(I) Crystal Transformation between Sheared and Layered Phases in Bi-2201

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A detail study on the equilibrium phase diagram around $Bi_2Sr_2CuO_\delta$ in the Bi-Sr-Cu-O system newly found a crystal transformation between the sheared and layered phases in Bi-2201 by changing the oxygen stoichiometry. The transformation occurs in the finite composition area surrounded by $Bi_{43-y}Sr_{40+y}Cu_{17}O_z$ ($0\leq y\leq 3$) and $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ ($0 \leq x< 0.1$). The phase stability sensitively depends on the temperature as well as the oxygen partial pressure.

Keywords: equilibrium phase diagram/ bismuth cuprate/ high-Tc superconductor

It is now well known that in $Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ (Bi-2201) two distinct phases appear depending on the details of preparation process. One phase has the so-called sheared structure (S-2201), an insulator with a monoclinic symmetry, a ~ 2.45nm, b ~ 0.54nm, c ~ 2.2nm, β ~ 106º and the other is the so-called layered one (L-2201), a superconductor with a tetragonal a ~ 0.54nm,c ~ 2.45nm. However, the monophasic compositional region and the phase stability of both phases are one of the controversial issues due to the sensitivity of both phases to the heating temperature and the reaction process in addition to the difficulty in phase identification. In the present work, we firstly determined the location of both phases in the phase diagram of Bi-Sr-Cu-O system which will provides us invaluable information on the stable synthesis of both phases.

The solid-solution of S-2201, $Bi_{43-y}Sr_{40+y}Cu_{17}O_z$ ($0\leq y\leq 3$), is newly found to exist in the $BiO_{1.5}$-SrO-CuO system at 830~860 ºC in air. In contrast, the solubility range of the S-2201 is found to extend toward the Cu-deficient region ($Bi_{2+x}Sr_{2-x}CuO_{6+\delta}$ $0\leq x<0.1$) by the heat treatment under Ar flow as shown in the figure. More interestingly, series of the S-2201 structure changes completely to the L-2201 upon annealing at 600ºC for 48h under high oxygen pressure (120atm) due to the change in the oxygen stoichiometry. The oxygen contents for cation stoichiometric $Bi_2Sr_2CuO_\delta$ is also determined to be δ=6 for the S-2201 and δ=6.2 for the L-2201. These results clearly demonstrate that the sheared phase has no excess oxygen. In the other word, the excess oxygen ions induce the layered structure to relaxing a mismatch between the Bi-double layer and the perovskite block accompanying with the incommensurable structural modulation.

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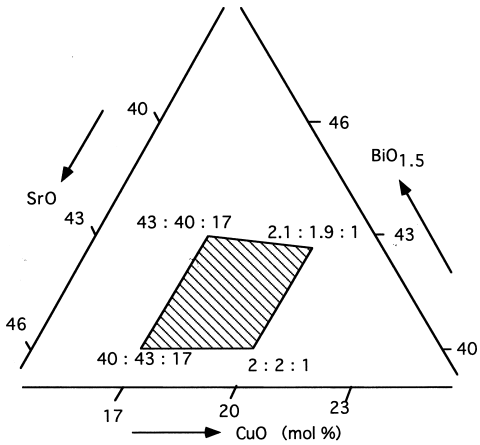

SOLID STATE CHEMISTRY — Quantum Spin Fluids —

Scope of research

Quantum spin oxide system such as high-T_c superconducting cuprates, $La_{2-x}Sr_xCuO_4$ and $Nd_{2-x}Ce_xCuO_4$ are synthesized in the form of single crystals using traveling-solvent-floating-zone method. Detailed equilibrium phase diagram of Bi cuprate systems is investigated. Main subjects and techniques are: mechanism of high-T_c superconductivity: origin of quantum phase separation in strongly correlated electron systems: spin excitations in quantum spin systems: interplay between spin and charge flow in doped spin system: neutron scattering by using triple-axis as well as time-of flight techniques.

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