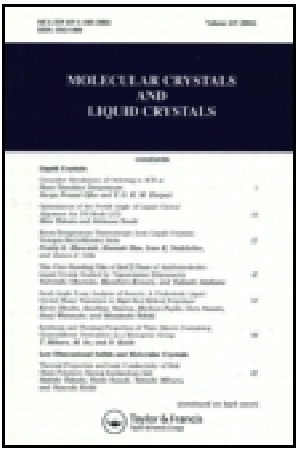

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Structural and Physical Properties in the Bi-Sr-Cu-O System

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STRUCTURAL AND PHYSICAL PROPERTIES IN THE BI-SR-CU-O SYSTEM

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Abstract The structure/property relationships in the Bi-Sr-Cu-O system have been investigated. This system includes $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$, the single Cu layer compound that is one member of the Bi-Sr-Ca-Cu-O family of superconductors. This family includes $Bi_2Sr_2CaCu_2O_8$, a 95K superconductor. We have determined that two structurally related phases exist near the composition $Bi_2Sr_2CuO_6$. One phase is a solid solution, $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$, with a wave modulated structure. The second phase, $Bi_2Sr_2CuO_6$, has a structure with a step dislocation. The former phase exhibits superconductivity while the latter phase is an insulator. The transition between structures is driven, atleast in part, by a change in cation ratios.

INTRODUCTION

The search for insight into the nature of superconductivity at high temperatures has, ironically, led to significant interest in the cuprate phase $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ which has the lowest T_c (<10K). This compound is a member of the Bi-Sr-Ca-Cu-O family of high T_c materials and a complete understanding of chemistry/property relationships in this phase may shed light on the more complex systems. Furthermore, the low T_c of the Bi-Sr-Cu-O superconductor allow measurements of the normal state properties to much lower temperatures.

A significant body of research on the Bi-Sr-Cu-O system, including studies of the phase diagram[1], crystal growth and characterization[2], single crystal x-ray diffraction[3], composition/property relations[4], doping effects[5], TEM[6], and oxygen effects[7], has already been published. Yet, no coherent picture of the structure/property relations in this system has emerged. The goal of this proceedings is to summarize our own experimental results in the $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ system and to incorporate these and other results into a unified description of the chemistry and properties of these materials.

EXPERIMENTAL

Ceramic samples were prepared from $Sr(NO_3)_2$, Bi_2O_3, and CuO. After an initial reaction at 810°C in alumina crucibles, samples were ground, pressed into pellets, and heated in air for 24 hours at 820°C on Ag foil. This last step was repeated, increasing the temperature by 10°C, until no change was observed in the powder diffractogram (typically 4-5 heatings to a maximum of 860°C). Resistivity measurements were performed on bars of sintered ceramics using a four-probe ac method. Contacts were made with indium metal with currents of 2mA being typical.

RESULTS AND DISCUSSION

Structure

The $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ system actually contains two distinct phases with closely related compostions[1a]. One compound has the formula $Bi_2Sr_2CuO_{6\pm\delta}$ and will be refered to as Phase A. The second phase is a solid solution of composition $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$ and will be refered to as Phase B. The Bi-Sr-Cu-O phase diagram showing these two phases is depicted in Figure 1. We have prepared ceramic samples in the system $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$ which includes both the top of the solid solution and Phase A. Figure 2 shows the evolution of x-ray powder diffraction patterns with changing composition in the $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$ system. From this data the following phase boundaries can be deduced: $Bi_2Sr_2CuO_{6\pm\delta}$ (Phase A) is only single phase at compositions very close to 2-2-1 while Phase B is stable for $x>0.16$. Phase A can be indexed on a monoclinic cell with a=24.45, b=5.412, and c=21.97Å and $\beta=105.75°$ while Phase B has a psuedo-tetragonal subcell with $a\approx b\approx 5.36$ and c=24.62Å. The substructure of Phase B has been determined and shows a layered structure similar to the other high T_c compounds. The actual structure is complicated by the presence of an incommensurate modulation along the layers. This modulation has been observed in TEM and the details of the modulation has been determined from a single crystal x-ray refinement for one composition within the solid solution[3b]. The substructure and modulated structure are depicted in Figure 3. The modulated structure is very similar (although more pronounced) to that found in the Bi-Sr-Ca-Cu-O system[8]. This modulation arises from a "lattice mismatch" between the repeat of the Bi-O layers and that of the Sr-O and Cu-O layers. The strain associated with this mismatch can be relieved

