JOURNAL OF SOLID STATE CHEMISTRY 114, 585–589 (1995)

BRIEF COMMUNICATION

Synthesis and Characterization of $Ba_{2-x}Bi_xCu_2O_5$ ($0 \leq x \leq 1.5$)

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Received April 27, 1993; in revised form February 22, 1994; accepted April 25, 1994

$Ba_2Cu_2O_5$ and its solid solutions with Bi_2O_3 have been synthesized and characterized using powder XRD, infrared spectroscopy, and DSC. The orthorhombic unit cell dimensions have been measured with the help of powder X-ray diffraction. The controversial valence state of copper, examined through electron paramagnetic resonance, was found to be divalent. The structural and magnetic resonance results are discussed in detail.

INTRODUCTION

The high-temperature superconductor $YBa_2Cu_3O_7$ is inherently mixed valent with the average valence of Cu between +2 and +3, which plays a crucial role in superconductivity. Thermodynamics, structure, and bonding in this superconductor are optimized to stabilize this fractional valence. In other words, nonstoichiometry requires an excess positive charge to reside somewhere in the lattice. Being completely ionic, Y and Ba cannot donate or accept excess charge. Thus they are trivalent and divalent, respectively, leaving Cu and O as possible candidates for "accepting" a positive charge (or a hole). There is thus a need to look for experimental evidence in favor of Cu^{3+} and O^{-1} (1). While there is convincing evidence for the presence of O^{-1} from X-ray absorption spectroscopy and photoemission studies (2), Cu^{3+} has not been identified yet. This aspect of nonstoichiometry and mixed valence serves as a reasonable basis in the search for new systems with metallic/superconducting characteristics, starting from pure insulating systems, through a possible insulator-to-metallic transition upon introduction of nonstoichiometry in them. Indeed, on this very basis, the compound Y_2BaCuO_5 has been successfully used as a precursor and reacted again with proper oxides in the preparation of $YBa_2Cu_3O_x$ (3). On the contrary, in a similar attempt, a perfectly stoichiometric perovskite such as $BaZrO_3$ could not be made nonstoichiometric (and hence exhibit metallic behavior as expected) even up to a maximum doping of copper (4). Yet, it seems a worthwhile experiment to create nonstoichiometry and defects in a stoichiometric system which would induce a metallic nature in it, if not a superconducting transition. Another approach to studying this behavior would be to start with an average valence of III for Cu and do a substitution to cause a III → II + I transition and study the effect on physical properties. One such trial was the work of Straub *et al.* (5) on the ternary copper oxide system $Ba_2Cu_2O_5$ to confirm the Cu oxidation state as III. Along with other compounds of the formula $Ln_2Cu_2O_5$ (*Ln* = Tb, Dy, Ho, Er, Tm, Yb, and Lu), the compound $Y_2Cu_2O_5$ has been indexed based on powder XRD data (6, 7) and the previous indexing (8) has been proved to be incorrect. However, although known for some time now (8), $Ba_2Cu_2O_5$ still remains to be characterized and studied carefully. A nearer composition with an established structure is Ba CuO_2, a nonstoichiometric compound in which large deviations from ideal composition and cubic structure (a = 18.347 Å, space group $Im3m$) are known to occur (9). The observation of variable oxygen content (between 1.79 and 2.50) in $BaCuO_2$ (10) with a corresponding variation of cell parameters suggests the possibility of having the composition $Ba_2Cu_2O_5$ with different oxygen contents and distorted unit cells. The use of BaO_2 and a lower reaction temperature, 600°C (instead of 850°C for $BaCuO_2$ (8)), assures a distinct crystal structure for the title compound, and hence $Ba_2Cu_2O_5$ need not be considered as a variant of the $BaCuO_2$ structure.

