

LETTERS TO THE EDITOR

Superconductivity in $Ba_{1-y}Sr_yPb_{1-x}Bi_xO_3$ *

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Substitution of Ba by Sr in $BaPb_{1-x}Bi_xO_3$ narrows the superconducting composition range in addition to lowering the T_c ; the decrease in T_c with Sr content is nonlinear. The effect of Sr substitution is found to be more subtle than a mere chemical pressure effect. © 1990 Academic Press, Inc.

$BaPb_{1-x}Bi_xO_3$ is one of the unique oxide systems exhibiting a fairly high superconducting transition temperature (T_c) of 13 K (1). Among the parent oxides, $BaPbO_3$ ($x = 0.0$) is a nonsuperconducting metal, while $BaBiO_3$ ($x = 1.0$) is an insulator involving charge ordering of Bi^{III} and Bi^V (2). The mechanism of superconductivity in relation to the compositionally controlled metal-insulator (M-I) transition in $BaPb_{1-x}Bi_xO_3$ is a problem that is yet to be fully understood. Thus, the sharp phase boundary at the M-I transition where superconductivity disappears at $x \approx 0.35$ (3) has not been explained. We have been reexamining the $BaPb_{1-x}Bi_xO_3$ system for some time in view of its fundamental importance to the field of oxide superconductivity. Of interest to us was an examination of the effect of the substitution of Ba by Sr in $BaPb_{1-x}Bi_xO_3$ in order to understand the chemical pressure effect arising from such substitution, as

distinct from the effect of hydrostatic pressure on the transition. A letter by Bredthauer and Jansen (4) on this topic in this journal has just come to our attention, and we hasten to report complementary results of our investigations on Sr substitution in the $BaPb_{1-x}Bi_xO_3$ system.

Several compositions in the $Ba_{1-y}Sr_yPb_{1-x}Bi_xO_3$ system were prepared by the usual ceramic method starting from BaO_2 , $SrCO_3$, PbO , and Bi_2O_3 . Samples were prepared at 850–900°C in air for 48 hr. Pseudocubic lattice parameters were determined from powder X-ray diffraction data. Superconducting transition temperatures were obtained from resistivity measurements down to 4.2 K. Thermoelectric power was measured down to 12 K using a closed-cycle helium cryostat.

X-ray diffraction data (Fig. 1) show that a considerable amount of strontium substitutes for barium in the system which retains the pseudocubic perovskite structure (y up to 0.3 for $x = 0.2$ and y up to 0.2 for $x = 0.25$). We have shown resistivity plots of

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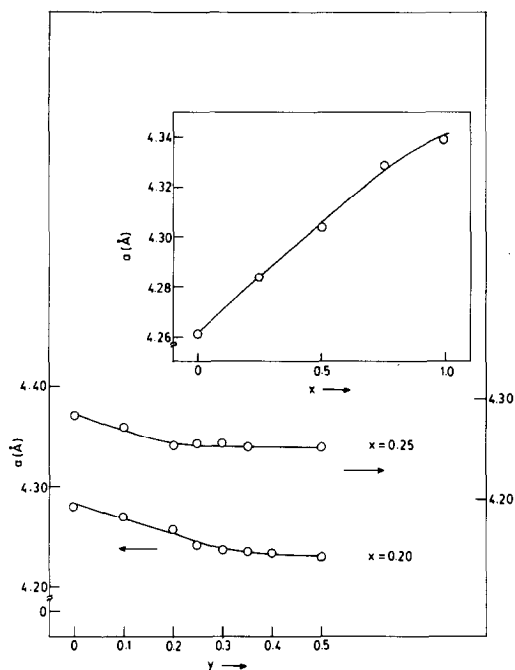


FIG. 1. Variation of the pseudocubic lattice parameter of the $\text{Ba}_{1-y}\text{Sr}_y\text{Pb}_{1-x}\text{Bi}_x\text{O}_3$ system as a function of x and y .

selected samples of $\text{Ba}_{1-y}\text{Sr}_y\text{Pb}_{0.8}\text{Bi}_{0.2}\text{O}_3$ in Fig. 2 to illustrate the effect of Sr substitution in place of Ba. Increasing the concentration of Sr decreases the T_c significantly. The variation of T_c (onset) as a function of x and y is shown in Fig. 3. For the purpose of comparison, we have also shown our data on the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ ($y = 0.0$) system. We see that when $y = 0$, the samples are superconducting in the range $0.05 \leq x \leq 0.30$ with a maximum T_c of 11 K occurring at $x = 0.25$. These results are in agreement with the literature report of Uchida *et al.* (3). The effect of Sr substitution at a given x ($0.05 \leq x \leq 0.30$) is not only to decrease the T_c but also to narrow the superconducting composition range, as can be seen from the plots shown in Fig. 3. We also find the decrease in T_c with increase in Sr substitution to be nonlinear, as noted by Sakudo *et al.* (5, 6). Accordingly, when $y = 0.25$, we find

