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SYNTHESIS, CONDUCTIVITY, AND X-RAY PHOTOELECTRON SPECTRUM OF $\text{Bi}_2\text{Sr}_2\text{Cu}_7+x$. A NEW TERNARY BISMUTH-OXIDE SYSTEM EXHIBITING METALLIC CONDUCTIVITY

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The preparation and some of the properties relating to the superconductive state of the newly discovered ternary bismuth oxide, $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$, are described. Conductivity behavior ranging from semiconductive to metallic is observed when four-probe AC resistivity measurements are carried out on pressed pellet specimens that have been annealed under different conditions. From a determination of the total oxygen present by an iodometric titration, it was found that metallic conductivity was associated with a higher oxygen content. An X-ray photoelectron experiment was carried out in order to determine whether bismuth or copper was present as the mixed-valent species. The XPS spectrum of the Bi 4f orbital electrons in the oxide was nearly identical to that observed in Bi_2O_3 , with no evidence of any Bi^{5+} .

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Our interest in the structures and conductivity properties of layered metal-oxide compounds led us to examine new ternary systems in which bismuth(III) was a component. We considered bismuth a good candidate for these investigations since the ability of bismuth(III) to form lamellar metal-oxides has been previously established.¹ One of the newly found phases in this system is $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$, an oxide that has very recently been reported to be superconductive at 20 K.² In this communication we report the preparation and some of the properties of this oxide related to its superconductive state: (a) the apparent melting temperature, (b) the X-ray powder pattern of the melted, re-frozen material, (c) the oxygen content, (d) its variation of resistance with equilibrating conditions, and (e) the results of an examination with XPS.

The starting materials, Bi_2O_3 , CuO , and SrCO_3 (all dry, reagent grade powders) were weighed, intimately mixed, and ground in a ball-mill for 15 minutes. The grey powder that resulted was then calcined in an alumina boat inside a muffle furnace at 800 °C. After a period of 24 hours the material was reground, calcined in air for another 24 hours, then removed and quenched rapidly in air. The purity of the resulting material was assessed by X-ray powder diffraction and the composition was analyzed by ICP atomic emission spectroscopy (*vide infra*). In order to insure reproducibility, all analyses were carried out on samples that had been melted for a period of 1 hour followed by quenching in air. From the X-ray powder pattern (Figure

1), we find no evidence of the presence of any of the starting materials or the known binary metal oxides SrCuO_2 ,^{3a} Sr_2CuO_3 ,^{3b} and Bi_2CuO_4 .⁴ Sample melting appears to be complete at 860 °C with an onset temperature ca 840 °C. In a sketch of the ternary phase diagram with $\text{BiO}_{1.5}$, SrO , and CuO located at the apices, this product is located at the center of the diagram, with phase boundaries demarcated by lines to each of the three corners. From the results of the ICP atomic emission spectroscopic analysis, the mole ratios of the bismuth, strontium, and copper ions were found to be 1.0:0.94:1.0. Two samples, samples A and B, were oxygen annealed in the form of pressed pellets for varying lengths of time (100 hours maximum) and were used both for resistivity measurements and for the analysis of total oxygen content. In both cases, no significant changes in resistivity were noted as the annealing time was increased beyond 24 hours. For samples A and B, O_2 annealing was carried out under an atmosphere of flowing oxygen at temperatures of 820 and 340 °C, respectively. Sample C, a solid fragment of the quenched material, was not treated further. Analysis of the total oxygen content in the annealed samples by an iodometric titration yielded values of x in the formula above of 0.12 and 0.16 for samples A and B, respectively.⁵

The resistivities of these oxide materials as a function of temperature were determined from standard 4-probe resistance measurements employing low-frequency AC currents with phase-sensitive detection of

voltage. The relative resistivities (R_T/R_{297}) as a function of temperature for three different specimens are illustrated in Figure 2. Curves A and C in this figure show that the variation is dominated by the semiconducting component, whereas curve B is dominated by the metallic component. Apparently, specimens A and C have comparable oxygen contents; very little equilibration must have occurred in specimen A. The two kinds of variations shown in figure 2 are those observed in the recently discovered high- T_C superconducting oxides;⁶ generally, the variation for the superconducting composition is located between these two curves and usually near that for the metallic-like behavior. We surmise that in the present case this state was not observed because it occurs at a temperature below that attainable with our equipment. For material prepared using commercial oxides, Michel et al.² found a value of 7 K for the transition.

In an attempt to determine whether copper or bismuth provides the dual valence required for conductivity in the oxide, we have measured the X-ray photoelectron spectra of the Bi 4*f* and Cu 2*p* orbital electrons using Mg K radiation. The spectra of bismuth 4*f* electrons in Bi₂O₃ and in specimen B are shown in Figure 3. If two valence states of bismuth were present in specimen B, the curve for Bi 4*f* 7/2 (right hand peak) would be asymmetric on the left side. As shown in Figure 3, the curve is quite symmetric and nearly the same as that for Bi₂O₃ which contains only one valence state.

The binding energy for the Bi 4f 7/2 in the mixed oxide occurs at 0.55 eV lower than that for Bi₂O₃. This shift is probably associated with that expected for a conductor compared with an insulator, both having the same valence state.⁷ We therefore adduce that, in the oxide described here, all of the bismuth is present in the form of Bi³⁺. Because of the overlap of O 1s Cu 2p 3/2 peaks, the spectrum for the Cu 2p 3/2 in the oxide was not observable. This result implies that the copper is strongly covalently bonded.⁸

A principal result of this investigation is the similarity, with respect to conductivity, between the compound described here and other metal-oxide systems that have been shown to be superconducting. The conductivity behavior is similarly strongly dependent on annealing conditions. Metallic conductivity is associated with high oxygen content, which, from the results of an XPS study, likely involves a concomitant increase in the Cu³⁺/Cu²⁺ ratio.

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FIGURE CAPTIONS

Figure 1. The X-ray powder pattern of $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$ obtained from a calcined mixture of the oxides.

Figure 2. Four-probe AC resistance measurements of three samples. Curves A and B were obtained following oxygen annealing at 384 and 820 °C, respectively. The resistivity of the product prior to oxygen annealing is shown in curve C.

Figure 3. The XPS spectrum of the Bi 4f orbital electrons in a Bi_2O_3 reference sample (solid line) and that of a $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$ pellet fragment (sample B) exhibiting metallic conductivity. The curves have been shifted by 0.55 eV with respect to each other and normalized so that they can be superimposed for comparison.

COUNTS PER SECOND