JOURNAL OF SOLID STATE CHEMISTRY 79, 177–180 (1989)

$Bi_{2-x}Pb_x(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ (n = 1, 2, 3, and 4) Family of Superconductors*

C. N. R. RAO,† R. VIJAYARAGHAVAN, L. GANAPATHI, AND S. V. BHAT

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Communicated by J. M. Honig, December 29, 1988

Superconducting oxides of the $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ series with n = 1, 2, 3 and 4 have been characterized. The superconducting transition temperature increases markedly with n up to n = 3, but the T_c of the n = 4 member is not much higher than that of the n = 3 member. The T_c does not change significantly in $Bi_{2-x}Pb_xCaSr_2Cu_2O_{8+\delta}$ with x ($0.1 < x \leq 0.5$).

Superconductivity in the Bi–Ca–Sr–Cu–O system above liquid nitrogen temperature has been a subject of intense investigation in recent months and the first three members of the $Bi_2(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ series have been characterized (*1*). During the course of our investigations of this series, we found that partial substitution of Bi by Pb not only favors the formation of the higher members of the series but also leads to better superconducting characteristics. In this letter we communicate the results of systematic studies on the $Bi_{2-x}Pb_x(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ series. Of special interest is the characterization for the first time of the n = 4 member with four Cu–O sheets and the preparation of the pure n = 3 member.

In order to synthesize the various compositions of the $Bi_{2-x}Pb_x(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ series, we employed the ceramic method, involving heating of the appropriate mixtures of the corresponding carbonates and oxides. In Table I we have provided the conditions of preparation of the various members. The duration of the heat treatment given in the table is the minimum period required to form the particular member of the series. Longer heating periods were, however, employed by us to obtain good monophasic compositions with reproducible properties. By this procedure we could obtain the pure n = 3 member of the series. Only mixtures of n = 3 with n = 2 and other members have been reported in the literature (*2, 3*). By prolonged heating of the appropriate mixture of oxides, we obtained the first evidence for the n = 4 member not reported hitherto. We also prepared the n = 2 and n = 3 members by reacting the Ca–Sr–Cu–O precursor of the required

* Contribution No. 589 from the Solid State and Structural Chemistry Unit.

† To whom all correspondence should be addressed.

0022-4596/89 $3.00

TABLE I

PREPARATIVE CONDITIONS AND LATTICE PARAMETERS OF $Bi_{2-x}Pb_x(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$

Starting composition	Phase present	Conditions[a]	Lattice parameters (Å) *a*	*b*	*c*
$Bi_{1.75}Pb_{0.25}CaSrCuO_{6+\delta}$	$n = 1$	1020 K 12 hr 1070 K 24 hr	5.404	5.404	24.500
$Bi_{1.5}Pb_{0.5}CaSrCuO_{6+\delta}$	$n = 1$	1020 K 12 hr 1070 K 24 hr	5.396	5.396	24.450
$Bi_{1.85}Pb_{0.15}CaSr_2Cu_2O_{8+\delta}$	$n = 2$	1020 K 12 hr 1130 K 24 hr	5.412	5.412	30.800
$Bi_{1.75}Pb_{0.25}CaSr_2Cu_2O_{8+\delta}$	$n = 2$	1020 K 12 hr 1130 K 24 hr	5.410	5.410	30.820
$Bi_{1.5}Pb_{0.5}CaSr_2Cu_2O_{8+\delta}$	$n = 2$	1020 K 12 hr 1130 K 24 hr	5.376	5.416	30.800
$Bi_{1.5}Pb_{0.5}Ca_{2.5}Sr_{1.5}Cu_3O_{10+\delta}$	$n = 3$	1020 K 12 hr 1110 K 36 hr	5.400	5.400	36.900
$Bi_{1.5}Pb_{0.5}Ca_3Sr_2Cu_4O_{12+\delta}$	$n = 4$	1020 K 12 hr 1120 K 48 hr	5.400	5.400	44.000

[a] Minimum heating period is indicated; considerably longer heating periods are necessary to get good samples.

stoichiometry with calculated amounts of Bi_2O_3 and Pb_3O_4. The $n = 2$ member could be prepared by the decomposition of a mixture of nitrates and oxalates as well. All the samples were characterized by powder X-ray diffraction, as well as by electrical and magnetic measurements.

We measured the nonresonant microwave absorption of these cuprates employing a Varian EPR spectrometer operating at 9.1 GHz. This is a sensitive technique for the detection of superconductivity (*4, 5*).

