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## **Abstract**

Ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  samples have been prepared with  $x = 0.00, 0.25, 0.50, 0.55, 0.75,$  and  $1.00$  in order to study the change in lattice constants with the ratio of Sr/Ca. This phase is frequently an impurity phase in the fabrication of Bi–Sr–Ca–Cu–O superconductors, and it is important to be able to connect the lattice constants with stoichiometry. The behavior of the lattice constants closely follows Vegard's law.

## **Keywords**

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## **Disciplines**

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## **Comments**

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# Synthesis and characterization of ceramic $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$

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Ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  samples have been prepared with  $x = 0.00, 0.25, 0.50, 0.55, 0.75,$  and  $1.00$  in order to study the change in lattice constants with the ratio of Sr/Ca. This phase is frequently an impurity phase in the fabrication of Bi–Sr–Ca–Cu–O superconductors, and it is important to be able to connect the lattice constants with stoichiometry. The behavior of the lattice constants closely follows Vegard's law.

## I. INTRODUCTION

Since the discovery of high  $T_c$  Bi–Sr–Ca–Cu–O superconductors, there has been considerable interest in the many phases that form at higher temperatures during the melt-texturing process. Second phase precipitates, for example, could be used as pinning centers in the superconducting Bi (2212) or Bi (2223) phases. For the Y (123) system the 211 phase seems to be the precipitate of choice for flux pinning, but no corresponding phase has emerged for Bi (2212). It has been shown<sup>1</sup> that Bi-based compounds have a very complicated melting process with more crystalline phases than in the superconducting Y (123) systems. Roth *et al.* have systematically studied the phase equilibria and crystal chemistry in the binary and ternary ceramic compounds related to Bi–Sr–Ca–Cu–O systems.<sup>2,3</sup> Schulze *et al.* have investigated phase diagrams in the system of  $\text{Bi}_2\text{O}_3$ –SrO–CaO–CuO for temperatures between 750 and 860 °C in air<sup>4,5</sup> and have mapped out the phases for Sr/Ca ratios of 1/1 and 2/1.

In flux pinning studies, it was found that the intragrain critical current density could be enhanced by introducing  $\text{Ca}_2\text{CuO}_3$  as the pinning center into the Bi–Sr–Ca–Cu–O system.<sup>6</sup> In recent studies of high temperature x-ray diffraction,<sup>1,7</sup> it has been shown that upon melting Bi (2212) powder at least three different insulating phases appear in the liquid in the 870 °C to 890 °C temperature range,  $(\text{Sr}_{1-x}\text{Ca}_x)\text{CuO}_2$ ,  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ , and  $(\text{Sr,Ca})\text{O}$ , during the melting process. During freezing, samples show a great deal of supercooling of the Bi (2212) liquid with nucleation of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  being favored over  $(\text{Sr}_{1-x}\text{Ca}_x)\text{CuO}_2$  and  $(\text{Sr}_{1-x}\text{Ca}_x)\text{O}$ . Although it has been claimed that the  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  system forms a complete series of solid solution,<sup>2,4</sup> detailed description and data, such as lattice parameters and their relations to the ratio of Sr/Ca, have not been reported to our knowledge. High temperature x-ray experiments show that various solid solutions can be formed with different ratios of Sr/Ca during the heating and cooling processes. Thus, information of crystalline  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  is necessary to identify the

phases appearing in Bi–Sr–Ca–Cu–O compounds at higher temperatures (850–890 °C).

The purpose of this work is to study the phase formation and crystalline properties of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ . Ceramic samples  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  with  $x = 0.00, 0.25, 0.50, 0.55, 0.75,$  and  $1.00$  have been prepared. The phases present in these samples have been determined by x-ray diffraction and scanning electron microscopy (SEM). Energy dispersive spectroscopy (EDS) and inductively coupled plasma (ICP) techniques have also been used to determine the chemical composition in ceramic samples of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ . The relationships between the lattice constants and the ratios of Sr/Ca have been obtained from x-ray diffraction data.

