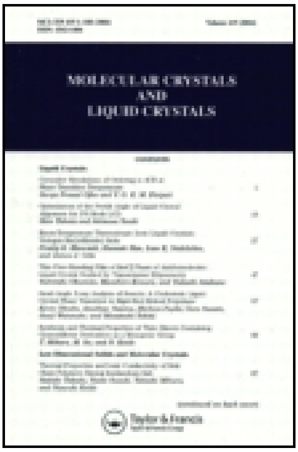

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The Subsolidus Phase Diagram of the $BiO_{1.5}$-SrO-CuO System and the Effect of Pb-Substitution

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Abstract Solid phases and their relations in the Bi-Sr-Cu-O system were investigated at 840°C in air. $Bi_{2+x}Sr_{2-x}Cu_{1+y}O_z$ ($0.1<x<0.6$, $0<y<x/2$), $Bi_{17}Sr_{16}Cu_7O_z$, $Bi_2Sr_3Cu_2O_z$, $Bi_4Sr_8Cu_5O_z$, and $BiSr_3O_z$ have newly been found. The superconductor with a $T_c \approx$ 10K corresponds to the Bi-poorest end of the solid solution mentioned above. Monophasic compositions of $Bi_{2-x+y}Pb_xSr_{2-y}Cu_{1+y/4}O_z$ with $0\leq x\leq 0.5$ and $0.1<y\leq 0.5$ were prepared. The modulation was found to completely disappear in a narrow range around the Pb solubility limit in the Bi-poor side of $x\geq 0.4$ and $y=0.125$.

INTRODUCTION

The Bi-Sr-Ca-Cu-O system is a rich system in which at least three superconducting phases have been found [1,2,3]. We have made effort to identify the solid phases formed in this system and reveal their relations [4,5,6] because this kind of research can afford a sound material-scientific base. Reported in this paper are the results obtained in the chemically most representative system, Bi-Sr-Cu-O. We found a series of solid solutions showing superconductivity only in it very narrow composition range. This allowed us to obtain some insight into the relation between chemical composition, structure, and superconductivity. More recently we have studied the Pb substitution effects to collect more systematic information.

EXPERIMENTAL

All the samples were prepared by a usual ceramic method starting from Bi_2O_3, $SrCO_3$, PbO, and CuO, each of a purity above 99.5%. Firing temperature ranged from 700°C to 1000°C, and the atmosphere was the air. Firing was continued for 48~ 180h in total, with intermittent grinding, mixing, and pelletizing processes. Phase identification was carried out using powder X-ray diffraction (XRD, CuKα), transmission electron microscopy (TEM, JEM-2000EX), electron microanalysis (EPMA, Hitachi X-650), measurement of dc magnetization (M) with a SQUID magnetometer and of dc resistance (R) with the four terminal method. Chemical compositions were examined by using inductively couples plasma atomic emission spectroscopy (ICP), nondispersive infrared oxygen analysis, and iodometry.

RESULTS AND DISCUSSION

The subsolidus phase diagram for the Bi-Sr-Cu-O system thus determined is presented in Fig. 1. The dotted lines connecting CuO, $Bi_{1-x}Sr_xO_z$, and Bi_2CuO_4 describe the relations established at 800°C, while partial melting occurs at 840°C. In the area connecting C, D, $SrCuO_2$, and $Sr_{14}Cu_{24}O_z$[7], two possibilities have remained unsettled as shown using a pair of dotted-and-dashed lines. In the binary $BiO_{1.5}$-CuO system, Bi_2CuO_4 has been isolated. In the SrO-CuO binary system, $Sr_{14}Cu_{24}O_z$, $SrCuO_2$ and Sr_2CuO_3 have been isolated. $Bi_{1-x}Sr_xO_z$ with 0.2<x<0.3, $Bi_{0.55}Sr_{0.45}O_z$, $BiSrO_{2.5}$, and $Bi_2Sr_3O_z$ have been isolated in the binary $BiO_{1.5}$-SrO system, and in addition a

