

PS10.05.18 YBa₂Cu₃O_{7-x} STRUCTURAL SYSTEMATICS FOR EQUILIBRIUM COOLED SAMPLES B. C. Chakoumakos¹, T. B. Lindemer², M. Yethiraj¹, ¹Solid State Division, ²Chemical Technology Division, Oak Ridge National Laboratory*, Oak Ridge, TN 37831

Constant wavelength neutron powder diffraction data have been refined using FAT-RIETAN for a new suite of YBa₂Cu₃O_{7-x} samples, specially prepared as a function of oxygen content, by dynamically changing the oxygen partial pressure during cooling while monitoring the sample weight. The lattice parameters variation as a function of oxygen content and the orthorhombic-to-tetragonal transition follow that observed by Anderson et al. (*Physica C* 172, 31, 1990) for *in situ* measurements, except that our *c* values are systematically larger by 0.03 Å. The oxygen contents determined by site occupancy refinements (no O(5) site included) agree within 1.5 s.u. of the nominal equilibrium values. From a bond valence sum analysis, the apparent copper valences vary from 1.3 to 2.3 for the chain site and from 2.15 to 2.20 for the plane site as the oxygen content is varied from 6.05 to 6.97 per formula unit. The hole content per CuO₂ sheet exhibits a parabolic dependence on T_c. For each *x* value a 12 g sample was prepared in a vacuum thermogravimetric apparatus by heating to equilibrium weight (±0.1 mg) at T-pO₂ conditions that would give the desired *x* value as calculated from the thermodynamic models that were fitted to experimental data for YBa₂Cu₃O_{7-x} (Lindemer et al., *J. Am. Ceram. Soc.* 72, 1775, 1989). The samples were then cooled at ≈200°C/h while decreasing the pO₂ to maintain the equilibrium specimen weight, i.e., the desired *x* value; about 75% of the specimens were equilibrated at lower T-pO₂ conditions to demonstrate that the desired *x* values were maintained. Reduction in flowing Ar-4%H₂ was used to verify the nominal *x* values of all samples after neutron diffraction. Neutron powder diffraction data were collected using the HB4 high resolution powder diffractometer (1.03 Å, *d*-spacing range = 0.55 - 5.38 Å) at the High Flux Isotope Reactor, ORNL.

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PS10.05.19 CRYSTAL CHEMICAL DESIGN OF HIGH-T_c SUPERCONDUCTORS ON THE GROUND OF OXIDE AND INTERMETAL LAYERS. L. M. Volkova, S. A. Polyshchuk, Institute of Chemistry, Far Eastern Branch of Russian Academy of Science, Vladivostok 690022, Russia, S. A. Magarill, Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Science, Novosibirsk 630090, Russia

The design of new compounds (B₂C₂)(MO₂) and A₂(B₂C₂)(MO₂)-candidates in superconductors of Nd₂CuO₄ and Sr₂Mn₃As₂O₂ structure types, which consist of alternating oxide planes of CuO₂-type and intermetal layers such as in compounds of the ThCr₂Si₂ or CaBe₂Ge₂ structure types will be presented. The paper will discuss the possibility of these systems formation on the ground of B and M = Cu, Mo, Nb, Ta, Re, W, Ru or Ti and C = Si, Ge, P, As, Bi or Te. The double role of B₂C₂-layer will be shown. It combines the functions of CuO₂-layers and interstitial layers (CuO, TiO, Bi₂O₂ and so on) in high-T_c cuprates.

This design was carried out on the base of our own crystal chemical concept of appearing "conductance coupled oscillating displacements of atoms" by transition in superconducting state. On the ground of the crystal chemical investigations of the high-T_c superconductors we proposed that the appearance of high-T_c superconductivity near the Mott metal-insulator phase boundary is associated with transition of system in dynamic state with coupled oscillating atom displacements. The correlation between the coupled oscillating displacements of atoms, changes of magnetic properties and transfer of charge carriers determines the transition of materials in superconducting state. 2D-systems with mutual controllability of layers by the presence of atoms at critical near-neighbor distances are favorable to appearance the dynamic state. The mixed valent compounds of the transition metals with low energy of intervalent transfer, where one of the states has a magnetic moment, may be a basis for these systems.

PS10.05.20 THE PLANE BUCKLING ANOMALIES AND SUPERCONDUCTIVITY OF COPPER OXIDE MATERIALS. A.V. Klochkov, O.A. Usov, Ioffe Physico-Technical Institute, Polytechnical str., 26, 194021 St.Petersburg, Russia

The interplay between the copper oxide plane buckling parameters and superconducting properties of cuprate high-temperature superconductors (HTSC) and related materials including Pr anomalies are discussed. The structure parameters are determined by X-ray diffraction data analysis and were shown to correlate with free hole carrier concentrations and critical temperature of superconductors. From consideration of local structure of copper oxide layers all cuprate HTSC compounds are found to be separated for two different types: buckled SC plane (BSP) like Y123, Bi2212 etc and flat plane (FSP) like 1201, 214(T') etc. For FSP type compounds the critical temperature has optimal value for flat copper layers and Pr anomalies were not observed. If buckling increases the critical temperature of FSP compounds decreases. For BSP one it increases, the Pr anomaly being observed. From analysis of structure parameters of R123 compounds (R - rare earth elements) we found that buckling of CuO layers increase but BaO decrease on ionic radius and for Pr they should be equal. But the buckling of CuO layers are found to abrupt to value known for insulators. Thus for Pr123 the layers assumed to be unstable due to large ionic radius of Pr and redistribution of charges between the layers. The analysis of buckling anomalies and its influence on the electronic properties are supposed to be important step for discovering of physical factors responsible for high critical temperatures.

PS10.05.21 USEFUL TOOLS FOR HIGH T_c SINGLE CRYSTALS ON THE DIFFRACTOMETER: TESTING, DATA COLLECTION AND REFINEMENT OF CRYSTAL STRUCTURES. V.N.Molchanov, Institute of Crystallography, Moscow 117333, Russia

Several useful tools were accumulated especially for high-T_c single crystals during more than 7 years of their studies in the X-ray Lab. of the Institute of Crystallography. The set of these tools covers all stages of diffraction experiment, starting from sample preparation, and includes effective strategy for evaluation of systematic errors in the course of crystal structure refinements. The following short list includes some of these methods.

Two-dimensional ω/2θ angle maps of special type reflections (e.g. h00, 0k0, hh0 and 00l) were widely used for checking crystal quality, twinning and distribution of mosaic spread. The sensitivity of this procedure is so high that enables to detect 1:500 volume ratio of twin domains for Y-123 samples. Apart from that the pin hole collimator may be used to visualize the distribution of twin domains at different parts of small single crystals.

Intensity measurements of specially chosen strong and weak reflections at different ψ-angles are very effective to check anisotropy of extinction for plate-like single crystals. Side faces of small single crystal cut from a big one are usually very rough for unambiguous indexing under a microscope. In this case rocking curves measured may be used also for improvement of absorption correction by fitting the best set of indices for side faces.

Typical refinement procedure includes subsequent statistical analysis of F_{obs}/F_{calc} and F_{obs}-F_{calc} values for each reflection from the reflection set along different variables, such as setting angles, index L for layered structures, extinction coefficient, mean path length, sin(θ)/λ and others. In many cases such a distribution served as a criteria of systematic errors absence.

Examples of effective using these tools are discussed.