The present work was undertaken to explore the possibility of inducing metallicity in a stoichiometric system, $Ba_2Cu_2O_5$, by doping it with Bi and to check the oxidation state of Cu in the latter along with the possible changes in its physical properties. The choice of bismuth for this purpose was based on the fact that even though $BaBiO_3$ crystallizes in a distortion of the perovskite structure, a new compound (phase) with the formula $BaBiO_{2.5}$ has been found to have a layer-like structure (11). By substituting a *trivalent* Bi for a *divalent* Ba, we are introducing a "hole" into the system. This excess charge carrier would be mobile by itself thereby increasing the overall

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0022-4596/95 $6.00

carrier concentration and hence a possible transition to a metallic state. However, it may not be directly compared with a nominally octahedral coordination of Bi in a rock-salt-like layer in high T_c superconductors, where the environment is highly distorted and complicated by the presence of structural modulations and variable oxygen content. Furthermore, the introduction of Bi_2O_3—which acts as an oxygen buffer due to its inherent oxygen nonstoichiometry—helps in optimizing the oxygen stoichiometry. For this study we have used powder X-ray diffraction (XRD), infrared (IR) spectroscopy, dc resistivity measurements, differential scanning calorimetry (DSC), and electron paramagnetic resonance (EPR) spectroscopy.

EXPERIMENTAL

Samples having the composition $Ba_{2-x}Bi_xCu_2O_5$ (x = 0.00, 0.5, 1.0, and 1.5) were prepared by mixing the required amounts of BaO_2, $Cu(NO_3)_2 \cdot 3H_2O$ and Bi_2O_3 and sintering the mixture at 580°C for 24 hr. It is to be noted that these preparation conditions are quite different from those for $BaCuO_2$, which needs a heat treatment at 850°C for 48 hr (8). XRD patterns for the samples were recorded on a Seifert X-ray diffractometer (Cu$K\alpha$, λ = 1.5418 Å with Ni filter) at room temperature. Perkin–Elmer double beam IR and JEOL FE-3X ESR spectrometers were also used in characterizing the compound. The thermal analysis of the compositions was performed over the temperature range 150–650 K using a DuPont 9900 DSC. The dc electrical resistivity was measured from 140 to 300 K by a two-probe technique. All the samples have been synthesized more than once to confirm the reproducibility.

RESULTS AND DISCUSSION

Structural Aspects

The XRD pattern of the compound $Ba_2Cu_2O_5$ (x = 0.00) consists of about 25 reasonably resolved reflections. These observed d values are compared with the only available data, that of Arjomond and Machin (8). Except for the reversal of intensities of maximum intensity and the next lower intensity lines, all the other lines are practically coincident. We have analyzed this observed pattern following Ito's method as explained by Azaroff (12). This method is an iterative procedure based on the assumption that the reflections are from a high symmetry unit cell and consists in assigning the most frequent occurrences in the interpolation of Q_i (= $1/d_i^2$) to the (h00), (0k0), and (00l) planes. Once the principal planes are assigned, it is only a matter of time to determine $d_{i(\text{cal})}$ and check with the $d_{i(\text{obs})}$. The reasonable condition imposed for finalizing the best fit among the three sets given by Wu's program (13) is

$$\min\left(\frac{\sqrt{\varepsilon(\Delta d_i)^2}}{N}\right),$$

where $\Delta d_i = d_{i(\text{obs})} - d_{i(\text{cal})}$ and N is the total number of observations. With this we could achieve the best fit of observed d-values to an orthorhombic system and the unit cell parameters are given in Table 1 along with those of the similar systems $Sc_2Cu_2O_5$, $Y_2Cu_2O_5$, and $In_2Cu_2O_5$. The (hkl) indices for all the reflections are given in the Table 2. Even though small, systematic changes have occurred in unit cell dimensions upon bismuth substitution, as seen from Table 1, pointing out the progressive

TABLE 1
Lattice Parameters of Orthorhombic $A_2Cu_2O_5$ (A = Sc, Y, Bi, In, and Ba)

Compound	a (Å)	b (Å)	c (Å)	Ref.
$Sc_2Cu_2O_5$	18.60	20.05	8.23	(8)
$Bi_2Cu_2O_5$	8.57	15.81	6.49	
$In_2Cu_2O_5$	24.62	10.54	3.27	
$Y_2Cu_2O_5$	10.793	3.493	12.45	(6, 7)
$Ba_{2-x}Bi_xCu_2O_5$				
x = 0.00	8.564(2)	7.415(2)	20.827(3)	This work
x = 0.10	8.569	7.026	20.729	
x = 1.00	8.563	7.426	20.827	
x = 1.50	8.581	7.422	20.729	

