

## Effect of Sb substitution on the superconductivity of $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{4n+2}$ ( $n = 1, 2$ and $3$ ) systems\*

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**Abstract.** Effect of incorporation of Sb in place of Bi in the bismuth cuprate superconductors has been examined. The nominal compositions studied are  $\text{M}\text{Ca}_{1.5}\text{Sr}_{1.5}\text{Cu}_2\text{O}_{8+\delta}$  and  $\text{M}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10+\delta}$ , where  $\text{M} = \text{Bi}_{2-x}\text{Sb}_x$  or  $\text{Bi}_{1.5-x}\text{Sb}_x\text{Pb}_{0.5}$ . Different preparative routes such as the ceramic method, the matrix route as well as the melt route were employed to prepare the materials. No indication of either Sb entering the lattice or enhancement of  $T_c$  is noted from resistivity, magnetic susceptibility and microwave absorption measurements.

**Keywords.** Oxide superconductors; bismuth; antimony; dopant effect.

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### 1. Introduction

In the recently discovered superconducting Bi–Ca–Sr–Cu–O oxide system, phases with the general formula  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n+1}\text{Cu}_n\text{O}_{4n+2}$ , with  $n = 1, 2$  and  $3$  have been synthesized and characterized (Maeda *et al* 1988; Rao and Raveau 1989). The superconducting transition temperature appears to scale with  $n$ , but pure phases are seldom formed. At the microscopic level, intergrowth structures with different  $n$  values are observed (Ganapathy *et al* 1988) and mostly the bulk preparations contain a mixture of phases with different values of  $n$ .

The Bi–Ca–Sr–Cu–O system has at least two superconducting phases namely  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ , a low  $T_c$  (80 K) phase and  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+\delta}$ , a high  $T_c$  (110 K) phase. Synthesis of the high  $T_c$  phase has been problematic and requires long sintering under carefully controlled preparative conditions. The addition of foreign elements to the Bi–Ca–Sr–Cu–O system could change the free energy of formation of the high and low  $T_c$  phases (Luo *et al* 1989). Partial substitution Pb ions into the Bi site enables a larger volume fraction of phases with higher  $n$  values to be formed and hence higher  $T_{c(0)}$  can be observed (Takano *et al* 1988). Recently Hongbao *et al* 1989 and Chandrachood *et al* 1989 had reported enhancement of  $T_{c(0)}$  up to 120 K and 132 K in Sb doped Bi–Ca–Sr–Cu–O with and without Pb. However, many research groups have not been able to reproduce these results (Maeda *et al* 1989; Pissas and Niarchos 1989). We have investigated the effect of Sb substitution in the Bi–Ca–Sr–Cu–O system by preparing the required compositions by different preparative routes. Our

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studies show no enhancement of  $T_c$  by such substitution as seen from dc conductivity, magnetic susceptibility and non-resonant microwave absorption measurements.

## 2. Experimental

Various nominal compositions mentioned in table 1 were prepared by the ceramic method, the matrix method and the glass-recrystallization method. High purity oxides and carbonates were sintered at reaction temperatures mentioned in table 1 in the ceramic method. In the matrix method higher homogenization temperature (1000°C) of starting materials, except  $\text{Bi}_2\text{O}_3$ ,  $\text{Sb}_2\text{O}_5$  and  $\text{PbO}$  was used and followed by final