In Fig. 1 we show typical powder X-ray diffraction patterns of the n = 1, 2, and 3 members of the series $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$. The pattern of the $n = 4$ member with about 30% of the $n = 3$ member is shown in the figure to indicate that the patterns of the two members are distinctly different. All members except $n = 2$ possess a pseudotetragonal structure. The $n = 4$ member has a *c*-parameter of ~44 Å compared to ~37 Å of the $n = 3$ member. The unit cell parameters of all the members are listed in Table I. In Fig. 2 we show the pow-

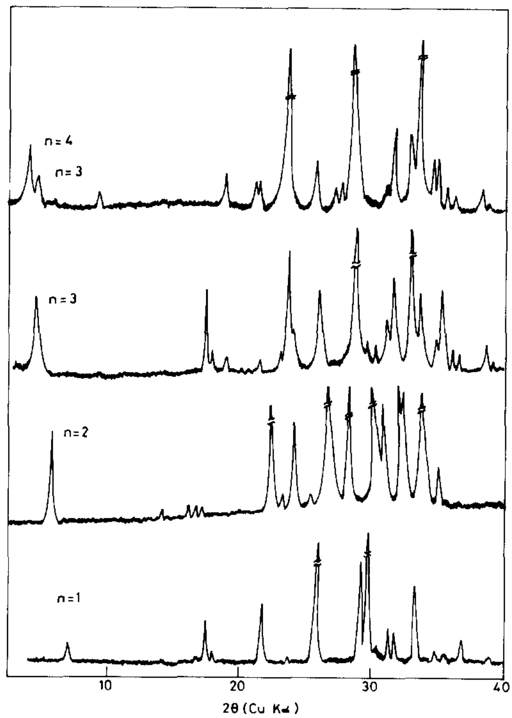

FIG. 1. Powder X-ray diffraction patterns of the n = 1, 2, 3, and 4 (with 30% $n = 3$) members of the $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ series.

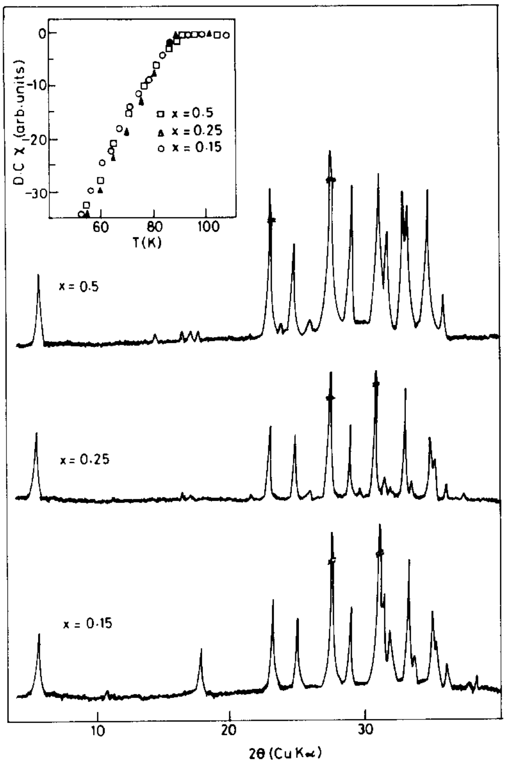

FIG. 2. Powder X-ray diffraction patterns of $Bi_{2-x}Pb_xCaSr_2Cu_2O_{8+\delta}$. Inset shows the dc susceptibility versus temperature plots for the different compositions.

der X-ray diffraction patterns of $Bi_{2-x}Pb_xCaSr_2Cu_2O_{8+\delta}$ for different values of x to show the monophasic nature of these compositions. The lattice parameters of these compositions are also listed in Table I. It is interesting that the compositions with $x = 0.15$ and 0.25 are pseudotetragonal, while the $x = 0.5$ composition is orthorhombic.

Superconductivity in the different members of the series $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ was first examined by the nonresonant microwave absorption technique. The normalized intensity of absorption versus temperature plots (Fig. 3) give the onset temperatures of 87, 92, and 112 K for the $n = 1$, 2, and 3 members, respectively. The $n = 4$ member shows only a slightly higher onset temperature than the $n = 3$ member. It should be noted that characterization of the $n = 1$ phase is rather elusive (*1*); high-T_c superconductivity in this member manifests itself only at certain critical compositions (Ca/Sr ratio) since the $n = 1$ member with no Ca has very low T_c (*6*). We notice that microwave absorption of $Bi_{1.5}Pb_{0.5}CaSrCuO_{6+\delta}$ (*1*) signals a slightly higher onset temperature than for the Pb-free $Bi_2CaSrCuO_{6+\delta}$ (*1*).