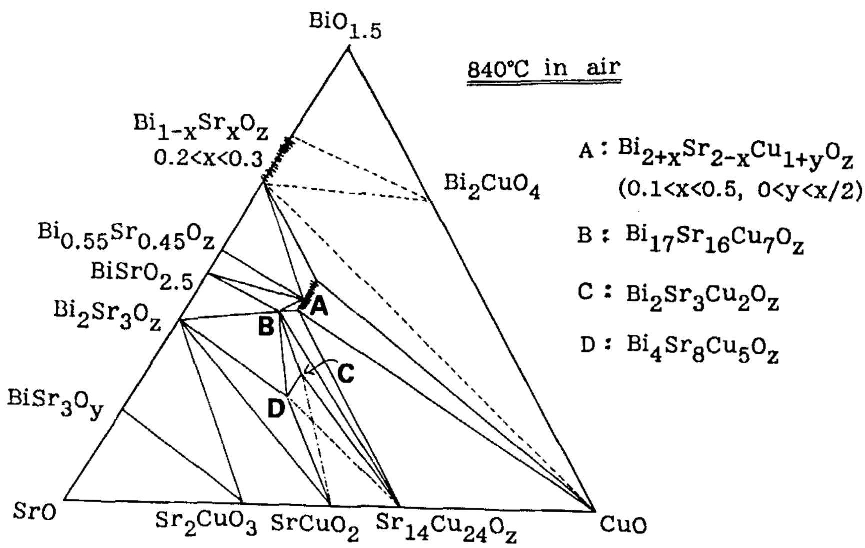

Fig.1.Phases and their relations in the Bi-Sr-Cu-O system.

new compound $BiSr_3O_y$ has been found. It has orthorhombic cell with a=8.57Å, b=8.38Å, and c=8.50Å. New compound that have been found in the ternary system $BiO_{1.5}$-SrO-CuO are $Bi_{2+x}Sr_{2-x}Cu_{1+y}O_z$ ($0.1<x<0.6$, $0<y<x/2$), $Bi_{17}Sr_{16}Cu_7O_z$, and compounds with compositions near $Bi_2Sr_3Cu_2O_z$ and $Bi_4Sr_8Cu_5O_z$. These are marked A, B, C, and D in Fig. 1. It should be noted that $Bi_2Sr_2CuO_z$, the ideal superconducting phase, does not exist. The XRD data for x=0.125 and y=0.031 is shown in Figure 2(a). The peaks marked with * in Figure 2(a) are satellite peaks due to the modulation. The modulation mode has more directly been observed by means of TEM[8,9]. Plotted in Figure 3 are the composition dependences of the modulation length along the b axis determined by XRD and TEM and of the nominal Cu valence determined from the compositional and iodometric analyses assuming the coexistence of Bi^{3+}, Sr^{2+}, and O^{2-}. Figure 4(a) and (b) show the superconducting transition in resistivity and magnetization, respectively, for x=0.1. The superconducting composition range is limited very sharply below $x<0.13$ as compared in Figure 4(c). The formation of this phase for $0<y<x/2$ suggests that considerable amounts of vacancies may be formed in the BiO and SrO layers and/or Cu substitutes at the Bi and/or Sr sites. It is interesting to note here that relatively alkaline-earth poor compositions have been reported also for both the double- and triple-CuO_2 layered phases[8,10] and that the modulation mode shows a stepwise change depending upon the Pb content substituting for Bi [10]. Comparing these with the present results, close relations with respect to the structure and composition between the mono-, double-, and triple-CuO_2 layered phases can be noticed. Especially, the stepwise changes of the modulation mode in the Pb-substituted triple-layered phase strongly suggests an ordered arrangement of Pb in the BiO layer. Besides, the solid solution of $Bi_{2-x+y}Pb_xSr_{2-y}Cu_{1+y/4}O_z$ ($0<x<0.5$ and $0.1<y<0.5$) has been found to exist in the PbO-$BiO_{1.5}$-SrO-CuO system. XRD charts for the series of y=0.125 are compared in Figure 2. All peaks could be indexed by assuming a tetragonal (x=0) or an orthorhombic cell ($x\geq0.1$) with $a\geq b=5.3\sim5.4$ Å and $c\approx24.6$Å. The most remarkable feature of this system is the fact that the modulation finally disappears as the Pb content increases. Figure 5