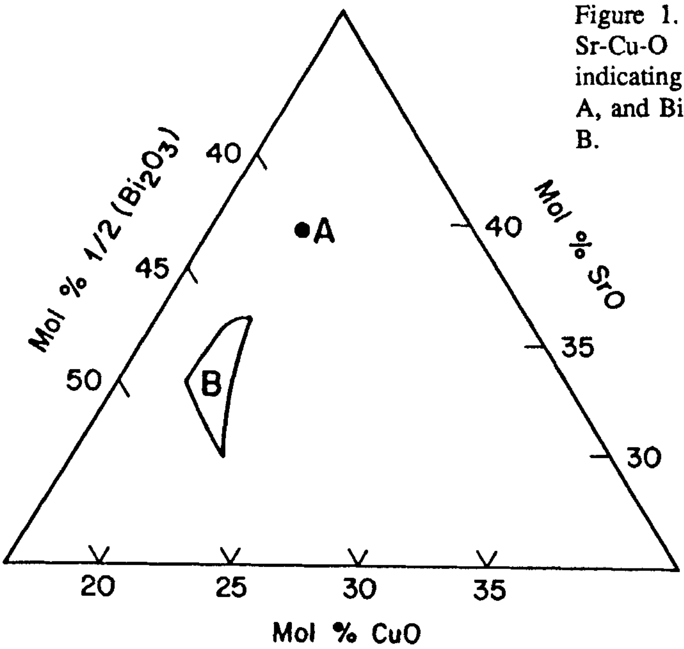

Figure 1. A portion of the Bi-Sr-Cu-O phase diagram indicating $Bi_2Sr_2CuO_6$, Phase A, and $Bi_{2+x}Sr_{2-y}CuO_{6\pm\delta}$, Phase B.

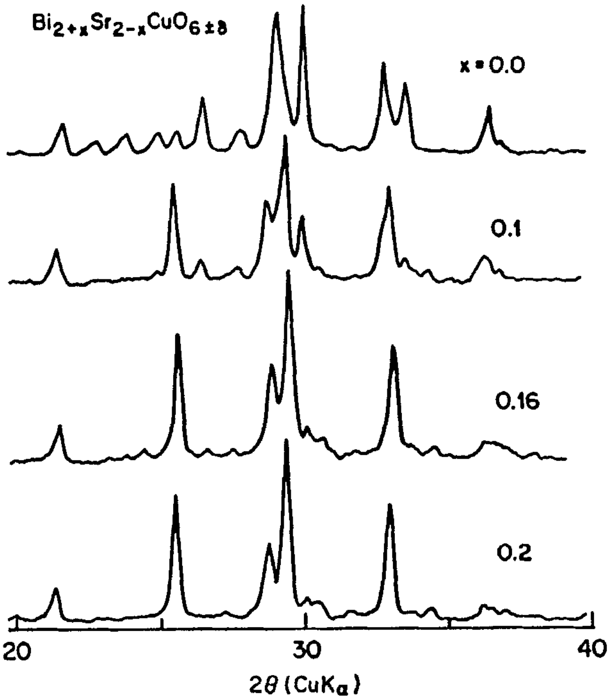

Figure 2. Evolution of x-ray diffractograms with x in $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$.

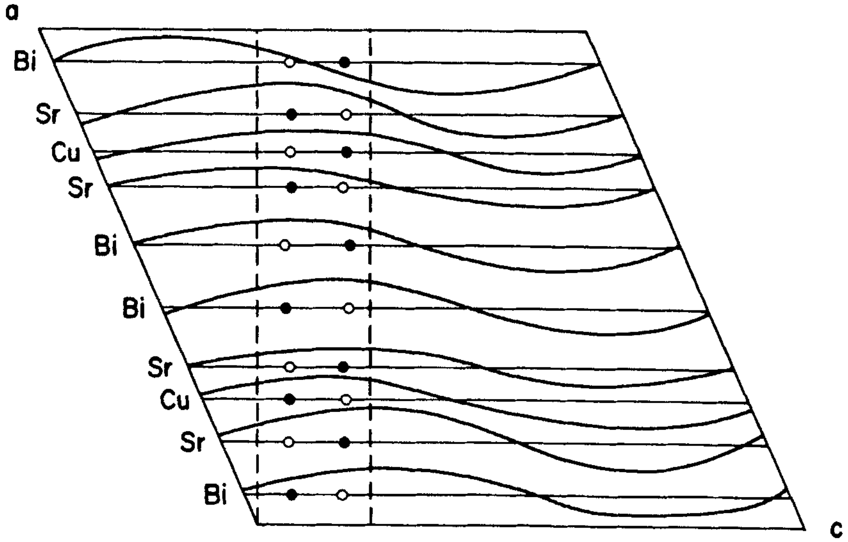

Figure 3. Modulated structure of Phase B showing subcell atom positions.

