

## ELECTRONIC STATE AND SUPERCONDUCTIVITY OF $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ (M=Al, Zn and Sn) SYSTEMS

Y. Zhao, and Q.R. Zhang, Department of Physics, Zhejiang University, Hangzhou, Zhejiang, P.R. China; H. Zhang, Department of Applied Chemistry, University of Science and Technology of China, Hefei, Anhui, P.R. China

A series of  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$  (M=Al, Zn and Sn) single-phase samples are prepared, and the measurements of the crystal structure, oxygen content, electric resistivity, thermoelectric power, Mössbauer spectrum, XPS and superconductivity have been performed. The experimental results of X-ray powder diffraction, Mössbauer spectrum and oxygen content show that the  $\text{Zn}^{2+}$  and the  $\text{Al}^{3+}$  occupy the Cu(2) site in Cu-O planes and the Cu(1) site in Cu-O chains respectively, but the  $\text{Sn}^{4+}$  occupies both the Cu(1) and Cu(2) sites. As regards the properties in superconducting state, both the  $\text{Zn}^{2+}$  and the  $\text{Al}^{3+}$  depress  $T_c$  strongly, but the  $\text{Sn}^{4+}$  does not. As for the electronic transport properties in normal state, the system doped by  $\text{Al}^{3+}$  displays a rapid increase of resistivity and some electron-localization-like effects, and the thermoelectric power enhances obviously; the series contained  $\text{Zn}^{2+}$  almost shows no changes of electric resistivity but the sign of the thermoelectric power is reversed. The experimental results also reveal that, although both the replacements for Cu(1) and for Cu(2) can suppress  $T_c$  and modify the electronic structure, the mechanism in these two kinds of replacements is not the same. The substitution of  $\text{Al}^{3+}$  for Cu(1) weakens the coupling intensity between the Cu-O planes, making the electron energy band narrow and the electrons localized; the replacement for Cu(2) with  $\text{Zn}^{2+}$  mainly influences the Cu-O plane itself, changing the structure of the Fermi surface. The simultaneous substitution of  $\text{Sn}^{4+}$  for Cu(1) and Cu(2) make the electronic structure vary complexly: sometimes it makes  $T_c$  high, sometimes low, depending on the preparation conditions. In additions, another noticeable phenomenon in this substitution study is the appearance of the  $\text{Cu}^{3+}$  oxidation state. Our XPS study shows when the Cu(1) was replaced by  $\text{Al}^{3+}$  or by  $\text{Sn}^{4+}$ , a peak corresponding to the  $\text{Cu}^{3+}$  oxidation state appears in the core level spectrum  $\text{Cu}_{2p}$ , but this phenomenon can not be observed in Zn-doped system. As we all know, it was believed that the presence of the  $\text{Cu}^{3+}$  plays a predominant role on high- $T_c$  superconductivity, and the most probable candidate of the  $\text{Cu}^{3+}$  is at the Cu(1) site. The XPS data show that the  $\text{Cu}^{3+}$  do exist in the Cu(1) site. Unfortunately, our experimental results also reveal that there is no intrinsic relationship between the  $\text{Cu}^{3+}$  oxidation state and the high- $T_c$  superconductivity. Observing and studying all our results noted above, at least one conclusion can be drawn as the following: intact Cu-O planes and strong coupling between these planes are two absolutely necessary conditions for the high- $T_c$  superconductivity in 1:2:3 compounds.