

10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

MS-10.01.03 NEUTRON-POWDER-DIFFRACTION STUDIES OF CRYSTAL AND DEFECT STRUCTURES FOR HIGH- T_c SUPERCONDUCTORS. By F. Izumi, *National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba, Ibaraki 305, Japan.*

A variety of superconducting oxides with two-dimensional CuO_2 conduction sheets has been found since the discovery of superconductivity in $(\text{La}_{1-x}\text{Ba}_x)_2\text{CuO}_4$ in 1986. They are all nonstoichiometric compounds except for $\text{Ba}_2\text{YCu}_4\text{O}_8$ self-doped with holes. Carriers are doped through the introduction of substitutional and/or interstitial defects in charge reservoirs sandwiched between two CuO_2 sheets. Thus, the arrangements, oxidation states, and occupation probabilities of atoms in the charge reservoir markedly affect superconducting properties such as T_c (Jorgensen, J.D., *Phys. Today*, 1991, 44(6), 34-40).

Neutron-powder diffraction has been extensively used to understand relationships between defects and physical properties in superconductors. In particular, it has been successfully applied to structural studies of O defects, e.g., interstitial O atoms between two TIO sheets in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+z}$ (Shimakawa, Y. *et al.*, *Phys. Rev. B*, 1990, 42, 10165-10171), those between two CuO_2 sheets in $\text{La}_{1.87}\text{Ca}_{1.18}\text{Cu}_2\text{O}_{6+z}$ (Kinoshita *et al.*, *Phys. Rev. B*, 1992, 45, 5558-5562), structural changes on oxidation of $\text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{8+z}$ (Marezio, M. *et al.*, *Physica C*, 1992, 199, 365-374), and the one-dimensionally modulated substructure of O atoms on BiO sheets in $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CuO}_{6+z}$ (Yamamoto, A. *et al.*, *Physica C*, 1992, 201, 137-144).

Up to 1991, the structures of superconducting copper oxides had been regarded as the stacks of slabs closely related to perovskite-, rock-salt-, and fluorite-type structures along the [001] direction. This structural condition was broken through by the appearance of two new compounds containing novel structural blocks: $\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{GaO}_7$ (Vaughney, J.T. *et al.*, *Chem. Mater.*, 1991, 3, 935-940) and the oxide carbonate $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_{1+y}\text{O}_{2+2y+z}(\text{CO}_3)_{1-y}$ (Kinoshita, K. & Yamada, T., *Nature*, 1992, 357, 313-315). In $\text{Sr}_2(\text{Y}_{1-x}\text{Ca}_x)\text{Cu}_2\text{GaO}_7$, Sr_2GaO_3 slabs between two CuO_2 sheets contain those $(\text{GaO}_3)^{3-}$ zigzag chains of $[\text{GaO}_4]$ tetrahedra which run parallel with the CuO_2 sheet by sharing two corners of each tetrahedron. Two remaining O atoms in $[\text{GaO}_4]$ occupy apical positions of Cu on the conduction sheet. Evidently, the Sr_2GaO_3 block is not associated with any of the perovskite-, rock-salt-, and fluorite-type structures. The $(\text{GaO}_3)^{3-}$ chain somewhat resembles $(\text{SiO}_3)^{2-}$ chains of $[\text{SiO}_4]$ tetrahedra in pyroxenes such as MgSiO_3 . Similar infinite chains also lie in the crystal lattices of CuGeO_3 , CrO_3 , SO_3 , and $\text{Pb}(\text{PO}_3)_2$.

In $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_{1+y}\text{O}_{2+2y+z}(\text{CO}_3)_{1-y}$, CuO_2 sheets and carbonate slabs, $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_y\text{O}_{2y+z}(\text{CO}_3)_{1-y}$, alternate with each other along the c axis (Izumi, F. *et al.*, *Physica C*, 1992, 196, 227-235). Substitution of Ba^{2+} ions for Sr^{2+} ions makes it possible to replace a part of carbonate ions, $(\text{CO}_3)_y$, randomly with excess Cu atoms (Cu_y) to which interstitial O atoms (O_{2y+z}) are coordinated. Such extraordinary defects in the charge reservoir increase the hole concentration on the CuO_2 sheet to such an extent that the oxide carbonate shows superconductivity at 40 K. Two new types of superconductors found later have carbonate slabs where C and Cu atoms are not randomly distributed but ordered to form superlattices. One is similar in structure to the OII phase of $\text{Ba}_2\text{YCu}_3\text{O}_{7-z}$ (Akimitsu *et al.*, *Physica C*, 1992, 201, 320-324), and the other to $(\text{Ba}_{1-x}\text{Nd}_x)_2(\text{Nd}_{1-y}\text{Ce}_y)_2\text{Cu}_3\text{O}_{8+z}$ (Miyazaki *et al.*, *Physica C*, 1992, 202, 162-166).

