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# LETTERS TO THE EDITOR

## Superconductivity at 34 K in the K/Ba/Bi/O System

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The critical temperature for superconductivity in the (Ba, K)$BiO_3$ system has been increased to 34 K. With each such increase of $T_c$ in a system containing no copper it becomes increasingly likely that the mechanisms for superconductivity in the Bi-based and the Cu-based oxide superconductors are very closely related to each other. Since the (Ba, K)$BiO_3$ superconductors possess the cubic perovskite structure, the mechanism for high $T_c$ would then not related directly to the two-dimensional character of the copper oxide superconductors or to the magnetism in such systems.

Superconductivity in the (Ba, K)(Bi, Pb)$O_3$ system was reported at 13 K in 1975 (*1*). At that time, superconductivity was observed only in samples containing Pb, and the effect of potassium was to give sharper, more complete transitions rather than increased $T_c$'s. Samples then prepared of the type (Ba, K)$BiO_3$ contained no detectable superconducting component. More recently (*2–5*), new synthesis conditions have yielded (Ba, K)$BiO_3$ superconductors with $T_c$ approaching 30 K. We defined synthesis conditions for which $T_c$ = 34 K.

The synthesis procedure was similar to that first reported by Wignacourt *et al.* (*6*). A mixture of $Bi_2O_3$, $Ba(OH)_2$, and KOH was heated in open gold containers at 360°C in air for 2 hr, followed by slow cooling at 6°/hr to 70°C. The $Ba(OH)_2$/KOH flux was in an approximate fivefold excess over that required for a given (Ba, K)$BiO_3$ composition. A $T_c$ of 34 K was obtained when using a K : Ba ratio of 9 : 1.

X-ray diffraction powder patterns indicated the presence of one or more phases with the perovskite structure for all superconducting products. The presence of superconductivity was established by the ac mutual inductance technique. Our samples showing sharp superconducting onsets at 34 K (Fig. 1) contain at least two perovskite phases, one with a cell edge of 4.30 Å and another with a cell edge of 4.24 Å. Small amounts of $Bi_2O_3$ were also frequently observed in our samples. As noted by earlier workers (*4, 5*), decreasing $x$ in $Ba_xK_{1-x}BiO_3$ leads to a decreased cell edge. The smallest cell edge reported by previous workers is 4.27 Å. We prepared a (Ba, K)$BiO_3$ perovskite with a cell edge of 4.24 Å, indicating a significantly higher level of potassium. Using the relationship between the cubic cell edge and the composition derived in Ref. (*4*), we conclude that our new composition with $a$ = 4.24 Å is $Ba_{0.4}K_{0.6}BiO_3$.

Neutron diffraction studies have been the

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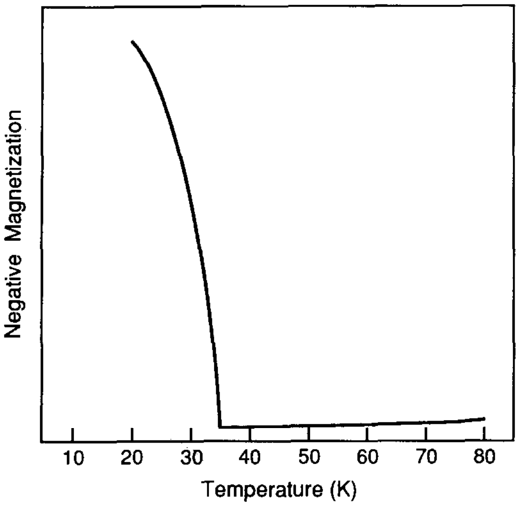

FIG. 1. Alternating current mutual inductance signal (arbitrary units) vs temperature (K).

most reliable method of determining structure and composition in the K/Ba/Bi/O system (*4*). Thus, neutron diffraction experiments were undertaken at Brookhaven National Laboratory using conditions recently described (*7*). These studies confirmed the cubic perovskite structure and the $Ba_{0.4}K_{0.6}BiO_3$ formula for the phase with the smaller cell edge. The analysis was more difficult and ambiguous for the phase or phases giving rise to the pseudo-cubic pattern with the larger cell edge. This pattern cannot be accounted for on the basis of one cubic phase. Instead, it is apparently due to the presence of more than one perovskite phase, at least one of which possesses symmetry lower than cubic. Our various refinements of this part of the pattern, however, all indicated a lower potassium content, consistent with the larger cell volume. More definitive neturon diffraction studies must await the availability of single-phase samples. This could be difficult to impossible if phase segregation occurs on cooling. At the present time, we cannot be certain which of the perovskite phases in our sample gives rise to the $T_c$ value of 34 K. It is tempting to attribute this behavior to the new phase with the higher potassium content which is the dominant phase in our product. On the other hand, previous work (*4*) has indicated a decreasing $T_c$ with increasing potassium content.

There have been two recent reports of $T_c$'s in the K/Ba/Bi/O system substantially higher than 30 K. In one publication a $T_c$ of 32 K (*8*) has been reported, but no X-ray diffraction data are provided. Thus, more than one phase may have been present, and the composition and cell edge of the $T_c = 32$ K phase are unknown. In a second paper a $T_c$ of 34 K is reported (*9*), but no cell edge is given for this product. The preparation used in both of these studies was the sealed-tube, high-temperature route which is very different from the synthetic route which we employed.

