Application of High Pressure to Complex Copper Oxide Systems as a Way to Find New Superconductors

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Effects of high pressure and high oxygen pressure on the formation, structure, oxygen content, and electrical and magnetic properties of copper oxide superconductors crystallizing in perovskite-related structures have been studied. Under 6 GPa at 1223 K $ACuO_2$ (A: $Ba_{1/3}Sr_{2/3}$–$Sr_{1/3}Ca_{2/3}$) is stabilized in the $Ca_{0.84}Sr_{0.16}CuO_2$ type structure (so-called infinite-layer structure) and R_2CuO_4 (R: Y, Dy, Ho, Er, Tm) in the Nd_2CuO_4-type structure. We have found superconductivity with T_c of 110 K in the $Sr_{1-x}Ca_xCuO_2$ system, free from any rare earth ion, Bi^{3+}, and Tl^{3+}, treated at 6 GPa and 1273 K.

Keywords: High-T_c superconductor/ High pressure synthesis/ Infinite-layer structure/ $ACuO_2$/ R_2CuO_4

All the known cupric oxide superconductors contain CuO_2 sheets made of corner sharing CuO_4 squares, and these are intergrown with counter layers having different compositions and structures like $(La_{1-x}Sr_xO)_2$ in $(La_{1-x}Sr_x)_2CuO_4$. It is known that the CuO_2 sheets change their properties depending upon the oxidation state from an antiferromagnetic semiconductor to a superconductor and then to a Pauli-paramagnetic metal. The oxidation state has been controlled by chemical modification of the counter layers. Superconducting properties such as transition temperature (T_c) and stiffness of the magnetic flux lattice which determines the critical current density, and so on strongly depend upon the chemical composition and the structural features of counterlayers. For example, the T_c of $YBa_2Cu_3O_7$ (YBCO), 93 K, is considerably lower than that of $HgBa_2CaCu_2O_{6+\delta}$, 125 K, while the stiffness of the magnetic flux lattice, a very important parameter from the viewpoint of practical application, is considerably larger for YBCO. YBCO consists of a superconducting $/CuO_2/Y/CuO_2/$ unit and a counter unit of /BaO/CuO/BaO/, while the Hg-based phase contains corresponding units of $/CuO_2/Ca/CuO_2/$ and $/BaO/HgO_\delta/$ BaO/. Optimization of superconducting properties thus requires a further search for new counterlayers.

Since the discovery of the high-T_c superconductor by Bednorz and Müller [1] the search for new superconducting compounds has been pursued mainly by exploring a range of chemical compositions (counter cations and oxygen content) and reaction temperatures. To such a trend, we have added one more degree of freedom, pressure, and found some new complex cupric oxides including three superconductors [2–4]. Since the Cu-O bond and the counter cation-O bond should have different compressibilities, it is quite reasonable to assume that use of high pressure leads us to finding new

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Scope of Research

Inorganic materials that have new and useful functions such as superconductivity and ferromagnetism are synthesized by novel methods. Particularly the search for new high-T_c superconductors is intensively conducted using a high pressure synthesis technique at a pressure range of 3–8 GPa, where materials of high density unavailable under ambient pressure can form.

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phases and new compositions.

The simplest composition and structure containing the above type of CuO_2 sheets can be seen in $ACuO_2$ having the so-called infinite-layer structure. This structure was reported for the first time by Siegrist *et al.* for $Ca_{0.84}Sr_{0.16}CuO_2$ [5]. Along the tetragonal *c* axis regular CuO_2 sheets alternate with A layers without oxygen as shown in Fig. 1. Although a monophasic sample can be obtained only for a narrow composition range of $A{\sim}Ca_{0.9}Sr_{0.1}$ at ambient pressure, we found that application of high pressure stabilizes this structure for a wide composition range of $A=Ba_{1/3}Sr_{2/3}$–$Sr_{1/3}Ca_{2/3}$ at least [6]. It is noticed from a comparison of specific density that application of high pressure induces a crystalline transition to a high density form. In the case of A=Sr, the ambient pressure phase contains double Cu-O chains bundled by edge-sharing, which are sandwiched by a pair of SrO layers of the rock-salt type. In comparison with this the high pressure form is more compact, higher in specific density by more than *7%*.

Goodenough and Manthiram pointed out the relation between the sign of carriers to be injected into CuO_2 sheets and the mechanical stress imposed upon the CuO_2 sheets. Bond-length mismatch across the interface between the CuO_2 sheets and the counter layers creates a tensile stress within one layer and a compressive stress in the other. CuO_2 sheets under compression as in La_2CuO_4 are readily doped p-type, but those under tension as in Nd_2CuO_4 are doped n-type, because the mismatch can be eased by contraction and expansion of the CuO_2 sheets on oxidation (p-type) and reduction (n-type), respectively.

The CuO_2 sheets in $ACuO_2$ may be subject to a considerably strong tensile stress for a composition range around A=Sr. This structural instability may be relaxed in the following ways. One is to make the Cu-O bond longer by injecting excess electrons into the CuO_2 sheets. The other is to introduce vacancies to the A cation sites and, thereby, make the average A ion size smaller. We reported the presence of superconducting phases in the Sr(Ba)-Cu-O system with T_c=60–100 K [7], while Smith *et al.* found superconductivity with a $T_c\sim$40 K in the Sr-Nd-Cu-O system more recently [8]. In the latter system the superconducting phase seems to be of the infinite-layer structure formulated as $Sr_{1-x}Nd_xCuO_2$. As *x* increases, the *a* axis is elongated but the *c* axis is shortened as expected above.

Another remarkable result of our high pressure synthesis under 6 GPa at 1223 K–1273 K is the stabilization of R_2CuO_4 with R=Y, Dy, Ho, Er, and Tm in the Nd_2CuO_4-type structure [9]. Under ambient pressure this structure is stabilized only for R ions larger than Gd^{3+}. These results are consistent with a general tendency that high pressure increases the coordination number of a small cation.

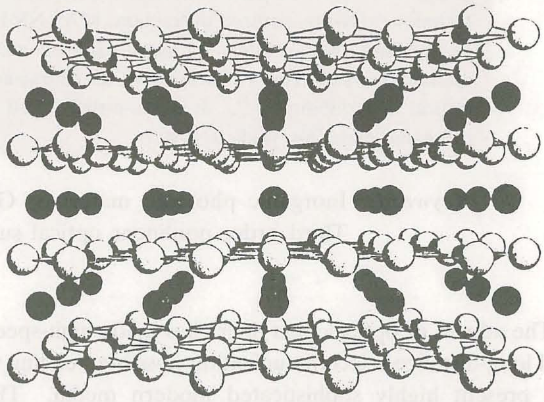

Figure 1. Infinite-layer structure, the parent structure of all the known cupric oxide superconductors. The CuO_2 planes and the alkaline-earth atom planes stack alternately along the *c* axis. Large dark and bright spheres represent A and oxygen atoms, respectively, and small dark spheres copper atoms.

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