

## Effect of Ga addition to $\text{YBa}_2\text{Cu}_3\text{O}_7$

Youwen Xu, R. L. Sabatini, A. R. Moodenbaugh, and M. Suenaga

*Division of Materials Science, Brookhaven National Laboratory, Upton, New York 11973*

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The effect of Ga substitution for Cu in  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_y$  has been investigated for nominal compositions  $x \leq 0.10$ . Samples are tetragonal for  $x > 0.03$ . For  $x \geq 0.05$ , evidence for second phase appears in x-ray-diffraction diagrams. Superconducting transition temperature  $T_c$  falls systematically with increasing  $x$ . The systematic variations in  $T_c$  and lattice parameters with nominal  $x$  suggest that Ga solid solution may extend to  $x = 0.05$ . However, electron microprobe results indicate that Ga incorporation into the superconducting phase is extremely limited; the Ga content  $x$  of the superconducting phase appears to be  $x \leq 0.01$ . A Ga-rich second phase is also observed by microprobe for  $0.01 \leq x \leq 0.10$ .

In at least three previous instances<sup>1-3</sup> the effect of Ga substitution into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (1:2:3) has been studied. It has been assumed that Ga substitutes for copper<sup>1,2</sup> or yttrium<sup>3</sup> in the superconducting compound. Xiao *et al.*<sup>1</sup> suggest that through interpretation of results on Ga and Zn substitution for Cu in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , oxygen-vacancy ordering (on Cu-O chains) is demonstrated to be unimportant for superconductivity in these high- $T_c$  compounds. We have prepared a series of samples with nominal composition  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_y$  in a manner described below, and one sample based directly on the recipe in Ref. 1. Our results suggest that Ga substitution may be inappropriate for systematic studies of superconductivity. Superconducting properties appear to be inconsistent from investigation to investigation. Further, it appears doubtful, in our samples at least, that Ga substitutes into  $\text{YBa}_2\text{Cu}_3\text{O}_7$  above the  $x = 0.01$  level.

Powders of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$ , and  $\text{Ga}_2\text{O}_3$  were ground thoroughly, pelletized, and heated in air at  $900^\circ\text{C}$  for  $\sim 20$  h. After regrinding and pelletizing the samples underwent an identical heat treatment. Again the samples were ground and pelletized. A final heat treatment took place in oxygen ( $\sim 48$  h at  $962^\circ\text{C}$ , then 8 h at  $865^\circ\text{C}$ , then a furnace cool to below  $100^\circ\text{C}$ ). We also prepared a sample (Ga content  $x = 0.08$ ) based directly on the procedure of Ref. 1. This sample, named 1, was sintered three times at  $950^\circ\text{C}$  in oxygen, with intermediate grindings and pelletizings.

Superconducting transitions were recorded using a mutual inductance method (ac susceptibility) operating at 200 Hz. X-ray diffraction data were acquired using a conventional setup utilizing Cu  $K\alpha$  radiation with a diffracted beam monochromator. Powdered silicon was mixed with samples to provide a reference. Lattice parameters were determined by a least-squares fit to the positions of ten or more diffractions peaks. An electron microprobe (with a wavelength dispersive spectrometer) was used to determine composition and degree of homogeneity for several samples. Optical micrographs at magnifications  $200\times$  and  $800\times$  were obtained for polished surfaces of all samples. Electrical resistivity measurements were performed on a selection of samples.

Superconductivity as a function of nominal composition

(ac susceptibility data) is shown in Fig. 1 as filled circles and a square (for sample 1). The data of Ref. 1 (also ac susceptibility results) are represented by the curved line in the figure. The discrepancy between the data of Ref. 1 and the present investigation is not simply explained. Our sample 1, made according to the procedure of Ref. 1, agrees well with our data, not that of Ref. 1. The data of Maeno<sup>2</sup> (from resistivity data) are represented by the two open circles. Although resistively determined  $T_c$ 's are normally higher than inductively determined  $T_c$ 's, that is not the case when comparing Maeno's data with the other results. The agreement among the three investigations is not good.