TABLE 2

d_{obs}	I/I_o	d_{cal}	h k l
3.7078	66	3.7078	0 2 0
3.6509	55	3.6509	2 1 1
3.4930	16	3.4930	0 2 2
3.4597	11	3.4713	0 0 6
3.2147	11	3.2171	1 0 6
3.0789	66	3.0554	1 2 3
2.8506	100	2.8484	1 2 4
2.7549	11	2.7532	3 0 2
2.6292	27	2.6281	1 1 7
2.5996	22	2.5992	2 2 3
2.1511	24	2.1507	3 2 3
2.0632	11	2.0632	1 3 5
2.0412	22	2.0403	2 2 7
2.0196	22	2.0181	4 0 9
1.9529	22	1.9524	1 1 10
1.9333	27	1.9236	3 0 8
1.6908	33	1.6902	5 0 2
1.6800	27	1.6790	2 4 2
1.5655	11	1.5659	1 3 10
1.4250	22	1.4242	2 4 8
1.3786	11	1.3790	1 5 5
1.3654	11	1.3648	0 1 15
1.1685	13	1.1676	0 5 11

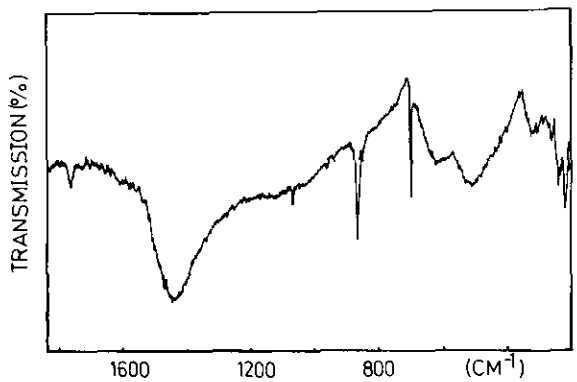

FIG. 1. The room-temperature infrared spectra of $Ba_2Cu_2O_5$.

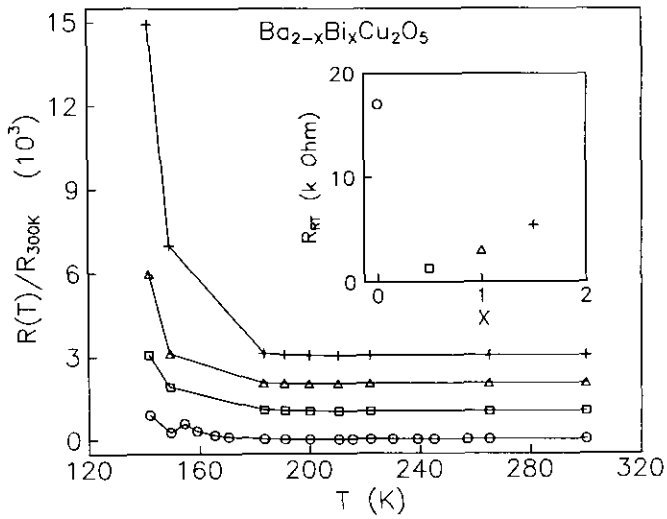

FIG. 2. The temperature dependence of normalized (with corresponding RT resistance) resistance of $Ba_{2-x}Bi_xCu_2O_5$ (x = 0.00, 0.50, 1.0, and 1.50) sintered pellets. For clarity, each curve is shifted up making the Y-scale arbitrary. The inset shows the response at RT. The symbols, ○, □, △, and + represent x = 0.00, 0.50, 1.0, and 1.50, respectively.

entry of bismuth into the unit cell and showing that Bi substitution to even more than 50% preserves the $Ba_2Cu_2O_5$ structure. Thus any consequent changes in physical properties must be atrributed to nonstoichiometry (developed in $Ba_2Cu_2O_5$ due to the doping of bismuth) alone. However, a few reflections (Table 2) can be seen to have somewhat larger Δd, indicating the presence of minor impurity phases, most probably BaO_2 and/or $BaCO_3$. This makes it clear that to get detailed structural information, single-crystal X-ray diffraction data on $Ba_2Cu_2O_5$ has to be obtained.