by buckling the Bi-O layer resulting in the incorporation of additional oxygen in the Bi-O layer which gives rise to the holes responsible for conduction in these materials. Different superlattice periodicities have been reported but the origin of these differences have not been detailed[2i,3].

We have monitored the superlattice periodicity throughout the solid solution region. High-intensity high-resolution powder diffractograms can be indexed with four parameters, a_T, c_T, s_a, and s_c where a_T and c_T are the a and c lattice parameters of the tetragonal subcell and s_a and s_c are the a and c components of the incommensurate superlattice modulation. Thus, s_a is the periodicity of mass-density waves along the a direction while s_c is the periodicity of the stacking of these waves along the c direction. While s_a shows little variation, we find a direct correlation between s_c and the Bi/Sr ratio (Figure 4). This correlation is most dramatic at the Sr-rich end of the solid solution. Strontium deficient samples with Bi/Sr=>1.4 exhibit broadening of superlattic peaks indicating a large number of defects in the superlattice for these compositions.

To determine the structure of Phase A, $Bi_2Sr_2CuO_6$, we have collected data on a single crystal. This data suggests a "stepped" version of the structure of Phase B (Figure 5). Indeed, a similar feature has been observed by TEM in ceramic samples having a local composition as determined by microprobe of

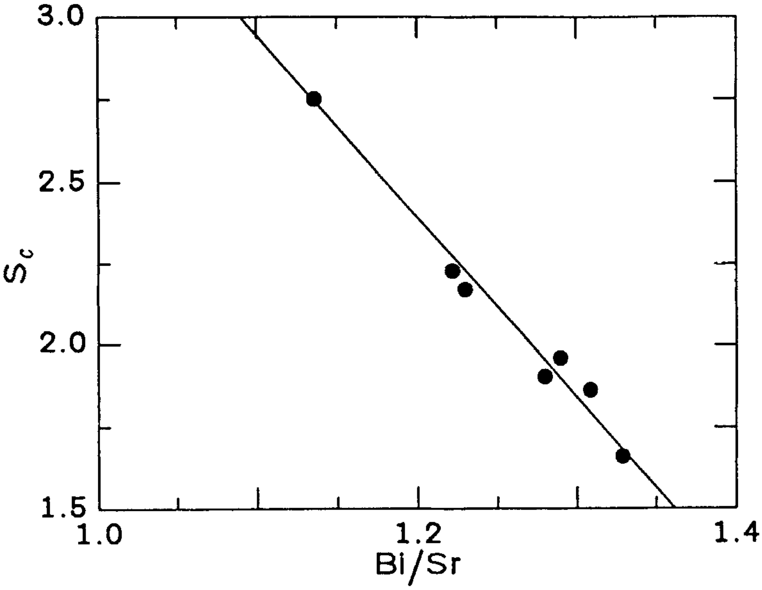

Figure 4. Superlattice modulation s_c as a function of Bi/Sr ratio.

