

Superconducting properties of phosphorus added (Bi, Pb)–Sr–Ca–Cu–O system

M.A.K.L. Dissanayake^{a,b}, K. Tennakone^a, S.H.S.P. Samarappuli^a,
O.A. Ileperuma^{a,b} and N.D. Karunasinghe^a

^a *Institute of Fundamental Studies, Hantana Road, Kandy, Sri Lanka*

^b *Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka*

Received 18 May 1990; in final form 4 July 1990

Superconducting properties of phosphorus added $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_{1.5}\text{O}_y$ system using two mixing ratios, $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ and $1:1$, have been investigated using electrical resistivity, ac magnetic susceptibility and X-ray powder diffraction measurements. The results show that phosphorus substitution for bismuth using phosphates in a solid state reaction is unlikely to be realised easily. This method results in the formation of a multiphase material with a lower transition temperature.

1. Introduction

Work of Michel et al. [1], Maeda et al. [2], Chu et al. [3,4], Tanako et al. [5] and others [6–8] has led to the discovery of (Bi, Pb)–Sr–Ca–Cu–O superconducting systems with resistivity onsets in the 100–120 K range. Effects of Sb substitution [9,10] and Ni substitution [11] on T_c in the (Bi, Pb)–Sr–Ca–Cu–O system have recently been investigated. P belongs to the same group as Bi in the periodic table and therefore, the valence electron configuration of P is the same as that of Bi. However, the atomic radius of P is smaller than that of Bi. Thus one would expect the superconducting properties of the (Bi, Pb)–Sr–Ca–Cu–O material to be affected if P can be substituted for Bi. In this paper we report the electrical resistivity, magnetic susceptibility and XRD studies of the $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_{1.5}\text{O}_y$ material where phosphorus has been introduced as $\text{Ca}_3(\text{PO}_4)_2$ with two mixing ratios, $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ and $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:1$.

2. Experimental

Bi_2O_3 , PbO, SrCO_3 , CaCO_3 , $\text{Ca}_3(\text{PO}_4)_2$ and CuO powders of purity better than 99% were used as starting raw materials. The powders were mixed with the

nominal cation ratio Bi:Pb:Sr:Ca:Cu=0.7:0.3:1:1:1.5. Phosphorus was introduced as $\text{Ca}_3(\text{PO}_4)_2$ using two mixing ratios to produce two sets of samples; set B with $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ and set C with $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:1$. After mixing appropriate quantities, the samples were prepared by dry grinding and firing the powders at 820°C in air for 12 h. Pellets were pressed from the calcined powders and sintered at 860°C in air for 60 h. Resistivity of the pellet samples were measured in a closed cycle refrigerator, Daikin model V202A5L using the four-probe technique with pressed indium contacts. The sample currents used were in the 1–5 mA range. The sample temperature was measured by a gold–chromel thermocouple. For superconducting samples, the Meisner effect was demonstrated by observing the reflection of a vertically suspended small SmCo magnet. The ac magnetic susceptibility was measured by using a Hartshorn bridge arrangement. Both coils were fixed to the cryo-tip and the sample was inserted into one coil, after making the null adjustment. Phase setting of the lock-in analyser was adjusted so as to measure the in-phase signal, corresponding to the variation in the bridge inductance. Both the resistivity and the susceptibility measurements were computer controlled. X-ray powder diffraction measurements were performed using a Shi-

madzu model XD-7A X-ray diffractometer using Cu $K\alpha$ radiation of wavelength 1.54 Å.

3. Results and discussion

Figs. 1 and 2 depict the temperature dependence of the electrical resistance and the ac magnetic susceptibility of the samples of set B, having nominal composition $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{Sr}_1\text{Ca}_1\text{Cu}_{1.5}\text{O}_y$ with $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$, along with those of the

pure material A, without phosphate doping. The undoped material exhibits superconductivity with onset of resistivity transition at 120 K and zero resistivity at 100 K, as has been reported by earlier workers [6–9]. Phosphate doping has not changed the resistivity onset at 120 K but shifted the zero resistivity transition temperature T_c down to 70 K. Further, a second resistivity onset appears at 80 K. The ac magnetic susceptibility of the undoped material shows a sharp onset at 110 K which corresponds to the mid-point of the resistivity transition. Phosphate-doped samples exhibit a sharp susceptibility transition at ≈ 80 K and the volume fraction of the superconducting phase has reduced considerably in comparison with the undoped material.