Pressure influences the interatomic distances and bond angles in superconductors, causing the variation of T_c . Structural changes in several superconductors under high pressure were studied by TOF neutron-powder diffraction using He-gas pressure cells (Izumi, F. *et al.*, *Physica C*, 1992, 193, 426-436 and references therein). The resulting crystal data revealed pressure-induced charge transfer in $\text{Ba}_2\text{YCu}_4\text{O}_8$ and a hysteresis effect of pressure on the lattice constants of $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+z}$. In addition, the bulk moduli and compressibilities of Cu-O bonds in the superconductors could be determined reliably.

MS-10.01.04 STRUCTURAL PHASE TRANSITIONS IN INSULATING AND METALLIC La_2CuO_4 .

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La_2CuO_4 can exist in two structural forms, one with I4/mmm space group symmetry and a second with Bmab symmetry. Recently, two new structural modifications have been discovered in $\text{La}_{2-x-y}\text{RE}_y\text{M}_x\text{CuO}_4$ (RE = rare earth and $\text{M} = \text{Sr}^{2+}$ or Ba^{2+}), the first with $\text{P4}_2/\text{ncm}$ symmetry and the second with Pccn symmetry. These four structures have different CuO_6 -octahedra tilts about the [1 1 0] or [1 $\bar{1}$ 0] axes of the I4/mmm phase. Superconductivity occurs in all four structural modifications, with $T_c(\text{I4/mmm}) > T_c(\text{Bmab}) > T_c(\text{Pccn}) > T_c(\text{P4}_2/\text{ncm})$ at fixed doping. Substitution of La with RE can be used to control which phases exist at which temperatures. Fixing the RE concentration but varying the doping has reaffirmed the special nature of the electronic or magnetic structure at a doping level of 1/8 hole per Cu atom.

MS-10.01.05 $(\text{B}_x\text{Cu}_{1-x})\text{Sr}_2\text{YCu}_2\text{O}_7$, A NEW LAYERED CUPRATE WITH BORON-OXYGEN GROUPS. By W.J. Zhu*, Y.Z. Huang, J.Q. Li and Z.X. Zhao, National Laboratory for Superconductivity, Institute of Physics, Academia Sinica, Beijing 100080, China.

New layered cuprates $(\text{B}_x\text{Cu}_{1-x})\text{Sr}_2\text{YCu}_2\text{O}_7$ have been synthesized with various boron contents. Their crystal structures resemble that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, but contain boron-oxygen groups connecting (CuO_2) sheets beside Y layers. $(\text{B}_x\text{Cu}_{1-x})$ forms solid solution with an approximate range of $x = 0.1-0.9$. The compound of idealized composition $(\text{B}_{0.5}\text{Cu}_{0.5})\text{Sr}_2\text{YCu}_2\text{O}_7$ crystallizes in the orthorhombic structure with cell parameters $a=0.383$, $b=0.381$ and $c=1.096\text{nm}$. There is a strong incommensurate modulation in the (100) plane with wave vector $\mathbf{q} = \mathbf{c}^*/2 + \mathbf{b}^*/4.81$. Electrical resistivity measurements indicates metallic or semiconducting behaviour depending on the boron content. No superconducting transition was observed for these samples. In the $(\text{B}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{1-y}\text{Ba}_y)_2\text{YCu}_2\text{O}_7$ series, Ba doping at the Sr site induces superconductivity with optimum $T_c=51\text{K}$ for $(\text{B}_{0.5}\text{Cu}_{0.5})(\text{Sr}_{0.4}\text{Ba}_{0.6})_2\text{YCu}_2\text{O}_7$. These samples remain single-phase up to Ba content $y = 0.8$.

MS-10.01.06 SYSTEMATIC STUDY OF THE STRUCTURE OF $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. By Hoong-Kun Fun, Arlohun Wang, Cheng Hung Chou, Tsong-Jen Lee, Horng-Yi Tang & M.K. Wu, Department of Physics and Materials Science Center, National Tsing Hua University, Taiwan.