## II. EXPERIMENTAL DETAILS

The ceramic compounds were prepared by a solid reaction technique. Starting materials of  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  were weighed with atomic ratios of  $x = 0.00, 0.25, 0.50, 0.55, 0.75,$  and  $1.00$ . The weighed powders of 5 g for each composition were thoroughly ground by a mortar and pestle for about 20 min. The mixed powders were placed in an  $\text{Al}_2\text{O}_3$  crucible and calcined at 800 °C for 12 h in air followed by a furnace cool. The calcined powders were reground and the calcination processes were repeated two times at 870 °C and 900 °C. The calcinated powders were pressed into pellets with diameters of about 12 mm using a uniaxial pressure at 4000 psi. The pellets were sintered at 950 °C in air for 12 h. The sintered pellets were then broken and ground into powder. The sintering procedure was repeated at 970 °C followed by a furnace cool.

X-ray diffraction data were taken using a Philips powder diffractometer with  $\text{Cu K}\alpha$  radiation operating at 40 kV and 20 mA. Microstructure and phase composition were examined by a Cambridge S. 200 scanning electron microscope (SEM) equipped with a Tracor-Northern energy dispersive spectrometer (EDS) and operated at 15 kV. Standards for analysis were determined by chemical analysis using the inductively coupled plasma (ICP) technique.

### III. RESULTS AND DISCUSSION

Samples studied in this work readily formed nearly phase-pure ceramic. Analyses by IPC and EDS do not indicate the presence of any impurities. The chemical analyses also show that there is no variation in the stoichiometry of each sample from the starting composition, and SEM examination of portions of each sample using backscatter imaging reveals no additional phases. Therefore, we have obtained the samples with compositions very close to the ideal stoichiometry in the ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ . X-ray diffraction results show that almost all diffraction peaks result from a single phase with very small amounts of impurity phases, such as CuO, in the sample of  $\text{Ca}_2\text{CuO}_3$ . Very weak peaks belonging to  $(\text{Sr}, \text{Ca})\text{CuO}_2$  phases have also been observed by x-ray diffraction in two of the ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  with  $x = 0.50$  and  $0.55$ . The SEM photographs of the samples with  $x = 0.25$  and  $0.50$  are shown in Fig. 1. The SEM pictures also indicate that these samples are essentially single phase.

Both XRD and SEM results show that the Ca can replace the Sr position in the ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$

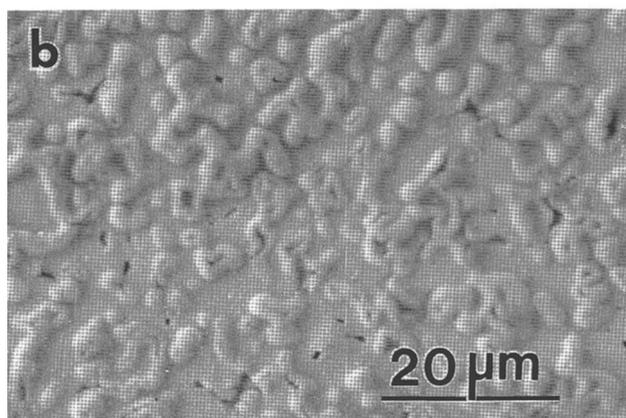
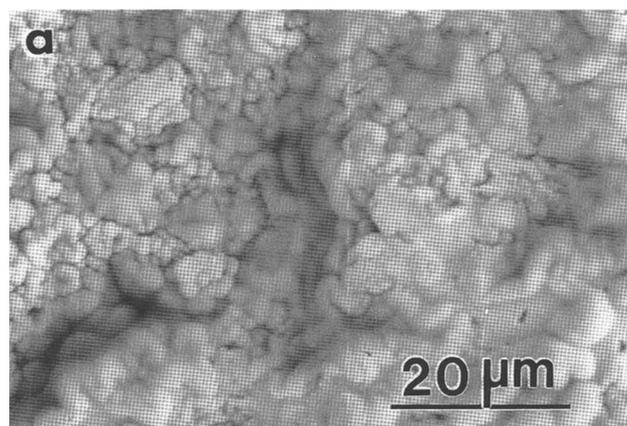