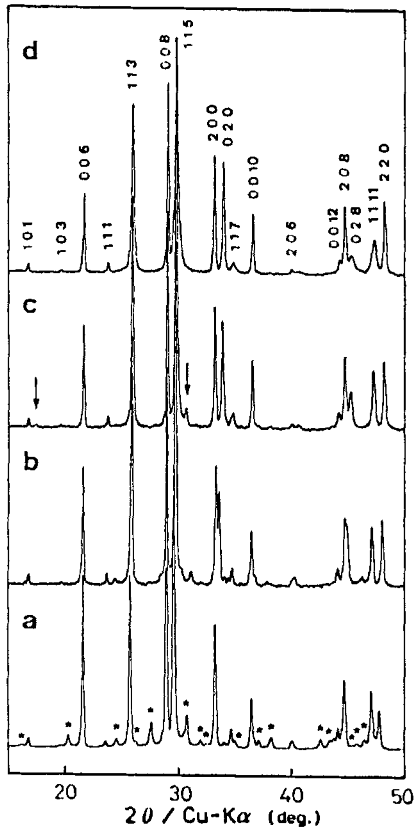

Fig.2 Powder XRD patterns for $Bi_{2.125-x}Pb_xSr_{1.875}Cu_{1.03}O_z$. (a) x=0.0, (b) x=0.2, and (c) x=0.4 prepared at 820°C in air and (d) x=0.4 finally treated at 700°C in Ar. The sample of x=0.4 prepared in air includes a small amount of $Sr_3Pb_2CuO_z$ as marked with arrows in (c), while it disappears after the treatment in Ar as seen in (d).

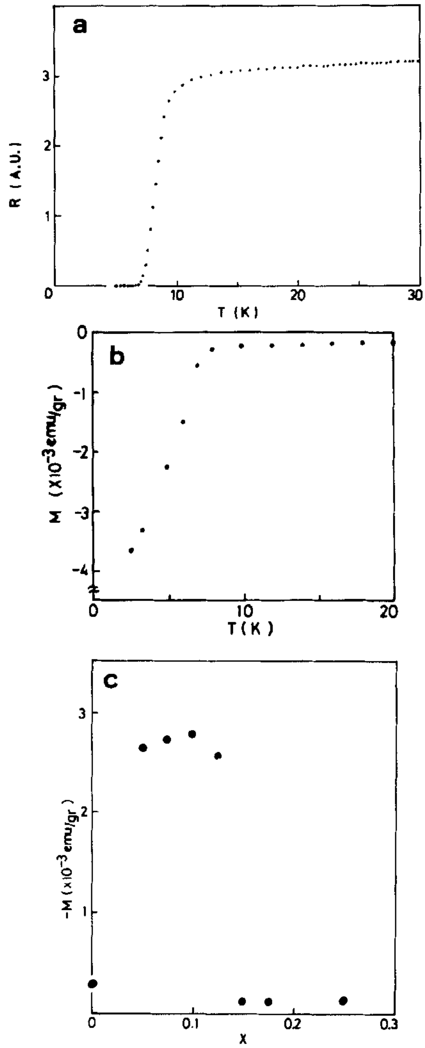

Fig. 4 Temperature dependences of resistivity (a) and magnetization (b) for $Bi_{2.1}Sr_{1.9}CuO_z$. Magnitude of the diamagnetism at 5K plotted vs. x (c).

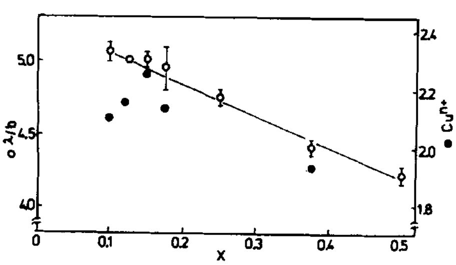

Fig. 3 Modulation wave length, λ, in units of the *b* axis length (○) and the nominal Cu valency (●).

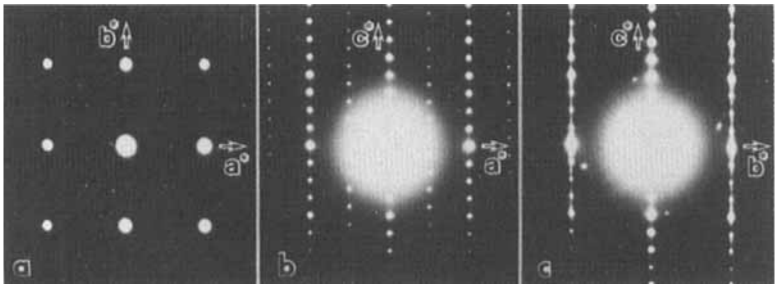

Fig.5 ED patterns of the modulation-free composition of (x, y)=(0.4, 0.125) showing the a^*-b^* (a), a^*-c^* (b), and b^*-c^* (c) reciprocal lattice sections. Note the lack of satellite spots due to modulation.

shows the ED patterns of the modulation-free composition of (x,y)=(0.4, 0.125). It shows superconductivity with $T_c \approx$ 14K. Further details will be described elsewhere.[11]

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