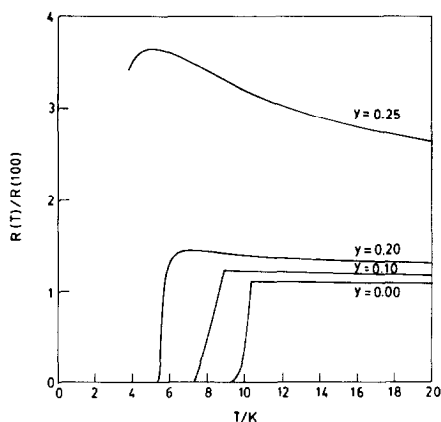


FIG. 2. Temperature-dependence of the normalized resistance of $\text{Ba}_{1-y}\text{Sr}_y\text{Pb}_{0.8}\text{Bi}_{0.2}\text{O}_3$.

superconductivity ($T_c \sim 5$ K) only in the $x = 0.2$ composition.

Since Sr^{II} is smaller than Ba^{II} , one would expect the effect of Sr substitution to be similar to that of hydrostatic pressure. However, the effect of Sr substitution on T_c is much more drastic than that of hydrostatic pressure (5). The effects of replacing the larger Ba^{II} (1.61 Å) by the smaller Sr^{II} (1.44 Å) would be twofold. One effect is, of course, the chemical pressure effect arising from the smaller size of Sr, which manifests itself as a contraction of the lattice. The other effect is related to the fact that Sr-O

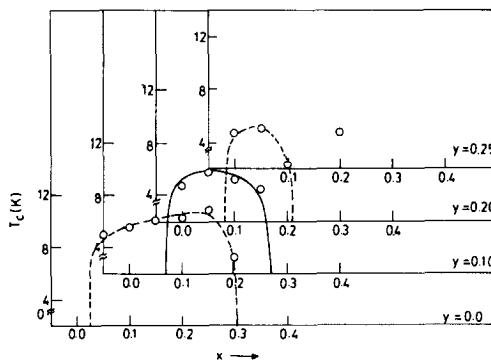


FIG. 3. Variation of T_c with x and y in the system $\text{Ba}_{1-y}\text{Sr}_y\text{Pb}_{1-x}\text{Bi}_x\text{O}_3$.

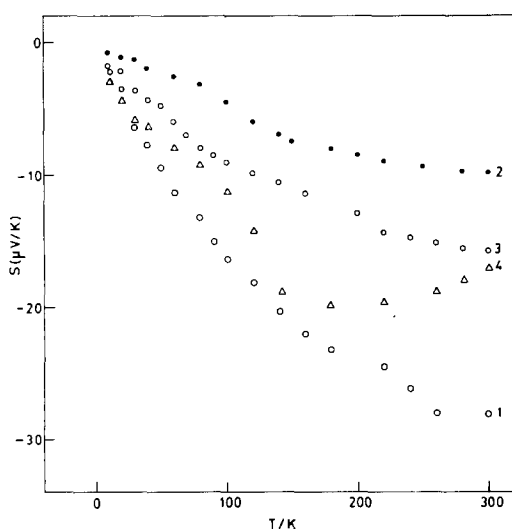


FIG. 4. Temperature dependence of the thermoelectric power of selected samples in the $\text{Ba}_{1-y}\text{Sr}_y\text{Pb}_{1-x}\text{Bi}_x\text{O}_3$ system: 1, $x = 0, y = 0$; 2, $x = 0.25, y = 0.0$; 3, $x = 0.2, y = 0.1$; 4, $x = 0.2, y = 0.2$.

bonds would be more covalent than Ba–O bonds, because Sr^{II} is more acidic than Ba^{II} . Larger covalency of Sr–O bonds would mean that the Pb/Bi–O bonds are less covalent. This would have the effect of narrowing the conduction band of Pb/Bi: $6s\text{--}O:2p$ parentage. This would naturally affect the density of states at the Fermi level. Our thermoelectric power data (Fig. 4) provide some support to this line of

thinking. The thermoelectric power is negative for all compositions and the absolute value increases with the increase in Sr substitution. The increase would indicate that the carrier density decreases with increasing Sr content. This is consistent with the argument that the effect of strontium substitution in the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system is not merely a pressure effect. The larger covalency of Sr–O bonds seems to significantly affect the electronically active Pb/Bi: $6s\text{--}O:2p$ band. Further work is needed to understand the subtle effect of strontium substitution on the superconducting properties of the $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ system.

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References

1. A. W. SLEIGHT, J. L. GILLSON, AND P. E. BIERSTEDT, *Solid State Commun.* **17**, 27 (1975).
2. D. E. COX AND A. W. SLEIGHT, *Acta Crystallogr. B* **35**, 1 (1979).
3. S. UCHIDA, K. KITAZAWA, AND S. TANAKA, *Phase Trans.* **8**, 95 (1987).
4. J. BREDTHAUER AND M. JANSEN, *J. Solid State Chem.* **86**, 327 (1990).
5. T. SAKUDO, H. UWE, T. FUJIWARA, J. FUJITA, AND J. SHIOZAWA, *Japan. J. Appl. Phys.* **23**, L496 (1984).
6. T. SAKUDO AND H. UWE, *Phase Trans.* **8**, 147 (1987).