FIG. 1. SEM (backscattering electron) photographs for samples of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  with (a)  $x = 0.25$  and (b)  $x = 0.55$ .

over a wide region of Sr/Ca ratio or composition ( $x$ ). The unit cell of each composition becomes larger as more Sr atoms substitute for Ca in the  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  structure with most of the change (relative change) in the unit cell occurring along the  $c$ -axis.

The compounds  $\text{Ca}_2\text{CuO}_3$  and  $\text{Sr}_2\text{CuO}_3$  were reported by Ref. 8 and their structures were determined by Refs. 9 and 10. After identifying the diffraction peaks, the crystal lattice constants can be calculated. Calculation of the lattice constants is quite straightforward since the ceramic  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  has an orthorhombic structure. At least seven stronger peaks were taken to estimate the lattice constants, where the long lattice constant has been chosen as the  $a$ -axis. The final values of the lattice constants were obtained by determining the lattice constants  $a$ ,  $b$ , and  $c$  from several diffraction peaks and then averaging these values to obtain overall average values for these parameters. The results are listed in Table I for the different ratios of Sr/Ca. The errors in Table I are chosen from the standard deviation values. The relationships of the lattice constants and compositions ( $x$ ) for the  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  are plotted in Fig. 2. Based on the data of Table I, we find that the unit cell dimensions vary linearly with composition. The lattice parameters  $a(x)$ ,  $b(x)$ , and  $c(x)$  can be written as

$$a(x) = 12.754 - 0.485x, \quad (1)$$

$$b(x) = 3.925 - 0.143x, \quad (2)$$

$$c(x) = 3.515 - 0.249x, \quad (3)$$

where the units of  $a(x)$ ,  $b(x)$ , and  $c(x)$  are in Å, and the relations were obtained by a computer fitting program to observe lattice constant data.

### IV. SUMMARY

A series of samples of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$  have been prepared with  $x = 0.00, 0.25, 0.50, 0.55, 0.75,$  and  $1.00$ . The lattice constants have been estimated and the relationships between the lattice constants and the ratios of Sr/Ca have been established. The lattice constants for all three axes vary linearly with the concentration, in

TABLE I. Lattice constants versus the compositions ( $x$ ) in the  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ .

$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)
0.00	$12.769 \pm 0.036$	$3.926 \pm 0.003$	$3.511 \pm 0.005$
0.25	$12.639 \pm 0.012$	$3.894 \pm 0.002$	$3.460 \pm 0.002$
0.50	$12.501 \pm 0.018$	$3.856 \pm 0.003$	$3.392 \pm 0.012$
0.55	$12.466 \pm 0.031$	$3.838 \pm 0.012$	$3.376 \pm 0.006$
0.75	$12.371 \pm 0.014$	$3.813 \pm 0.002$	$3.325 \pm 0.003$
1.00	$12.299 \pm 0.019$	$3.789 \pm 0.004$	$3.267 \pm 0.002$

