PS10.05.22 STRUCTURAL ANOMALY INDUCED IN YBa2Cu3O7−δ (6<δ<7) BY H2O ABSORPTION. S. Edo and T. Takama*, Department of Mechanical System Technology, Hokkaido Polytechnic College, Nakhito 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 YBa2Cu3O7−δ (6<δ<7) into an anomalous structure having an extraordinary long spacing (>12.5 Å) along the c-axis (Takama and Edou, Physica C 235-240, 1994, 401-402). In the present paper, the cause of the transformation is investigated. Polycrystalline samples of YBa2Cu3O7−δ with δ of 0.1 K were annealed at 998 K for 6 h 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, N2, Ar, O2 and the mixture of Ar and H2) at pressure of 1 atm for 30-230 h. The X-ray diffraction profiles were measured by step scanning. A magnetic susceptibility was measured using the Hartshorn bridge circuit. The X-ray profiles for the samples annealed in N2, Ar and O2 were analyzed by the Rietveld method assuming a space group of Pnma. For annealings in N2 and Ar, the lattice parameters varied slightly without a detectable weight change. For annealing in Ar, 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+H2O, 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 of 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+H2O. These observations suggest that the anomalous structure is induced by absorption of H2O 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 Pb2Sr2Y0.3Ca0.7Cu0.8O6.4. J.E. Jørgensen, M. H. Iversen and N. H. Andersen*, Department of Chemistry, Aarhus University, DK-8000, Århus C, Denmark; *Reso National Laboratory, PO Box 40, DK-4000 Roskilde, Denmark.

Pb2Sr2Y0.3Ca0.7Cu0.8O6.4 is a high temperature superconductor for δ>0 with a critical temperature of 70 K. In contrast to the YBa2Cu3O7−δ compounds, superconductivity is destroyed by low temperature oxygen annealing. The stacking sequence of layers in Pb2Sr2Y0.3Ca0.7Cu0.8O6.4 is(Y/Ca)-Cu02 Sr0-Pb0-Cu02- Sr0-Pb0-Cu02- having a 4a x 2b x 2c superstructure, while the chain region remains unaffected. The electron diffraction patterns showed a 4a x 2b x 2c superstructure and the neutron data were analyzed by the Rietveld method. The refinement was done in space group Pnmm. The additional oxygen was found to be located in the 2r (0 1/2 2) and 2p (1/2 2 1/2) positions and the refinements yielded δ=0.66. Comparison of the structures of oxidized and unoxidized Pb2Sr2Y0.3Ca0.7Cu0.8O6.4 shows that the bond valency sum for Cu in the CuO2 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 CuO2 layers to the PbO2-Cu-PbO sandwich. The reduction in bond valency sum is responsible for the lack of superconductivity in the oxidized sample.