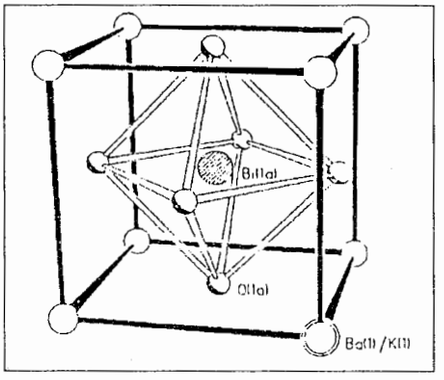
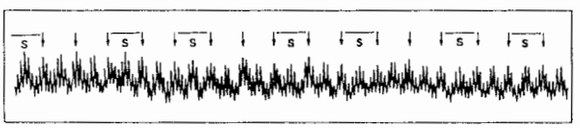
10-Physical and Chemical Properties of Materials in Relation to Structure (Superconductors, Fullerenes, etc)

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 $Bi_2Sr_2(Ca_{0.96}Pr_{0.04})Cu_2O_{8+\delta}$ SUPERCONDUCTIVE CERAMICS. By T. Onozuka, Institute for Materials Research, Tohoku University, Sendai 980, Japan.

The basic structure of $Bi_2Sr_2(Ca_{1-x}Ln_x)Cu_2O_{8+\delta}$ (Ln=rare earth) ceramics is of $Bi_3Ti_4O_{12}$-type with repeat b_0= 0.54nm. 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= 80K (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, ρ =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 $2\cdot\sqrt{2}\cdot a$ x $2\cdot\sqrt{2}\cdot a$ x 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 x b x 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 orderd 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 x 135b x 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 Tl-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 Tl-2212 single crystal with Tc=110K 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 Kα 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 60K. 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.

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