**Table 1.** Preparative conditions and superconducting properties of various nominal compositions studied.

Sl. No.	Nominal cation ratios						Electrical properties
	Bi	Sb	Pb	Ca	Sr	Cu	
$n = 1^{(a)}$							
1)	1.95	0.05	0.0	1.0	1.0	1.0	$T_{c(\text{on})} = 70 \text{ K}$ , $T_{c(0)} \sim 20 \text{ K}$
2)	1.90	0.10	0.0	1.0	1.0	1.0	semiconductor, $R_{RT} = 0.36 \text{ ohm}$ .
3)	1.85	0.15	0.0	1.0	1.0	1.0	insulator
4)	1.45	0.05	0.5	1.0	1.0	1.0	"
5)	1.40	0.10	0.5	1.0	1.0	1.0	"
$n = 2^{(b)}$							
6)	1.95	0.05	0.0	1.5	1.5	2.0	$T_{c(\text{on})} = 90 \text{ K}$ , $T_{c(0)} = 52 \text{ K}$
7)	1.90	0.10	0.0	1.5	1.5	2.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 43.5 \text{ K}$
8)	1.85	0.15	0.0	1.5	1.5	2.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 19 \text{ K}$
9)	1.45	0.05	0.5	1.5	1.5	2.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 25 \text{ K}$
10)	1.40	0.10	0.5	1.5	1.5	2.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 67 \text{ K}$
$n = 3^{(c)}$							
11)	1.95	0.05	0.0	2.0	2.0	3.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 20 \text{ K}$
12)	1.90	0.10	0.0	2.0	2.0	3.0	$T_{c(\text{on})} = 78 \text{ K}$ , $T_{c(0)} = 61 \text{ K}$
13)	1.85	0.15	0.0	2.0	2.0	3.0	$T_{c(\text{on})} = 80 \text{ K}$ , $T_{c(0)} = 63 \text{ K}$
14)	1.45	0.05	0.5	2.0	2.0	3.0	sharp drop at 110 K $T_{c(0)} = 60 \text{ K}$
15)	1.40	0.10	0.5	2.0	2.0	3.0	$T_{c(\text{on})} = 74 \text{ K}$ , $T_{c(0)} = 55 \text{ K}$
$n = 3^{(d)}$							
16)	1.85	0.15	0.0	2.0	2.0	3.0	not superconducting
17)	1.90	0.10	0.0	2.0	2.0	3.0	$T_{c(0)} = 78 \text{ K}$
18)	1.45	0.05	0.5	2.0	2.0	3.0	not superconducting
Glassy route (melt at 1400 K and quenched)							
19)	1.90	0.10	0.0	1.0	2.0	2.0	very high resistance
20)	1.90	0.10	0.0	1.0	2.0	2.0	$T_{c(\text{on})} = 90 \text{ K}$ , $T_{c(0)} = 60 \text{ K}$

(recrystallized at 850 C 120 h)

(a) Heat treatment: 600 C 12 h, 700 C 12 h, 820 C 73 h; (b) Heat treatment: 600 C 12 h, 700 C 12 h, 840 C 120 h; (c) Heat treatment: 600 C 12 h, 700 C 12 h, 820 72 h, 840 144 h; (d) Matrix method, Heat treatment: 1000 C for precursor compositions, followed by 500 C 12 h, 750 C 12 h, 800 C 36 h, 845 C 120 h (see text) (onset of diamagnetism from dc susceptibility of these samples are found to be 80 K, 110 K and 115 K respectively.)

heating with the addition of the above oxides. Bismuth cuprate glass was prepared by quenching the melt from 1100°C between precooled brass plates. This was followed by crystallization to get  $n=2$  phase the procedure for which has been described previously (Varma *et al* 1989). Characterization was done by X-ray diffraction and resistivity of all the samples. DC magnetic susceptibility and microwave absorption were done on selected samples to see the onset of superconductivity at higher temperatures. The nonresonant microwave absorption studies were done using a varian EPR spectrometer operating at 9.1 GHz. This is shown to be a sensitive technique for detection of superconductivity (Bhat *et al* 1987).

### 3. Results and discussion

X-ray diffraction patterns of the various Sb-substituted  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$  and  $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10+\delta}$  compounds indicate that the number and intensity of impurity lines increase with the increase in Sb content. The samples prepared by the glassy route and recrystallized are comparatively well formed. X-ray patterns of amorphous and recrystallized phases are presented in figure 1 for the nominal composition  $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$ . Lattice parameter calculations by least square fitting of the prominent lines indicate no observable systematic shifts (for example;  $a = 5.41 \text{ \AA}$ ,  $b = 5.44 \text{ \AA}$  and  $c = 30.77 \text{ \AA}$  for  $n = 2$  phases). This implies that Sb is not actually entering the lattice nor does it help in increasing the formation of a purer phase as observed in Pb.

The temperature variation of the normalized resistance of  $n = 2$  and 3 compositions is given in figures 2 and 3 respectively. The  $n = 1$  samples were metallic but not superconducting down to 15 K.  $T_c$  (zero) of  $n = 2$  and 3 compositions are low although the onset temperatures are quite high for many of them. R-T measurements are not the best way deciding whether phases with higher  $T_c$  are present or not, we can at best get an indication from these measurements. Magnetic susceptibility measurements were therefore carried out on selected samples and the results are presented as insets in figures 2 and 3. Here also there is no indication of the presence of higher  $T_c$  phase on Sb substitution. A few of the compositions with and without lead (Sl. nos 7, 9, 12 and 14 in table 1) were heated to 1110 K for 350 h to see the effect of long term annealing on the superconducting properties. In sample nos 7, 9 and 12 the remeasured  $T_{c(0)}$  were 58 K, 66 K and 71 K respectively. However all samples except no. 12 showed clear onset and substantial drop in the 100–110 K temperature range irrespective of starting compositions being  $n = 2$  or 3. This result shows the formation of  $n = 3$  phase on long term annealing for both the starting compositions. The Sb addition does not seem to affect the  $T_c$  on longterm annealing either. Nonresonant microwave absorption studies of some of the samples which showed higher onset temperatures in the resistivity measurements (see figure 3) were carried out. Thus the composition  $\text{Bi}_{1.45}\text{Pb}_{0.5}\text{Sb}_{0.05}\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10+\delta}$  shows an onset of 117 K (see curve no 2 in figure 5).