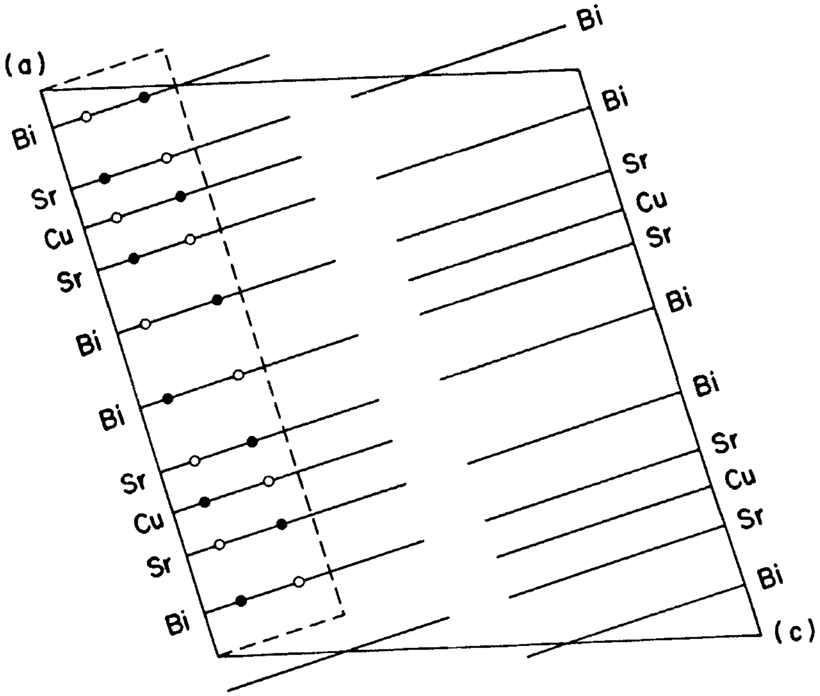

Figure 5. Possible description of the "step" structure of Phase A, $Bi_2Sr_2CuO_6$.

$Bi_{2.4}Sr_{2.4}CuO_x^{6b}$. Unfortunately, metal-atom disorder at the steps has made a complete structural refinement difficult. It is clear, however, that this "step" becomes favorable as the composition approaches $Bi_2Sr_2CuO_6$.

Properties

The evolution of resistance for ceramic samples of $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$ is shown in Figure 6. Phase A, $Bi_2Sr_2CuO_6$, is a semiconductor. As x increases, samples become metallic and a superconducting transition becomes apparent. At x=0.1, samples shows zero resistance above 4K. As the Bi content is increased further, properties degrade until the material is again insulating. At x=0.18 samples are semiconducting with no superconducting transition above 4K. It is important to compare these properties with the x-ray diffraction results discussed above. It should be noted that the best superconducting behavior is observed in multiphase samples. Indeed, other studies find that superconductivity occurs at compositions which are not within the single phase region[4b]. Furthermore, the superconducting

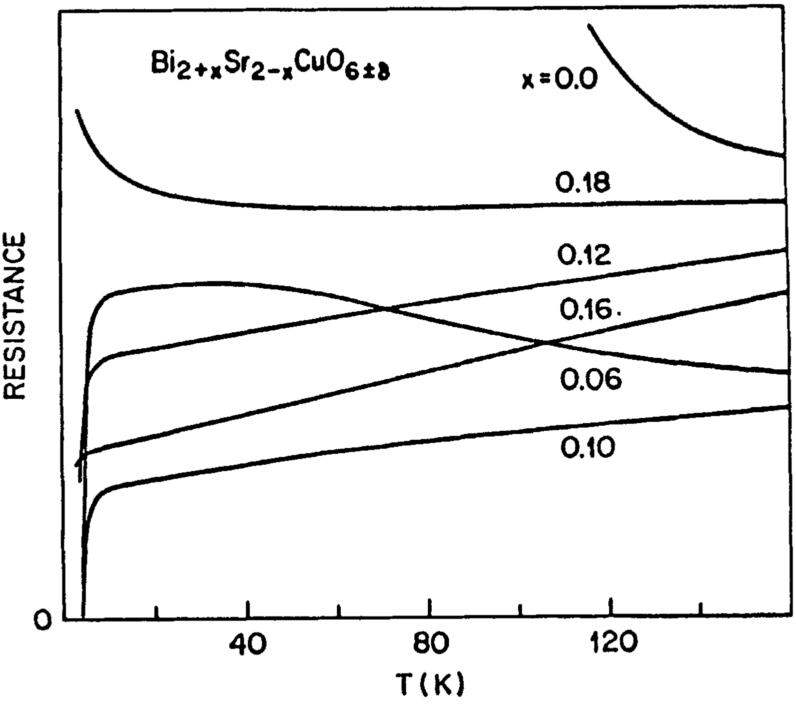

Figure 6. Resistance versus temperature for samples of $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$.

fraction is small in all samples. It seems apparent that the best superconducting properties would result if the structure of Phase B could be maintained at compositions closer to 2-2-1. This is consistent with the increasing degree of oxidation as x decreases in $Bi_{2+x}Sr_{2-x}CuO_{6\pm\delta}$. However, as x is reduced the wave-like modulation of Phase B becomes unstable with respect to the step dislocation of $Bi_2Sr_2CuO_6$ so that by $x \leq 0.16$ two phase samples result (A + B).

ACKNOWLEDGEMENT

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