with T_{cal} is observed.

The observed changes in the lattice parameters with T_{cal} could be related to the decreasing particle size. It has been found that the oxygen content in other related systems

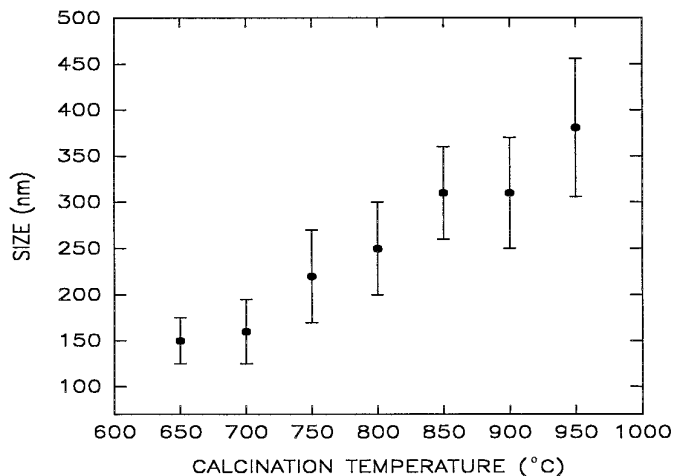


FIG. 7. Mean particle size vs T_{cal} obtained by TEM for Gd_2CuO_4 samples prepared by the sol-gel method.

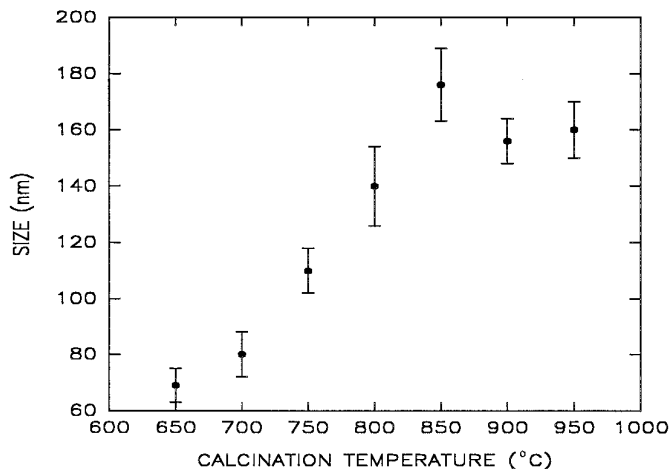


FIG. 8. Mean particle size vs T_{cal} obtained by Rietveld refinement for Gd_2CuO_4 samples prepared by the sol-gel method.

(15) increases when the particle size decreases, possibly due to the larger number of surface atoms in the particles calcined at low T_{cal} . This nonstoichiometric amount of oxygen located mainly at the surface layers of the grains could modify the lattice parameters (16). The influence of the structure on the magnetic properties of these compounds can be explained through the reduction of the oxygen distortion in the CuO_2 planes (17). Further studies to clarify the mechanisms of these phenomena are in progress.

CONCLUSIONS

Preparation of Gd_2CuO_4 and Nd_2CuO_4 by the sol-gel method allows control of the mean particle size by changing T_{cal} . The mean particle size increases with T_{cal} , and there is also an associated decrease in the lattice parameters and unit-cell volume. Samples prepared by a standard solid state reaction at 1050°C have a larger particle size and have smaller lattice parameters than those prepared by the sol-gel method. These results clearly show that the

preparation method, and in particular the T_{cal} employed in the sol-gel method, can have appreciable effects on cuprate structure. Thus, the observed (10) variation of the magnetic properties of Gd_2CuO_4 with mean particle size may also be due to small variations in the lattice parameters of this material.

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REFERENCES

1. Y. Tokura, H. Takagi, and S. Uchida, *Nature* **337**, 345 (1989).
2. J. T. Markert and M. B. Maple, *Solid State Commun.* **70**(2), 145 (1989).
3. S. B. Oseroff, D. Rao, F. Wright, M. Tovar, D. C. Vier, and S. Schultz, *Solid State Commun.* **70**(12), 1159 (1989).
4. K. A. Kubat-Martin, Z. Fisk, and R. R. Ryan, *Acta Crystallogr. Sect. C* **44**, 1518 (1988).
5. Y. Y. Xue, P. H. Hor, R. L. Meng, Y. K. Tao, Y. Y. Sun, Z. J. Huang, L. Gao, and C. W. Chu, *Physica C* **165**, 357 (1990).
6. S. B. Oseroff, D. Rao, F. Wright, D. C. Vier, S. Schultz, J. D. Thompson, Z. Fisk, S. W. Cheong, M. F. Hundley, and M. Tovar, *Phys. Rev. B* **41**(4), 1934 (1990).
7. P. Bordet, J. J. Capponi, C. Chaillout, D. Chateigner, J. Chenavas, Th. Fournier, J. L. Hodeau, M. Marezio, M. Perroux, G. Thomas, and A. Varela, *Physica C* **185-189**, 539 (1991).
8. A. Butera, A. Caneiro, M. T. Causa, L. B. Steren, R. Zysler, M. Tovar, and S. B. Oseroff, *Physica C* **160**, 341 (1989).
9. J. D. Thompson, S. W. Cheong, S. E. Brown, Z. Fisk, S. B. Oseroff, M. Tovar, D. C. Vier, and S. Schultz, *Phys. Rev. B* **39**(10), 6660 (1989).
10. J. Mahía, C. Vázquez-Vázquez, J. Mira, M. A. López-Quintela, J. Rivas, T. E. Jones, and S. B. Oseroff, *J. Appl. Phys.* **75**, 6757 (1994).
11. J. Mahía, C. Vázquez-Vázquez, M. I. Basadre-Pampín, J. Mira, J. Rivas, M. A. López-Quintela, and S. B. Oseroff, *J. Am. Ceram. Soc.*, in press.
12. L. Luterotti, P. Scardi, and P. Maistrelli, *J. Appl. Crystallogr.* **25**, 459 (1992).
13. H. M. Rietveld, *J. Appl. Crystallogr.* **2**, 65 (1969).
14. J. Mira, J. Mahía, C. Vázquez-Vázquez, J. Rivas, M. A. López-Quintela, and S. B. Oseroff, to be published.
15. J. Mahía, Doctoral Thesis, Universidad Santiago de Compostela, Spain, 1995.
16. M. Verelst, N. Rangavittal, C. N. R. Rao, and A. Rousset, *J. Solid State Chem.* **104**, 74 (1993).
17. L. B. Steren, M. Tovar, and S. B. Oseroff, *Phys. Rev. B* **46**, 2874 (1992).