

**PS10.05.22 STRUCTURAL ANOMALY INDUCED IN  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $6 < x < 7$ ) BY  $\text{H}_2\text{O}$  ABSORPTION.** S. Edo and T. Takama\*, Department of Mechanical System Technology, Hokkaido Polytechnic College, Zenibako 3-190, Otaru 047-02, Japan; \*Department of Applied Physics, Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo 060, Japan.

The present authors have found that heat-treatment in air between 373 K and 473 K transforms the structure of oxygen-reduced  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $6 < x < 7$ ) into an anomalous structure having an extraordinary long spacing ( $> 12.5 \text{ \AA}$ ) along the  $c$ -axis (Takama and Edo, *Physica C* 235-240, 1994, 401-402). In the present paper, the cause of the transformation is investigated. Polycrystalline samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.95}$  with  $T_c$  of 91 K were annealed at 998 K for 6 hr in air and quenched into liquid nitrogen to obtain oxygen content  $x$  of 6.40. The samples were pulverized and annealed at 473 K in atmospheres of several kinds of gases (air,  $\text{N}_2$ , Ar,  $\text{O}_2$  and the mixture of Ar and  $\text{H}_2\text{O}$ ) at pressure of 1 atm for 30-230 hr. The X-ray diffraction profiles were measured by step scanning. Ac magnetic susceptibility was measured using the Hartshon bridge circuit. The X-ray profiles for the samples annealed in  $\text{N}_2$ , Ar and  $\text{O}_2$  were analyzed by the Rietveld method assuming a space group of Pmmm. For annealings in  $\text{N}_2$  and Ar, the lattice parameters slightly varied without a detectable weight change. For annealing in  $\text{O}_2$ , the lattice parameters were consistent with those for an as-quenched sample with  $x=6.71$ . The oxygen content  $x$  estimated from the weight gain increased from 6.40 to 6.73 through oxygen absorption. The sample annealed in Ar+ $\text{H}_2\text{O}$ , however, showed a drastic change in the profile as did that for the sample annealed in air. The profile change indicated an increase of the lattice parameter  $c$  by about 18 % compared with that for the as-quenched sample. The weight gain during the annealing was 3.1 %. Similar changes were also observed for the fully oxidized sample with  $x=6.95$ . The two samples with different concentrations turned to normal conductors after annealing in Ar+ $\text{H}_2\text{O}$ . These observations suggest that the anomalous structure is induced by absorption of  $\text{H}_2\text{O}$  molecules in the atmospheres regardless of the oxygen content. When the annealed samples were re-heated to temperature above 673 K, the structure reverted to the orthorhombic structure and superconductivity was recovered along with a reduction in weight. It seems that the recovery takes place with desorption of water.

**PS10.05.23 ON THE STRUCTURE OF OXIDIZED  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$ .** J.E. Jørgensen, M. H. Iversen and N. H. Andersen\*, Department of Chemistry, Aarhus University, DK-8000, Århus C, Denmark; \*Risø National Laboratory, PO Box 49, DK-4000 Roskilde, Denmark

$\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+\delta}$  is a high temperature superconductor for  $\delta=0.0$  with a critical temperature of 70 K. In contrast to the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds, superconductivity is destroyed by low temperature oxygen annealing. The stacking sequence of layers in  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  is: (Y/Ca)- $\text{CuO}_2$ -SrO-PbO-Cu-PbO-SrOCuO $_2$ -. Additional oxygen is incorporated into the PbO-Cu-PbO sandwich during low temperature annealing. A  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  sample was oxidized at 345 °C for 2 hours and studied by powder neutron diffraction and electron diffraction. The electron diffraction patterns showed a  $4a \times 2b \times c$  superstructure and the neutron data were analysed by the Rietveld method. The refinement was done in space group Pmmm. The additional oxygen was found to be located in the  $2r$  ( $0 \ 1/2 \ z$ ) and  $2p$  ( $1/2 \ y \ 1/2$ ) positions and the refinements yielded  $\delta=0.71(4)$ . Comparison of the structures of oxidized and unoxidized  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  shows that the bond valency sum for Cu in the  $\text{CuO}_2$  layers is reduced from 2.284 to 2.189 in the oxidized sample. This reduction in bond valency sum is mainly due to an elongation of the axial Cu-O bond which links the  $\text{CuO}_2$  layers to the PbO-Cu-PbO sandwich. The reduction in bond valency sum is assumed to be responsible for the lack of superconductivity in the oxidized sample.

**PS10.05.24 Ca SUBSTITUTION AND OXYGEN DEFICIENCY IN  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .** P. Berastegui, S.-G. Eriksson, L.-G. Johansson, Dept. of Inorganic Chemistry, Chalmers University of Technology and University of Göteborg, S41296 Göteborg, Sweden

The structural changes that occur upon the non-isovalent substitution of Ca for Y, were studied in  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  samples with  $\delta=0, 0.4$  and 1. Polycrystalline samples with stoichiometry  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $x=0.0, 0.1, 0.2$ ) were prepared by the solid-state reaction route and annealed in controlled partial oxygen pressures in order to obtain samples with the desired oxygen content. Neutron powder diffraction data were collected at room temperature using the medium resolution-high intensity powder diffractometer POLARIS, at the ISIS spallation source, Rutherford Appleton-Laboratory. Data analysis were carried out using the modified time-of-flight Rietveld program TF15LS, in the space groups Pmmm (samples with  $\delta=0, 0.4$ ) and P4/mmm (samples with  $\delta=1$ ). Site occupancies were constrained at their nominal values except the oxygen occupancies at the  $\text{CuO}$  chain.

Ca doping in the fully oxidized high- $T_c$  superconductor  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  has been observed to result in a decrease of  $T_c$ . The differences in ionic size and valence induce changes in the interatomic distances around this site but have also a drastic effect on the rest of the structure. In both superconducting samples ( $\delta=0, 0.4$ ), a decrease of the oxygen content can be observed with increasing Ca substitution, while the whole structure responds to the change in charge at this site. On the contrary, the nonsuperconducting sample ( $\delta=1$ ) shows a constant oxygen content with Ca doping. This results in the  $\text{CuO}_2$  planes being doped with holes, while the chain region remains unaffected.

The effect that the substitution has on the superconducting transition and calculations of the Bond Valence Sum for the different ions will also be discussed.

**PS10.05.25 SYSTEMATIC X-RAY DIFFRACTION STUDY OF  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  SINGLE CRYSTALS.** Cheng-Hung Chou, A. Wang, H.K. Fun, T.J. Lee, H.Y. Tang, C.H. Lin, M.K. Wu, Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 30043, R.O.C

Crystal structures of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  single crystals (BKBO), grown by the anodic electrocrystallization process, were analyzed to compare with previous studies on sintered powder samples. Results show that BKBO prepared in this way exhibit the same crystal symmetry of space group Pm3m for a wide range of  $x$ -values (0.38 to 0.66). This work shows that the content of potassium change with depth.  $T_c$  vs. potassium solubility curve has been plotted. In order to assure the uniformity of the composition and to examine the dependence of  $T_c$  on oxygen content, thin films of BKBO on the MgO substrate were prepared by laser ablation technique and their compositions will be checked by grazing incident X-ray diffraction. Thereafter, the resistivity vs. temperature curve were plotted using four probed method. Electron density maps, calculated from room temperature X-ray diffraction data, do not show conspicuous difference between superconducting and nonsuperconducting samples.