Fig. 3 depicts the temperature variation of the electrical resistance and the ac magnetic susceptibility of the phosphate-doped samples of set C with $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:1$. This amount of phosphate doping has considerably increased the normal state resistivity of the sample. Two resistivity onsets are observed at 120 and 100 K respectively and the zero resistivity transition remains at 70 K as for the samples B with low phosphate doping. According to the magnetic susceptibility curve, a sharp transition occurs at ≈ 75 K and the material becomes superconducting at 70 K. However, the volume fraction of the superconducting phase has reduced to about 1/3 of that in the low-phosphate-doped samples.

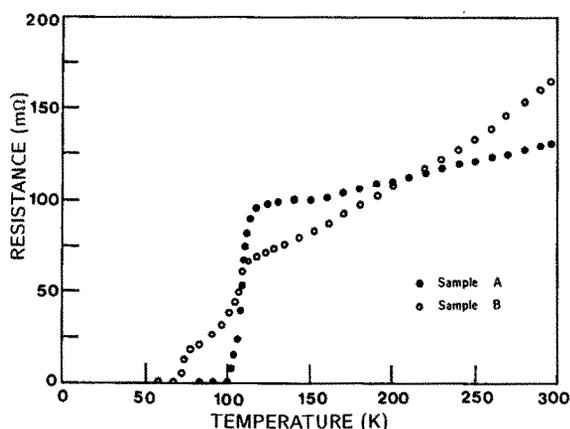


Fig. 1. Temperature dependence of the electrical resistance of pure $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{Sr}_1\text{Ca}_1\text{Cu}_{1.5}\text{O}_y$ (sample A) and that with phosphate added in the ratio $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ (sample B).

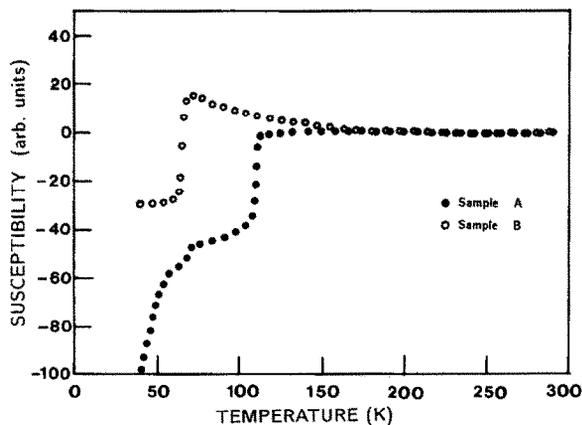


Fig. 2. Temperature dependence of the ac magnetic susceptibility of pure $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{Sr}_1\text{Ca}_1\text{Cu}_{1.5}\text{O}_y$ (sample A) and that with phosphate added in the ratio $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ (sample B).

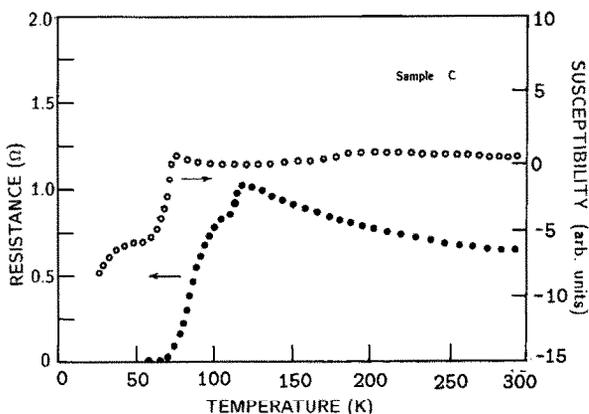


Fig. 3. Temperature dependence of the electrical resistance and the ac magnetic susceptibility of $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{Sr}_1\text{Ca}_1\text{Cu}_{1.5}\text{O}_y$ with phosphate added in the ratio $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:1$ (sample C).

Fig. 4 shows the X-ray diffraction patterns of the undoped material A, along with the two phosphate-doped samples B and C. It can be seen that the XRD pattern of the undoped material has peaks characteristic of both the 110 K phase and the 85 K phase reported in the literature [12,13]. Peaks corresponding to the 110 K phase can be indexed using $a=5.390$ Å, $b=5.390$ Å, and $c=37.100$ Å, whereas those of the 85 K phase can be indexed with $a=5.390$ Å, $b=5.390$ Å, and $c=30.900$ Å.