The infrared spectrum of the compound $Ba_2Cu_2O_5$, see Fig. 1, looks like that for a combination of calcite- and aragonite-type structures in general, but is different from that of BaO_2, $BaCO_3$, $Ba(NO_3)_2$, or any other possible impurities/secondary phases. As can be seen, all absorption bands are sharp and well resolved. The observed bands and their assignments are given in Table 3, and this assignment is based on the premise that a Ba_2CuO_3 + CuO_2-type combination would result in the absorption of a calcite-type group around 1065 cm^{-1}. $CaCO_3$ has a planar XO_3 group both of its forms calcite and aragonite giving rise to the IR-active vibrational frequencies (14)

TABLE 3

Absorption bands (cm^{-1})	Assignments
325, 510, 590	Lattice mode vibrations
610	
700	ν_4
845, 862	ν_2
1065	ν_1
1445	ν_3
1775	$\nu_1 + \nu_4$

Note. ν_1, ν_2, ν_3, and ν_4 are CO_3 modes of aragonite ($CaCO_3$).

879 (ν_2)	1429–1492 (ν_3)	706 (ν_4)
1080 (ν_1)	806 (ν_2)	1504, 1492 (ν_3)
		calcite
		711, 706 (ν_4) aragonite.

Similarly, a combination of ν_1 and ν_4 modes would thus produce a band at 1755 cm^{-1}. As the bismuth concentration is increased, the absorption becomes progressively smaller and, finally, for x = 1.5 only a broad band in the range 400–500 cm^{-1} remains in the spectrum. Thus the IR spectrum brings out the effect of Bi substitution by way of significant changes in the nature of the molecular groups. This rearrangement of IR-sensitive molecular groups because of Bi doping has shown its influence on the electrical response of the system, as explained in the following section.

Electrical Behavior

The dc electrical resistance in the range 140–300 K did show reduction with increasing Bi concentration. Figure 2 shows the normalised (with respect to ρ_{RT} of each composition) resistance plots for the compositions x = 0.00, 0.50, 1.00, and 1.50 as a function of temperature. The room-temperature resistances are shown as inset in the same figure. The normal state resistivity behavior of metallic and/or superconducting cuprates shows a similar trend, essentially due to overlapping of Cu–O orbitals despite minor/major structural variations. The observed temperature dependence of resistance is similar to that

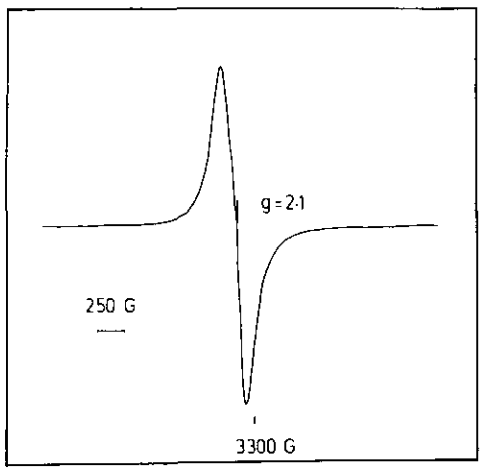

FIG. 3. The RT EPR spectrum (ν = 0.233 GHz, 1 mW and 5 × 10).

of the Bi–Sr–Ca–Cu–O system, where this kind of fall in resistivity upon warming is attributed to the increase in the overlapping of Cu–O orbital planes (15).

Even though we could not achieve the true metallicity upon Bi substitution into the $Ba_2Cu_2O_5$ system that we expected, at the same time it is interesting to note the nonnegligible drop in the room-temperature resistances. As the above data show, one can still hopefully attempt substitution of Bi $0 \leq x \leq 0.5$ to get an insulator-to-metal transition.

