07.3-1 PHASE DIAGRAM OF THE TETRAGONAL TO ORTHORHOMBIC STRUCTURAL TRANSITION IN $La_{2-x}Sr_xCuO_4$. By

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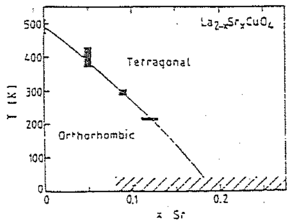
The relation between structural and superconducting instabilities is considered to play a crucial role in the behaviour of the new high T_c superconductors. In the $La_{2-x}Sr_xCuO_4$ materials it is usually admitted that the effect of Sr alloying to La is to suppress the orthorhombic distortion present in La_2CuO_4 and to stabilize the tetragonal phase which is superconducting.
We report here an X-ray scattering study of the structural phase diagram of $La_{2-x}Sr_xCuO_4$. For x = 0.12 a low T single crystal study reveals a tetragonal to orthorhombic transition at T_{T-O} = 215 ± 5 K. The intensity of the associated superstructure reflections and the orthorhombic distortion (c - a) (space group Cmca) were measured down to 12 K. Precursor diffuse scattering is observed up to room temperature and it is quasi-isotropic. Supplementary powder diffraction data for x = 0, 0.05 and 0.09 allow to construct a phase diagram of the tetragonal to orthorhombic distortion (see figure). From this result one can conclude that superconductivity (observed in the hatched region) coexists with the orthorhombic distortion in a broad concentration range, in contrast with previous hypotheses.



07.3-2 HIGH RESOLUTION SYNCHROTRON X-RAY STUDY OF $La_{2-x}M_xCuO_{4-y}$ (M = Ba, Sr). by

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High resolution X-ray diffraction of $La_{2-x}M_xCuO_{4-y}$ (M = Ba, Sr) reveals two macroscopically segregated phases of the K_2NiF_4-type with nearly identical lattice parameters. In the Sr-substituted material the minor phase shows considerably broader Bragg peaks than the major phase and it occurs in substantial amounts. The two phases are associated with phase separation within a nominally single phase field and are presumably sensitive to oxygen and/or thermal treatment. In a detailed study of $La_{1.8}Ba_{.2}CuO_{4-y}$, several peaks showed additional broadening on cooling. This broadening is consistent with a small spontaneous monoclinic distortion, with an onset temperature of ~150K, which is possibly relevant to the superconducting properties. Small single crystals within the powder aggregate are also studied and show a similar two-phase constituency and a resolvable peak splitting at low temperature.

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07.3-3 NEUTRON AND SYNCHROTRON X-RAY POWDER STUDIES OF A HIGH IONIC CONDUCTOR SYSTEM : $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$.

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It was recently reported that $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ solid solutions exhibit high ionic conductivity. This conductivity increases rapidly with increasing values of x. Arrhenius plots of log σT(x) versus the reciprocal of the absolute temperature show three extrema, 2×10^{-2}, 2×10^{-3} and 8×10^{-3} $(\Omega cm)^{-1}$ for x = 0.35, 1.0 and 1.8, respectively. It was also found that, depending on the substitution parameter x, the compounds in this solid solution adopt three structure types, corresponding to three different phases: Phase I is in the region 0 ≤ x ≤ 0.4, phase II in 0.4 < x ≤ 1.0 and Phase III in 1.0 < x ≤ 2.0. The x values corresponding to the maximum and minimum conductivities coincide approximately with phase transition boundaries.
In this paper results of our efforts to correlate structural changes with conductivity behaviour are presented:
a) Single crystal structure studies of $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ compounds with x = 0.0, 0.06, 1.0, 1.8 and 2.0 indicate that structure framework of compounds in phase I is an $R\bar{3}c$, Nasicon-type structure. Further insertion of trivalent In^{3+} ions induces much more complicated structural changes: compounds in phases II and III are found to be orthorhombic, Pbca, and monoclinc, $P2_1/n$, respectively. Crystal structures in phases I, II and III, and their relationships, are described.
b) Neutron powder refinements of highly conducting, polycrystalline samples with nominal compositions x = 0.25, 0.40 and 0.45 indicate that lithiums in the large eight-coordinated sites are in a highly disordered configuration, occuping only 6% of the site capacity, while the low energy octahedral sites are 95% filled. Such a site distribution, which is unfavorable for fast ion diffusion, may change in the highly conducting state: transfer of Li ions from octahedral sites into the large cavities is therefore expected at high temperature. Results of studies of site occupancies and structural changes as a function of temperature, at 40, 200, 600 and 800 K, along with electrical properties will be discussed.
c) Neutron studies have also suggested the existence of a parasitic phase in the $Li_{1+x}Ti_{2-x}In_xP_3O_{12}$ solid solution. This phase could not, however, be readily identified. Due its exceptionally high resolution a synchrotron x-ray diffraction pattern of $Li_{1.25}Ti_{1.75}In_{0.25}P_3O_{12}$ shows 26 extra reflections, well resolved from the expected lines. Rietveld refinement applied to the x-ray pattern confirms a neutron observation that the observed Ti/In ratio is substantially lower than it should be according to the chemical analysis. These extra reflections are indexed, and a space group and a solution of the crystal structure of this unwanted phase are proposed.