

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 $(\text{GaO}_3^{3-})_\infty$ 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 $(\text{GaO}_3^{3-})_\infty$ chain somewhat resembles $(\text{SiO}_3^{2-})_\infty$ 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 .

By R. Harlow and M. Crawford, Central Research and Development, Du Pont Company, Wilmington, DE 19880, U.S.A.

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 $P4_2/nm$ 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 $T_c(I4/mmm) > T_c(\text{Bmab}) > T_c(\text{Pccn}) > T_c(P4_2/nm)$ 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.

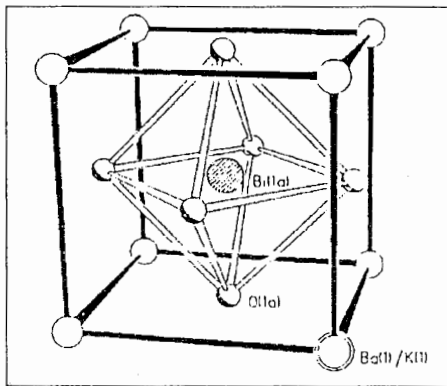
New layered cuprates $(\text{B}_x\text{Cu}_{1-x})\text{Sr}_2\text{YCu}_2\text{O}_7$ have been synthesized with various boron contents. Their crystal structures resemble that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, but contain boron-oxygen groups connecting (CuO_2) sheets beside Y layers. $(\text{B}_x\text{Cu}_{1-x})$ 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.

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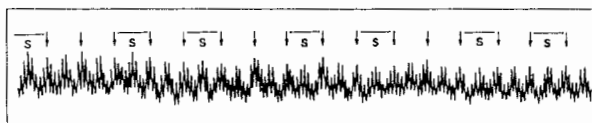
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Single crystals of $Ba_{1-x}K_xBiO_3$ (BKBO), with $x=0.35, 0.50$ and 0.55 , were grown by an anodic electrocrystallization process. Good single crystals for single crystal structure determination were selected by precession photographs. Powdered samples were also prepared for analysis of the powder pattern by the Rietveld method. Electron density maps from the results of the single crystal structure determination indicated non-localisation of the oxygen electrons. The detailed results of the systematic structure determinations, both with single crystals and with Rietveld analysis of powder data, will be presented. The structure of BKBO is shown below.



PS-10.01.07 MODULATION MODE OF LATTICE OF $Bi_2Sr_2(Ca_{0.96}Pr_{0.04})Cu_2O_{8.6}$ SUPERCONDUCTIVE CERAMICS. By T. Onozuka, Institute for Materials Research, Tohoku University, Sendai 980, Japan.

The basic structure of $Bi_2Sr_2(Ca_{1-x}Ln_x)Cu_2O_{8.6}$ (Ln =rare earth) ceramics is of $Bi_2Ti_4O_{12}$ -type with repeat $b_0 = 0.54$ nm. In addition, they display a long-period modulated structure in which domains with extent $b_1=4.5b_0$, $b_2=5b_0$ or $b_3=4b_0$ align along the b-axis with a mixing ratio. A [001] high-resolution image of the ceramics exhibits one-dimensional contrast modulation. The mixing mode of the two domains (modulation mode of the lattice) has been determined directly from the density distribution (Fig. 1) of the one-dimensional contrast modulation measured by photometry on the negative film of a sample of the title ceramic with $T_c = 80$ K (Onozuka (1993). J. Appl. Cryst. 26, in press.). The density distribution consists of two kinds of short units: b_1 and b_2 with nine and ten peaks, respectively. Unit b_1 is distinguished from unit b_2 by the existence of twin peaks in the middle, while unit b_2 has a single maximum peak. This density distribution occurs in an ordered sequence of the two units, namely two units b_1 , then one unit b_2 , then one unit b_1 , and one unit b_2 , etc.... The existence of the (2,1,1,1) modulation mode of the lattice in the crystal is thus revealed. This domain configuration is consistent with that of the ground state with the density of discommensuration, $\rho = 2/5$, in an one-dimensional competitive system described by the Frenkel-Kontorova model. The consistency with the model supports that the (2,1,1,1) modulated structure is induced by the lattice misfit between Bi-O double layers and perovskite layers in the compound.