Magnetic susceptibility measurements on $Bi_{2-x}Pb_xCaSr_2Cu_2O_{8+\delta}$ indicate that the temperature at which onset of diamagnetism occurs does not change significantly with x (see inset of Fig. 2). The onset of diamagnetism in the $n = 2$ and $n = 3$ members of $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ (Fig. 4) occurs around 90 and 106 K, respectively. Electrical resistivity measurements lead to similar transition temperatures for these members. The onset of diamagnetism in the case of the $n = 4$ member is 110 K (Fig. 4) indicating that T_c does not increase much on increasing the number of Cu–O sheets beyond three. These results are consistent with those from the microwave absorption results shown in Fig. 3. In Fig. 5 we plotted the onset temperatures of the four members of the $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}$

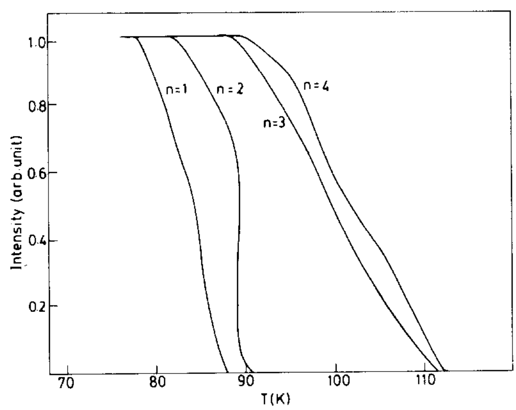

FIG. 3. Plots of the normalized nonresonant microwave absorption intensity of $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ against temperature.

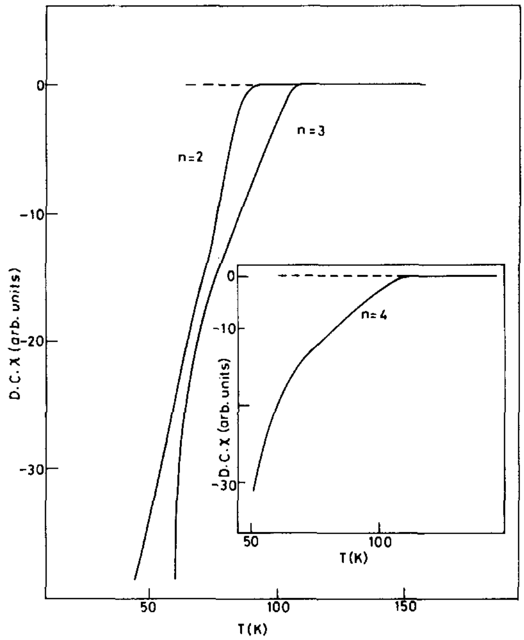

FIG. 4. Direct current magnetic susceptibility versus temperature plots of $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$.

$Cu_nO_{2n+4+\delta}$ series from magnetic and microwave absorption measurements against n in order to highlight the insensitivity of T_c to the number of Cu–O sheets beyond three.

Acknowledgment

The authors thank the Department of Science and Technology for support of this research.

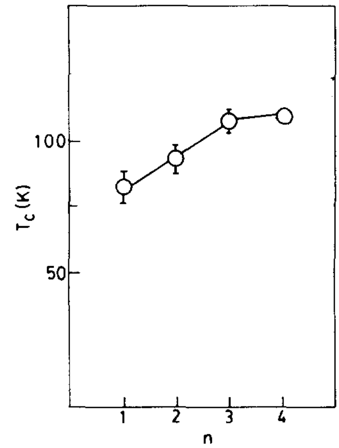

FIG. 5. Variation of T_c in $Bi_{1.5}Pb_{0.5}(Ca, Sr)_{n+1}Cu_nO_{2n+4+\delta}$ against the number of Cu–O sheets.

References

1. C. N. R. RAO, L. GANAPATHI, R. VIJAYARAGHAVAN, G. RANGA RAO, K. MURTHY, AND R. A. MOHAN RAM, *Phys. C* **156**, 827 (1988).
2. Z. CHEN, H. LIU, Z. MAO, K. WANG, X. ZHAN, AND Y. ZHAND, *Phys. C* **156**, 834 (1988).
3. J. L. TALLON, R. G. BUCKLEY, P. W. GILBERG, M. R. PRESLAND, I. W. M. BROWN, M. E. BOWDEN, L. A. CHRISTIAN, AND R. GOGUEL, *Nature (London)* **333**, 153 (1988).
4. S. V. BHAT AND C. N. R. RAO, *Rev. Solid State Sci.* **2**, 329 (1988), and references cited therein.
5. K. MOORJANI, B. F. KIM. J. BOHANDY, AND F. J. ADRIAN, *Rev. Solid State Sci.* **2**, 263 (1988).
6. C. MICHEL, M. HERVIEU, M. M. BOREL, A. GRANDIN, F. DESLANDES, J. PROVOST, AND B. RAVEAU, *Z. Phys. B* **68**, 421 (1987).