Electron Paramagnetic Resonance

The typical electron paramagnetic resonance spectrum of $Ba_2Cu_2O_5$ at room temperature is shown in Fig. 3. With an isotropic g of 2.1 and a line width of 237.5 G, this is in agreement with the literature (5). However, we feel that the signal is not due to Cu^{3+} as claimed by Straub *et al.* (5), who compared this g-value with the anisotropic g-tensor for Cu^{3+} in Al_2O_3 at 1.8 K, namely, $g = 2.0788$ and $g = 2.0772$, observed by Blumberger *et al.* (16) and quoted by Abragam and Bleaney (17). The Cu^{3+} with $S = 1$ should give two EPR transitions, $M_s = -1$ to $M_s = 0$ and $M_s = +1$ to $M_s = 0$ and hence must result in *two* EPR lines (18) instead of the one actually observed here. A recent EPR work by Armstrong *et al.* (19) on Ba_2CuO_{3+x} and $Bi_{2-x}Sr_xCu_2O_5$ may be compared with the present results. Though orthorhombic Ba_2CuO_{3+x} did not give any EPR signal, the *tetragonal* phase of Ba_2CuO_{3+x} gave a resonance absorption with $g_\parallel = 2.035$, $g_\perp = 2.114$, and $\Delta H_{pp} = 300 \pm 20$ G. The fact that $g_\parallel < g_\perp$ suggests that the environment of Cu^{2+} is either trigonal bipyramidal or distorted octahedral, which could not be determined unequivocally owing to the oxygen vacancies in the copper–oxygen sheets. In contrast, $Bi_{2-x}Sr_xCu_2O_{5-y}$ gave a single, broad isotropic EPR signal with g-values varying from 2.24 to 2.46 for $x = 0.00$ to 2.00. The Cu(II) g-factor values for an ideal octahedral field and that with tetragonal distortion are 2.2 and $g_\parallel = 2.4$ and $g_\perp = 2.1$, respectively (20). After a careful consideration of the EPR parameters for $x = 0.00$ ($g = 2.102$, $\Delta H = 237.5$ G), $x = 0.50$ ($g = 2.095$, $\Delta H = 240$ G), $x = 1.00$ ($g = 2.145$, $\Delta H = 1150$ G), $x = 1.50$ ($g = 2.094$, $\Delta H = 1262$ G), one can see that g-factor values are characteristic of the Cu(II) state rather than of Cu(III) state in $Ba_{2-x}Bi_xCu_2O_5$. This clearly indicates the possibility of having Cu in an oxidation state of II rather than III in $Ba_2Cu_2O_5$. At this point, it is pertinent to mention that formal valence rules would not always give actual valence states. For example, even though formal valence rules would assign a *trivalent* state for copper in the $LaCuO_3$, in the X-ray near-edge structure study of $LaCuO_3$, copper was found to be *divalent* as in La_2CuO_4 and $YBa_2Cu_3O_x$ (21). Similarly, in the compound $Ba_2Cu_2O_5$, even though the formal valence rule gives for copper a valence state of 3, our results assign it to a *divalent* state.

Differential Scanning Calorimetry

The differential scanning calorimetric scan of $Ba_2Cu_2O_5$ was performed to check for phase transitions. Other than the two endotherms, one at 243°C and another at 340°C (Fig. 4), it has no thermal event between −150 and +500°C. These two endotherms could represent the completion of reaction/formation of $Ba_2Cu_2O_5$ or a two-stage reduction of unreacted BaO_2 to BaO or structural phase transitions in $Ba_2Cu_2O_5$. The first possibility is based on the observation of three IR absorption bands, around 1755 and 860 cm^{-1} due to $BaCO_3$ and at 1440 cm^{-1} due to BaO_2, which could account for the presence of a few unindexable lines in the XRD. The other two possibilities arise from the rather low reaction and decomposition (650°C) tem-

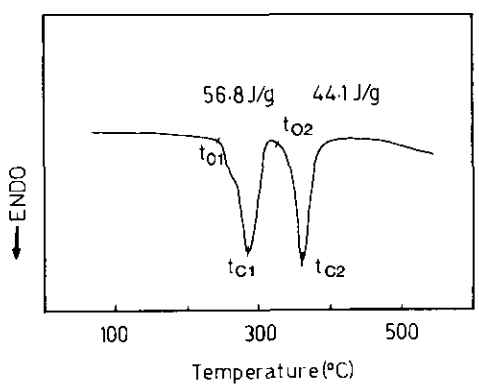

FIG. 4. The DSC scan of $Ba_2Cu_2O_5$ showing the two endotherms and the enthalpy involved. t_o and t_c represent the onset and completion of the thermal event(s).

peratures. Of these, we feel that two-stage reduction is a more plausible explanation of the DSC data.

