

### $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ : New High $T_c$ Superconducting Oxides\*

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The discovery of high-temperature superconductivity in perovskite-related oxides has generated an enormous amount of activity. Superconductivity above 30 K was initially reported by Bednorz and Muller [1] in a multiphase system having a nominal stoichiometry of  $\text{La}_{5-x}\text{Ba}_x\text{Cu}_5\text{O}_{5(3-y)}$ . Subsequent to this, Tanaka *et al.* [2] identified the superconducting compound as  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  ( $x = 0.15$  shows maximum  $T_c$ ) with the  $\text{K}_2\text{NiF}_4$ -type structure. Substitution of Ba by Sr was shown to produce relatively narrow superconducting transitions with zero resistance near 40 K [3]. Recently, Chu *et al.* reported superconductivity above 90 K in a multiphase sample having the nominal composition  $\text{Y}_{1.2}\text{Ba}_{0.8}\text{CuO}_{4-\delta}$  [4]. The composition of this superconducting phase in this multiphase sample was identified as  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  [5], a perovskite-related material. Both of these materials are thought to have perovskite-related structures, and while many of their physical properties are similar, there are also several important differences in their behavior.

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  can be viewed as a solid solution of  $\text{Sr}^{2+}$  and  $\text{La}_2\text{CuO}_4$ , with  $\text{Sr}^{2+}$  randomly replacing  $\text{La}^{3+}$  on the same crystallographic site. The solid solution range is from  $x = 0$  to as high as  $x = 0.6$  for rapidly cooled samples. Up to a concentration range of  $x = 0.15$ , the  $\text{Sr}^{2+}$  is incorporated into the lattice without creating oxygen defects as charge compensation, but as  $x$  increases from 0.15, there is a steady increase in oxygen vacancies, until the structure is no longer stable at  $x \sim 0.60$  [6]. This solid solution behavior influences the superconductivity in these materials, as indicated in Fig. 1. For  $x = 0$ , there is no superconducting transition above 4 K, but as the  $\text{Sr}^{2+}$  concentration increases, so does the critical temperature, to a maximum near 40 K at  $x = 0.15$ .

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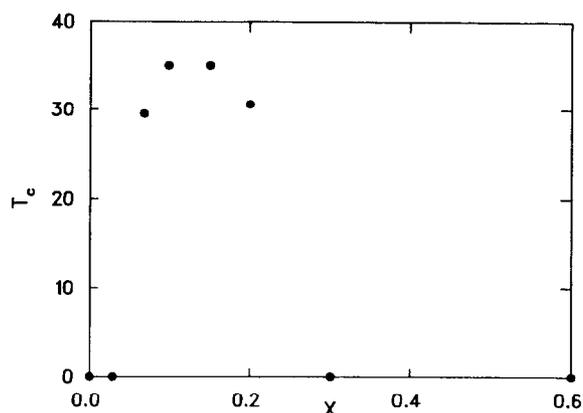


Fig. 1. The variation of the superconducting critical temperature with  $x$  in the compound  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

At  $x < 0.15$ , divalent strontium replaces trivalent lanthanum with charge balance maintained via the formation of  $\text{Cu}^{3+}$ . However, when  $x$  exceeds 0.15, oxygen vacancies begin to form because of charge compensation. These oxygen vacancies are located in the Cu–O plane, as determined by neutron diffraction. Since it is the Cu–O planes which are primarily involved in superconductivity, it is not surprising that at  $x$  greater than 0.15,  $T_c$  decreases very rapidly.

$\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ , on the other hand, exists as a stable compound, the Y and Ba each occupying different, ordered crystallographic sites and there appears to be no appreciable solid solution region for this material [5]. When the nominal stoichiometry deviates from  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ , impurity phases are formed, as evidenced from new peaks in X-ray powder patterns. The Y–Ba–Cu–O phase diagram is shown in Fig. 2. This phase diagram is a projection of a quaternary phase diagram onto the zero-oxygen

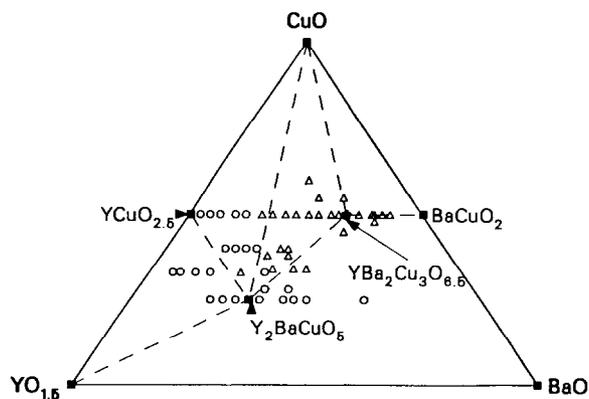


Fig. 2. The Y–Ba–Cu phase diagram: the projection of a quaternary phase diagram onto the zero-oxygen plane (nominal oxygen content is inferred assuming charge balance).

plane, with nominal oxygen content inferred by assuming charge balance. The initial atomic percent of the metals in the starting composition are used to determine the relative position of each sample. Four-probe resistivity, critical current and X-ray and neutron powder data were used to characterize the samples. It can be seen that there are relatively few stable quaternary compounds in this system. Because of this, superconductivity occurs over a large region in the phase diagram. Unlike  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ , the critical temperature does not vary in the phase region in which  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  is stable. This lends further support to the single-phase nature of this compound. This explains why the critical temperature does not vary in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  while there is a large variation in the case of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

While both  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  show zero resistance at 37 K and 92.5 K, respectively, their critical fields are quite different;  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  has a critical field estimated to be about 80 T, while there are initial indications of much higher critical fields in the yttrium compound. Critical currents in  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  are about 1 A/cm<sup>2</sup> at zero field [3], while  $J_c$  values of 500 A/cm<sup>2</sup> at zero field [7] have been measured in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ . Since critical currents are in part dependent on sample preparation techniques, and these values were obtained from sintered pellets of pressed polycrystalline samples with a density of about 85% of theoretical density, it is expected that the  $J_c$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  is in fact considerably higher than these initial measurements indicate.

One other major difference in behavior between these two materials involves the replacement of  $\text{La}^{3+}$  or  $\text{Y}^{3+}$  by other rare earth ions.  $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  is sensitive to changes at the  $\text{La}^{3+}$  site, with eventual conversion to another tetragonal structure at some rare earth ion concentration.  $\text{R}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$  (R = Nd–Eu) all exhibit another structure, and none of them is superconducting [8]. This is not the case for  $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_{6.5}$ , where  $T_c$  is not depressed, and may in fact slightly increase for some magnetic rare earth substitution.

It appears that, with some work,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  may play an important role in the future applications

of superconductivity. The most important area to be focused on is the improvement of the critical currents. The optimization of critical current densities in a superconductor generally involves adjusting the size and morphology of microstructural features in order to maximize the flux pinning in the superconductor. Critical current densities above 500 A/cm<sup>2</sup> (at  $H = 0$ ,  $T = 77$  K) in the absence of any such optimization suggest that practical applications involving current-carrying conductors at liquid nitrogen temperatures, such as power generation and transmission, high-field magnets, or magnetic levitation, are possible, perhaps probable, using  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$  superconductors.

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