PS-10.01.08 SUPERSTRUCTURES OF HTC Y-BA-CU-OXID BY X-RAY AND NEUTRON DIFFRACTION. By D.Hohlwein*, R.Sonntag and Th.Zeiske, Institut of Crystallography, University of Tübingen and Hahn-Meitner-Institut, Berlin, Germany.

In the System $YBa_2Cu_3O_{6+x}$ the superconducting transition, T_c , depends not only on the oxygen content, but also on the degree of oxygen order. Precise structure determinations, which can be done only by neutron or X-ray diffraction, were possible up to quite recently only for $x=0$ (no oxygen in the chains) and $x=1$. We succeeded in the determination of superstructures for $x=0.35, 0.40$ and 0.51 . For $x=0.35$ we found a well ordered oxygen structure with a $2\sqrt{2}a \times 2\sqrt{2}a \times c$ lattice by neutron diffraction (R.Sonntag et al., Phys.Rev.Lett. 1991, 66, 1497). At this concentration the compound is just not superconducting. The structure does not show the characteristic chains of the 90 K superconductor but instead there are half-filled chains alternating with quarter-filled ones. First and second neighbor oxygen places are not occupied, i.e., the structure is determined by the Coulomb repulsion of the oxygen atoms. Still more detailed results could be obtained by X-ray diffraction on a tiny piece of the neutron crystal (Th.Zeiske et al., Z.Physik, 1992, B86, 11). The above described tetragonal structure is a superposition of orthorhombic domains and the copper atoms in the neighborhood of oxygen atoms show small displacements. On a single crystal with slightly larger oxygen concentration, $x=0.40$, we detected the ortho-II Phase $2a \times b \times c$, for the first time with neutrons (Th.Zeiske et al., Nature, 1991, 353, 542). The ortho-II-phase is not long range ordered and $T_c = 38$ K. The order domains are along the chain direction (b-axis) twice as large ($24b$) as in a-direction ($10a$). Along the c-axis the order is only short ranged ($2c$). For the concentration $x=0.51$ we found by X-ray diffraction a well ordered ortho-II structure with $T_c = 56$ K (Th.Zeiske et al.; Physica C, 1992, 194, 1). The domain sizes are $18a \times 135b \times 6c$. The structure analysis revealed interesting displacements of Ba-atoms towards the Cu-O chains in an antiferro-distortive way.

PS-10.01.09 STRUCTURE OF TI-2212 ABOVE AND BELOW T_c . By V.N. Molchanov*, R.A. Tamzyan and V.I. Simonov, Institute of Crystallography, Russian Academy of Sciences, Moscow, Russia; M.K. Blomberg and M. Merisalo, Physics Dept., Helsinki University, Finland.

A Ti-2212 single crystal with $T_c=110$ K was investigated above and below the transition to the superconducting state using X-ray diffraction techniques. Data collections were carried out on a HUBER-5042 four-circle diffractometer (Mo $K\alpha$ radiation, graphite monochromator) equipped with a Displex-202 closed-type double-stage helium cryostat. Integrated intensities were measured on a spherical sample 0.266 mm in diameter at temperatures of 290, 160, 130, 90 and 60 K. The phase transition to superconducting state was not accompanied by change in symmetry (SG I4/mmm), appearing of satellite reflections, or of twinning.

Structural models were refined using full matrix least squares techniques. Anisotropic extinction parameters, anharmonic thermal motion parameters of heavy atoms were also tried. Models with small shifts of thallium and oxygen atoms from special positions were also tested. Final R-values did not exceed 0.028.

Analysis of changes in cell dimensions and interatomic distances reveals slight nonmonotonous dependence of some parameters on temperature in the phase-transition region. In this region, shortening of Cu-O (planar) bonds is clearly seen, while Cu-O (apical) bonds become slightly longer. These changes may be caused by increasing the local hole concentration around $Cu1$ at the superconducting phase transition.