Lattice parameters as a function of nominal Ga content are shown in Fig. 2. We observe the tetragonal phase to be stable above  $x = 0.03$ . While this is in essential agreement with Maeno,<sup>2</sup> Xiao<sup>1</sup> shows a slight orthorhombic distortion to higher  $x$ . The  $c$  lattice parameter for sample

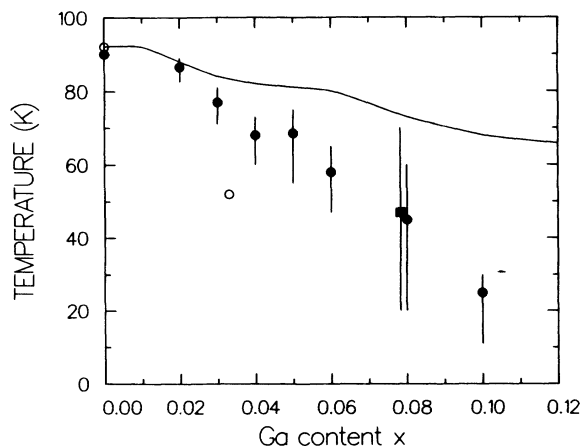


FIG. 1. Superconducting transition temperature vs nominal Ga content in  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_y$ . Filled symbols are midpoints of ac susceptibility transitions (circles for normally prepared samples; square for sample 1). Vertical lines through data points span 10% to 90% of transition. Curved line represents data of Ref. 1. Open circles represent the resistance data of Ref. 2.

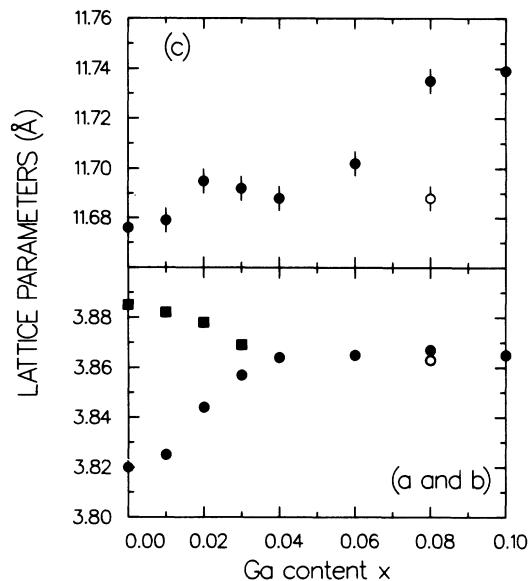


FIG. 2. Lattice parameters [(a), (b), and (c)] of  $\text{YBa}_2\text{-(Cu}_{1-x}\text{Ga}_x)_3\text{O}_y$ . Open symbols are for sample 1. In lower plot, (a) is represented by circles; (b) by squares. In both cases standard deviation of lattice parameter is equal to the height of the symbol. For (c), standard deviation is represented by the vertical line.

1 differs from that of our normally prepared sample at the same composition but is in agreement with Ref. 1. The observed systematic variation of lattice parameters suggests that Ga is incorporated into the 1:2:3 compound, at least below  $x = 0.05$ . X-ray-diffraction patterns for samples with  $x \geq 0.05$  clearly show peaks with intensity  $\geq 2\%$  of that of the most intense peak in the pattern which are not indexable with the 1:2:3 compound parameters. These extra peaks are evidence for the presence of a significant amount (several wt.%) of additional phase or phases. The diffraction pattern of sample 1 also shows such peaks although Ref. 1 describes its samples as single phase to  $x = 0.20$ . These results suggest that the solid solution  $\text{YBa}_2\text{-(Cu}_{1-x}\text{Ga}_x)_3\text{O}_y$  ends below  $x = 0.05$ . Taken together, the variation of lattice parameters below  $x = 0.05$  and the appearance of additional phases at  $x = 0.05$  suggest that the solid solution range may extend to  $x$  values between 0.03 and 0.05.