For both the $BaPb_{1-x}Bi_xO_3$ and $Ba_xK_{1-x}BiO_3$ systems, $T_c$ varies strongly with composition. In both $x = 0$ compounds, the electronic structure might be expected to be a filled oxygen $2p$ valence band just below an empty $6s$ conduction band. Due to high covalency, there would actually be a strong admixture of $2p$ and $6s$ in both bands. Metallic and superconducting properties ($T_c = 0.5$ K) are in fact found for $BaPbO_3$ which has the perovskite structure. This compound may then be viewed as a semimetal or a zero gap semiconductor due to overlap of the Pb$6s$ and O$2p$ bands. On the other hand, $KBiO_3$ with the perovskite structure is unknown. For $x = 1$ (i.e., $BaBiO_3$), the electronic configuration is formally $s^1$ for $Bi^{IV}$. However, such an oxidation state is unstable with respect to disproportionation into $Bi^{III}(s^2)$ and $Bi^{V}(s^0)$.[1] Insulating properties result from this disproportionation rather than from antiferromagnetism (*10*).

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[1] When writing $Bi^{III}$ and $Bi^{V}$, there is no implication that the real charges on these cations are close to +3 and +5, respectively, Instead, the $Bi^{III}$–O bonds contain more electrons than the $Bi^{V}$–O bonds. The extra pair of electrons in the $Bi^{III}$–O bonds are antibonding; thus, the $Bi^{III}$–O bonds are longer than the $Bi^{V}$–O bonds.

In the region intermediate between $x = 0$ and $x = 1$, the occurrence of superconductivity may be related to this tendency of $s^1$ cations to disproportionate (*11, 12*).

There are striking similarities between the bismuth oxide-based and copper oxide-based superconductors. In both cases, there is a band which would be filled with two electrons per active cation, i.e., a Bi6$s$–O2$p$ band or a Cu3$d_{x^2-y^2}$–O2$p$ band. At the half-filled level, the band splits to form the insulating state. This splitting may drive the filled half of the $\sigma^*$ band down close to or possibly below the $\pi^*$ band. Superconductivity might then result from a delicate interplay of these two bands. The splitting of the $\sigma^*$ band is caused by an electron pairing interaction which is different for $\mathrm{Cu^{II}}$ and $\mathrm{Bi^{IV}}$. Nonetheless, these tendencies to pair electrons may be related to the occurrence of superconductivity when the $\sigma^*$ band occupancy drops below the half-filled level. Alternately, superconductivity might be related to disproportionation for both the Bi-based and Cu-based systems (*11*): $2\mathrm{Bi^{IV}} \rightarrow \mathrm{Bi^{III}} + \mathrm{Bi^{V}}$ and $2\mathrm{Cu^{II}} \rightarrow \mathrm{Cu^{I}} + \mathrm{Cu^{III}}$.

## References

*1.* A. W. SLEIGHT, J. L. GILLSON AND P. E. BIERSTEDT, *Solid State Commun.* **17**, 27 (1975).

*2.* L. F. MATTHEISS, E. M. GYORGY, AND D. W. JOHNSON, *Phys. Rev. B* **37**, 3745 (1988).

*3.* R. J. CAVA, B. BATLOGG, J. J. KRAJEWSKI, R. FARROW, L. W. RUPP, A. E. WHITE, K. SHORT, W. F. PECK, AND T. KOMETANI, *Nature (London)* **332**, 814 (1988).

*4.* D. G. HINKS, B. DABROWSKI, J. D. JORGENSEN, A. W. MITCHELL, D. R. RICHARDS, S. PEI, AND D. SHI, *Nature (London)* **333**, 836 (1988).

*5.* L. F. SCHNEEMEYER, J. K. THOMAS, T. SIEGRIST, B. BATLOGG, L. W. RUPP, R. L. OPILA, R. J. CAVA, AND D. W. MURPHY, *Nature (London)* **335**, 421 (1988).

*6.* J. P. WIGNACOURT, J. S. SWINNEA, H. STEINFINK, AND J. B. GOODENOUGH, *Appl. Phys. Lett.* **53**, 1753 (1988).

*7.* J. B. PARISE, J. GOPALAKRISHNAN, M. A. SUBRAMANIAN, AND A. W. SLEIGHT, *J. Solid State Chem.* **76**, 432 (1988).

*8.* S. JIN, T. H. TIEFEL, R. C. SHERWOOD, A. P. RAMIREZ, E. M. GYORGY, G. W. KAMMLOTT, AND R. A. FASTNACHT, *Appl. Phys. Lett.* **53**, 1116 (1988).

*9.* S. KONDOH, M. SERA, K. FUKUDA, Y. ANDO, AND M. SATO, *Solid State Commun.* **67**, 879 (1988).

*10.* Y. J. UEMURA, B. J. STERNLIEB, D. E. COX, J. H. BREWER, R. KADONO, J. R. KEMPTON, R. F. KIEFL, S. R. KREITZMAN, G. M. LUKE, P. MULHERN, T. RISEMAN, D. L. WILLIAMS, W. J. KOSSLER, X. H. YU, C. E. STRONACH, M. A. SUBRAMANIAN, J. GOPALAKRISHNAN, AND A. W. SLEIGHT, *Nature (London)* **335**, 151 (1988).

*11.* A. W. SLEIGHT, *in* "Chemistry of High-Temperature Superconductors" (D. L. Nelson, M. S. Whittingham, and T. F. George, Eds.), pp. 2–12. Amer. Chem. Soc., Washington, DC (1987).

*12.* T. M. RICE, *Nature (London)* **332**, 780 (1988).