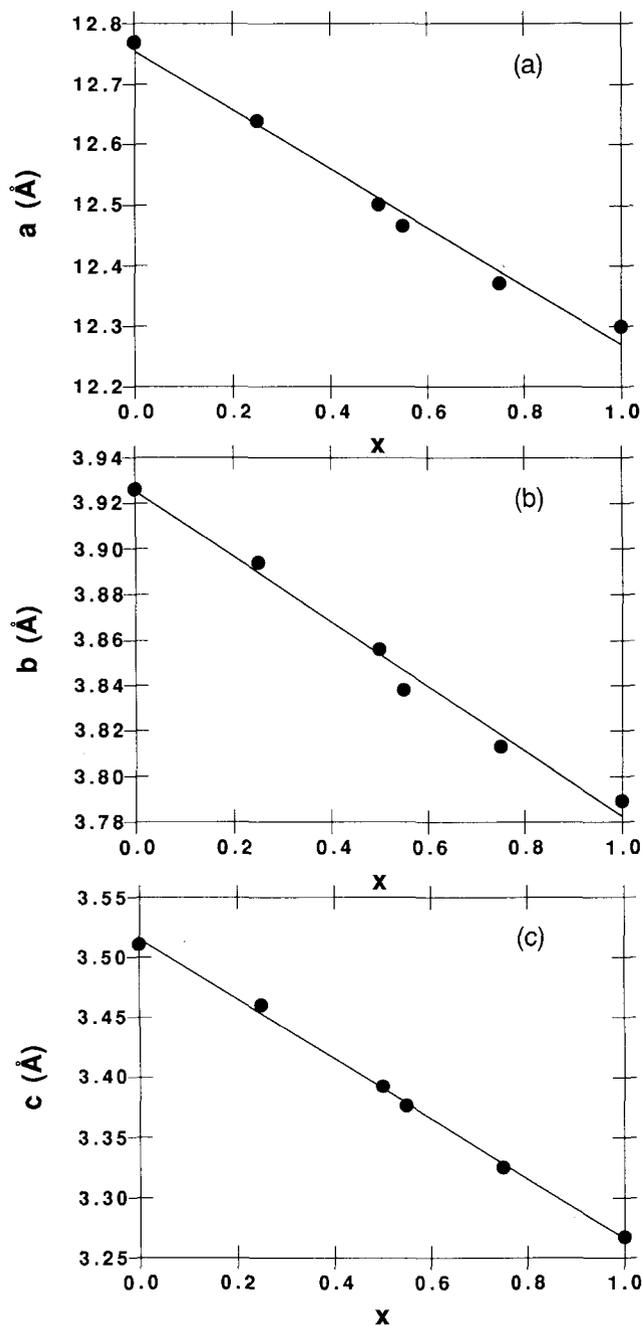


FIG. 2. Lattice constants  $a(a)$ ,  $b(b)$ , and  $c(c)$  versus  $(x)$  for the samples of  $(\text{Sr}_{1-x}\text{Ca}_x)_2\text{CuO}_3$ .

agreement with Vegard's law. The solid solutions have been found to be formed in the whole region with any ratio of Sr/Ca, in agreement with previous studies.

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#### REFERENCES

1. J. Polonka, M. Xu, A. I. Goldman, D. K. Finnemore, and Q. Li, *Supercond. Sci. Technol.* (1991, in press).
2. R. S. Roth, C. J. Rawn, J. D. Whitley, C. K. Chiang, and W. K. Wong-Ng, *J. Am. Ceram. Soc.* **72** (3), 395–399 (1989).
3. R. S. Roth, C. J. Rawn, J. J. Ritter, and B. P. Burton, *J. Am. Ceram. Soc.* **72** (8), 1545–1549 (1989).
4. K. Schulze, P. Majewaki, B. Hettich, and G. Petzow, *Z. Metallk.* (in press).
5. P. Majewaki, B. Hettich, H. Kaeger, and K. Schulze, *Adv. Mater.* (in press).
6. D. Shi, M. S. Boley, U. Welp, J. Chen, and Y. Laio, *Phys. Rev. B* **40** (7), 5255–5258 (1989).
7. J. Polonka, M. Xu, Q. Li, D. K. Finnemore, and A. I. Goldman, *Appl. Phys. Lett.* **59**, 3640 (1991).
8. A. M. M. Gadalla and J. White, *Trans. Br. Ceram. Soc.* **65** (4), 181–190 (1966).
9. G. L. Teske and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **371**, 325 (1969); **379**, 234 (1970).
10. K-H. Breuer, W. Eysel, and M. Behruzi, *Z. Kristallogr.* **176**, 216 (1986).