CONCLUSIONS

We have prepared and characterized the ternary copper oxide compound $Ba_2Cu_2O_5$ and its solid solutions with Bi_2O_3. We could fit the powder X-ray data to an orthorhombic cell. The IR spectroscopy and DSC study are in agreement with XRD results. The controversial valence state of copper in this compound which was thought to be *trivalent* was found to be more closely a *divalent* one through our EPR experiments. Even though we aimed at getting an insulator-to-metal transition with bismuth substitution, we could only achieve a marginal drop in resistivity. Based on our results, however, we predict a possible metallic transition in $Ba_{2-x}Bi_xCu_2O_5$ in the composition range $0 \leq x \leq 0.5$. Studies toward this goal are in progress.

ACKNOWLEDGMENTS

One of us (YSR) thanks the CSIR Govt. of India for financial assistance in the form of an SRF. We thank the referees for their helpful suggestions and comments.

REFERENCES

1. T. V. Ramakrishnan and C. N. R. Rao, "Superconductivity Today," p. 44. Wiley Eastern Ltd., New Delhi, 1992.
2. R. Schlogl, H. Eickenbusch, W. Paulus, and R. Schollhorn, *Mater. Res. Bull.* **24,** 181 (1989).
3. M. K. Wu *et al., in* "Superconductivity and its Applications" (H. S. Kwok and D. T. Shaw, Eds.), p. 25. Elsevier, Amsterdam, 1988.
4. Y. Srinivasa Rao and C. S. Sunandana, *J. Mater. Sci. Lett.* **10,** 927 (1991).
5. U. Straub, D. Krug, Ch. Ziegler, D. Schmeißer, and W. Gopel, *Mater. Res. Bull.* **24,** 681 (1989).
6. N. Kimizuka, E. Takayama, S. Horiuchi, A. Yamamoto, and T. Fujita, *J. Solid State Chem.* **42,** 322 (1982).
7. H. Fjellvag, P. Karen, and A. Kjekshus, *Acta Chem. Scand. A* **42,** 144 (1988).
8. M. Arjomond and D. J. Machin, *J. Chem. Dalton Trans.* **11,** 1061 (1975).
9. E. F. Paulus, G. Miche, H. Fuess, I. Yehia, and U. Lochner, *J. Solid State Chem.* **90,** 17 (1991).
10. S. Eriksson, L. G. Johansson, L. Boerjesson, and M. Kakihana, *Physica C* **59,** 162 (1989).
11. P. Lightfoot *et al., J. Solid State Chem.* **92,** 473 (1991).
12. L. V. Azaroff, "Elements of X-ray Crystallography," p. 483 McGraw–Hill, New York, 1952.
13. E. Wu, Flinders University of Australia, "POWD" software.
14. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds," p. 129. Wiley, New York, 1978.
15. A. Q. Pham, C. Michel, M. Herviev, A. Maignan, and B. Raveau, *J. Phys. Chem. Solids* **54,** 65 (1993).
16. W. E. Blumberger, J. Eising, and S. Geschwind, *Phys. Rev.* **130,** 900 (1963).
17. A. Abragam and B. Bleaney, "EPR of Transition Ions," p. 452. Clarendon, Oxford, 1970.
18. C. S. Sunandana, *Mater. Res. Bull.* **25,** 404 (1990).
19. A. R. Armstrong, R. Janes, K. K. Singh, and P. P. Edwards, *Bull. Mater. Sci.* **14,** 641 (1991).
20. C. J. Ballhausen, "Introduction to Ligand Field Theory," p. 270. McGraw–Hill, 1962.
21. A. W. Webb, K. H. Kim, and C. Bouldin, *Solid State Commun.* **79,** 507 (1991).