

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

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10.01 – Superconducting Materials

MS-10.01.01 STRUCTURAL EFFECTS OF ELEMENT SUBSTITUTION IN THE CUO PLANE OF THE 1-2-3 YBCO SUPERCONDUCTOR
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Changes in the crystal structure, as a result of different substitutions in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ have been studied by electron microscopy and have been related to the physical properties of these substituted materials. In this contribution we will limit ourselves to substitutions taking place in the CuO plane.

Oxygen ordering has been investigated in superconducting $\text{ABa}_2\text{Cu}_3\text{O}_{7-\delta}$ ceramic materials with $A = \text{Er, Nd, Sm, Y}$ and Yb , as well as in samples where the rare earth element is partially substituted by Pr. The critical temperature T_c is determined as function of oxygen deficiency. A distinct relationship is found between the width of the 60 K plateau and the Ortho II ordering. [Krekels et al. *Physica C* 196 (1992) 363]. These results show that the Ortho II ordered phase is a superconducting phase with a characteristic T_c of 60 K.

Small substitutions of iron (or cobalt) for copper have a dramatic impact on T_c as well as on the microstructure. The average size of the (110) twin domains decreases and a "tweed" pattern results.

Substituting the Cu by Co or Ga (and simultaneously replacing Ba by Sr so as to have a chemical formula $\text{YSr}_2\text{Cu}_2\text{GaO}_7$) does not alter the topology of the structure. However Co- or Ga-ions have a strong tendency to be tetrahedrally coordinated by oxygen ions. Therefore the CoO layer, which replaces the CuO chain layer, adopts a configuration of chains of corner sharing CoO_4 tetrahedra along the [110] or $[\bar{1}\bar{1}0]$ perovskite directions. These tetrahedra are rotated about an axis parallel to c. This rotation can take place with equal probability in the clockwise and the anti-clockwise sense. In the structure described by Roth [J. de Physique II (1991) 721] all chains are rotated in the same sense. We have found direct evidence that the unit cell is doubled because of an alternating clockwise and anti-clockwise rotation in successive chains. Moreover a number of interesting defects occurring in such structures are analysed using high resolution electron microscopy.

Recently it has been proven to be possible to substitute Cu in the CuO layer by carbonates, phosphates or sulphates. YBCO based material containing SO_4 -tetrahedra on the Cu(1) sites shows an incommensurate modulation which can be attributed to the ordering of b-oriented SO_4 -rich chains in the Cu-S-O layer and which can be described in terms of an SO_4 concentration wave.

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MS-10.01.02 SEARCH FOR NEW SUPERCONDUCTING LAYERED CUPRATES. By E.V. Antipov¹, A.V. Luzikova¹, A.L. Kharlanov¹, E.M. Kopnin¹, A.V. Mironov¹, S.N. Putilin¹, I. Bryntse² and M. Marezio^{3,4},
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The problem of obtaining a new superconducting material can be divided into two different tasks: synthesis of a new phase with a superconductor related structure and its proper modification for appearing the superconductivity.

1. Synthesis of new layered cuprates.

The main part of known superconducting cuprates have the layered structures with the (CuO_2) layers located in the perovskite slab "intergrown" with the rock salt or fluorite blocks. The possibility of synthesis of new phases with such structures is determined by matching of these slabs. The dimensions of the rock salt or fluorite blocks are determined by ionic radii of the cations located there and can be modified easily using different cations. To achieve block matching the perovskite block size should be appropriately changed. Its size is determined mainly by the length of the strong covalent Cu-O bonds in the (CuO_2) layers. The alteration of this bond length can be achieved by changing the copper valence using various synthesis conditions or non-isovalent substitution of cations in the structures. This approach has been used for the synthesis of the different cuprates with the fluorite slabs: T^* , Th-containing 223 and Sr-containing 223 and 1222, Bi-2222 phases.

New phases can be synthesized also by the modification of the composition of the rock salt slab by a location of the Hg^{2+} or Ga^{3+} cations inside this block. The new phases Hg-1201, Hg-1212 and Ga-1201 have been obtained applying such approach. The different crystallochemical behavior of Hg^{2+} and Ga^{3+} ions results in various oxygen arrangements of these cations: Hg^{2+} has the dumbbell coordination in contrast to the tetrahedral one for Ga^{3+} .

2. "Structure-property" relation for layered cuprates.

The composition of the layers neighboring the (CuO_2) ones influences significantly the superconducting properties of layered cuprates. The single crystal refinement of the Nd-containing 123 phase with partial replacement of Ba^{2+} cations by Nd^{3+} ones, Nd,Th-containing 223 phase and powder refinement of the Sr-containing 223 and 1222 phases revealed the existence of strong distortions in their structures. Such distortions caused by the statistical location of the different cations in one crystallographic position are possibly responsible for the charge localization in the (CuO_2) layers and the suppression of the superconductivity in these phases. We suppose that the phases with the highest T_c should not have such disorder in their structures (e.g. provided by different cation substitutions.)

The different crystallochemical behavior of the cations in the "insulator" slabs determines the methods of synthesis of phases with the desired formal copper valence in the (CuO_2) layers. The Hg and Ga-containing cuprates are given as examples.