The XRD peaks, characteristic of the undoped material, are retained even with phosphate addition. However, some new peaks have appeared at $2\theta=18^\circ$, 30° , and 39° . These peaks do not correspond to unreacted $\text{Ca}_3(\text{PO}_4)_2$, and their intensities have increased with increasing phosphate content. The phosphate-doped material evidently has a multiphase character, as can be seen also from the electrical resistivity and magnetic susceptibility data. The volume fraction of the superconducting phase has

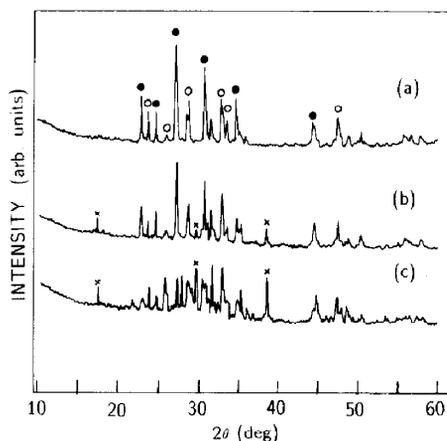


Fig. 4. X-ray diffraction patterns of pure $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{Sr}_1\text{Ca}_1\text{Cu}_{1.5}\text{O}_y$ (a), and that with phosphate added in the ratios $\text{Ca}_3(\text{PO}_4)_2:\text{CaCO}_3=1:4$ (b) and $1:1$ (c). Peaks due to 110 K phase (○), 85 K phase (●) and impurity phases (×) are indicated.

diminished and that of the new impurity phase has increased with phosphate addition.

Based on the above observations, we can conclude that it is unlikely that phosphorus can be substituted for bismuth using phosphates in a solid-state reaction. This method results in the formation of a multiphase material with a lower transition temperature possibly caused by the effect of non-superconducting impurity phases.

References

- [1] C. Michel, M. Hervieu, M.M. Borel, A. Grandin, F. Deslandes, J. Provost and B. Raveau, *Z. Physik B* 68 (1987) 421.
- [2] H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, *Japan. J. Appl. Phys.* 27 (1988) L209.
- [3] C.W. Chu, J. Bechtold, L. Gao, P.H. Hor, Z.J. Huang, R.L. Meng, Y.Y. Sun, Y.Q. Wang and Y.Y. Xue, *Phys. Rev. Letters* 60 (1988) 941.
- [4] R.M. Hazen, C.T. Prewitt, R.J. Angel, N.L. Ross, L.W. Finger, C.G. Hadjidakos, D.R. Veblen, P.J. Heaney, P.H. Hor, R.L. Meng, Y.Y. Sun, Y.Q. Wang, Y.Y. Xue, Z.J. Huang, L. Gao, J. Bechtold and C.W. Chu, *Phys. Rev. Letters* 60 (1988) 1174.
- [5] M. Tanaka, *Superconductor Week 2* (May 23, 1988) 1.
- [6] U. Balachandran, D. Shi, D.I. Dos Santos, S.W. Graham, M.A. Patel, B. Tani, K.S. Vandervoort, H. Claus and R.B. Poeppel, *Physica C* 156 (1988) 649.
- [7] C. Chen, J.Q. Li, Y.S. Yao, X.M. Huang, Z.X. Zhao and W.K. Wang, *Solid State Commun.* 68 (1988) 749.
- [8] L. Ganapathi, S. Krishna, K. Murthy, R. Vijayaraghavan and C.N.R. Rao, *Solid State Commun.* 67 (1988) 967.
- [9] S.X. Dou, H.K. Liu, N.X. Tan, Y.J. Sheng and W.K. Jones, *Physica C* 158 (1989) 97.
- [10] H. Liu, X. Zhan, Y. Chao, G. Zhou, Y. Ruan, Z. Chen and Y. Zhang, *Physica C* 156 (1988) 804.
- [11] M.A.K.L. Dissanayake, S.H.S.P. Samarappuli, K. Tennakone, O.A. Lleperuma and N.D. Karunasinghe, to be published.
- [12] J.M. Tarascon, W.R. McKinnon, P. Bardoux, D.M. Hwang, B.G. Bagley, L.H. Green, G.W. Hull, Y. le Page, N. Stoffel and M. Giroud, *Phys. Rev. B* 38 (1988) 8885.
- [13] E. Chavira, R. Escudero, D. Rios-Jara and L.M. Leon, *Phys. Rev. B* 38 (1988) 9272.