Electrical conductivity measurements also seem to confirm the systematic nature of the variation of properties with Ga content. Electrical resistivities for  $x \leq 0.08$  are metallic in character; resistivity falls as temperature is reduced. Room-temperature values of resistivity are comparable to those of Ref. 1. For  $x = 0$  we observe  $800 \mu\Omega \text{ cm}$ , while Ref. 1 reports  $1700 \mu\Omega \text{ cm}$ . For  $x = 0.08$  prepared normally we find  $8600 \mu\Omega \text{ cm}$ ; Ref. 1 sees  $7000 \mu\Omega \text{ cm}$ . Our values of resistivity at room temperature are generally lower than those of Ref. 1 for  $x \leq 0.03$  and higher for  $x \geq 0.04$ . Again these electrical resistivity measurements tend to support the picture that Ga is being dissolved into a solid solution in these samples. Here the apparent systematic behavior extends well beyond the  $x = 0.03\text{--}0.05$  solubility limit suggested by x-ray-

diffraction results.

Composition of the 1:2:3 phase and two impurity phases was determined by an electron microprobe of several samples. The majority 1:2:3 phase in all cases contained significantly less Ga than the nominal compositions. For example, the specimen with nominal  $x = 0.04$  had Ga content of the 1:2:3 phase determined at ten places. Nine of ten determinations of Ga content were between  $x = 0.00$  and  $x = 0.01$ ; the tenth determination gave  $x = 0.04$ . A reasonable explanation of these results is that the nine low determinations represent the actual composition of the 1:2:3 phase, while the  $x = 0.04$  determination is anomalously high because of the chance inclusion in the field of a Ga-rich second phase. A microprobe study of sample 1 gives similar results: Ga content of the 1:2:3 phase is found to be below  $x = 0.01$ , compared to the nominal  $x = 0.08$ . It may be useful to compare these results to those of a parallel investigation into the alloying of Fe into the 1:2:3 compound.<sup>4</sup> In the case of Fe for nominal  $x = 0.05$ , five determinations of the Fe content resulted in values  $4.7 \leq x \leq 5.2$ . For Fe, the content of the 1:2:3 phase determined by microprobe agrees well with the nominal composition. The electron microprobe determinations of Ga content in this investigation indicate that no more than about  $x = 0.01$  Ga is incorporated into the 1:2:3 compound.

A gallium-rich second phase with about 12.5 at.% Ga occurs in all Ga-substituted samples. The approximate ratio of metal atoms (not including oxygen) in this compound is, from microprobe results,  $\text{Y}_4\text{Ba}_{10}\text{Cu}_1\text{Ga}_5$ . In addition to this phase we observe CuO. A trend exists for increasing volume of the Ga-rich phase with Ga substitution. For nominal  $x = 0.10$  this second phase constitutes perhaps 15% to 20% of the volume of the sample as determined optically. It appears, then, that much of the Ga introduced into the sample precipitates out into a second phase. An attempt to determine the composition of the second phase occurring in sample 1 was unsuccessful because of the small size of the precipitates,  $\leq 5 \mu\text{m}$ . The authors of Ref. 1 determined composition of their samples by energy-dispersive fluorescence analysis, which is somewhat less accurate than the microprobe, especially when examining small regions. Their findings agree with their conclusion, based on x-ray-diffraction results, that their samples are single phase up to  $x = 0.20$ .

Evidence from our composition determinations of the 1:2:3 compound compositions, supplemented by observations of the occurrence of the second Ga-rich phase, strongly suggests that the solubility of Ga in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is severely limited, perhaps to  $x \leq 0.01$ . This conflicts with our own estimate of solubility of Ga ( $x \leq 0.05$ ) made from x-ray-diffraction data. However, we feel that the microprobe data are more reliable. The x-ray-diffraction data may be misleading, possibly for the following reason. Variation in lattice parameter above  $x = 0.01$  may perhaps be influenced by microstructural changes (perhaps related to variations in oxygen stoichiometry or ordering) leading to systematic variation of lattice parameters. Note that systematic variations in  $T_c$  (Fig. 1) and resistivities exist all the way up to  $x = 0.10$ , in spite of the fact that the solubility range ap-

pears to end below  $x = 0.05$ .

We suggest that any conclusions based on the apparent behavior of Ga-doped samples are premature. Specifically we feel that Ga is inappropriate for the systematic study of doping in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  for the two following reasons. Electron microprobe determinations of composition suggest that Ga is not actually incorporated into the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in the amount of the nominal (starting) com-

positions. Also, the superconducting transition temperatures vary from investigation to investigation (Fig. 1).

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