Our best sample was the one obtained by glass recrystallization method having the composition  $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$ . The R-T and  $\chi$ -T results presented in figure 4 fail to show any indication of higher  $T_c$ . Non-resonant microwave absorption measurement also did not show any indication of higher  $T_c$  phase being present. The zero field microwave absorption intensity as function of temperature is shown in figure 5 for selected samples.

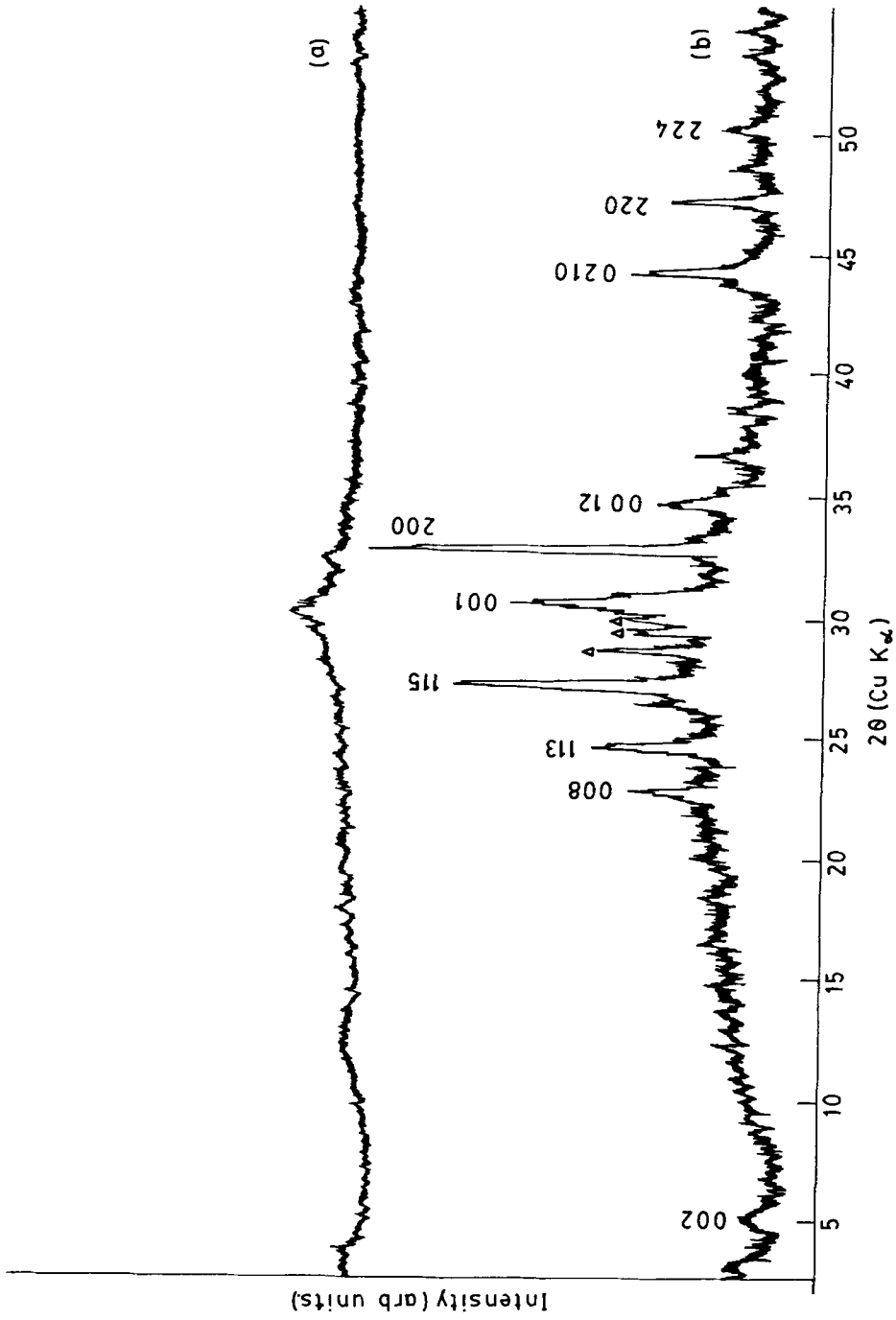


Figure 1. X-ray pattern of (a) glassy and (b) recrystallized samples of  $\text{Bi}_{1.9}\text{Sb}_{0.1}\text{CaSr}_2\text{Cu}_2\text{O}_{8+x}$ . Lines due to impurity phases are marked by triangles.

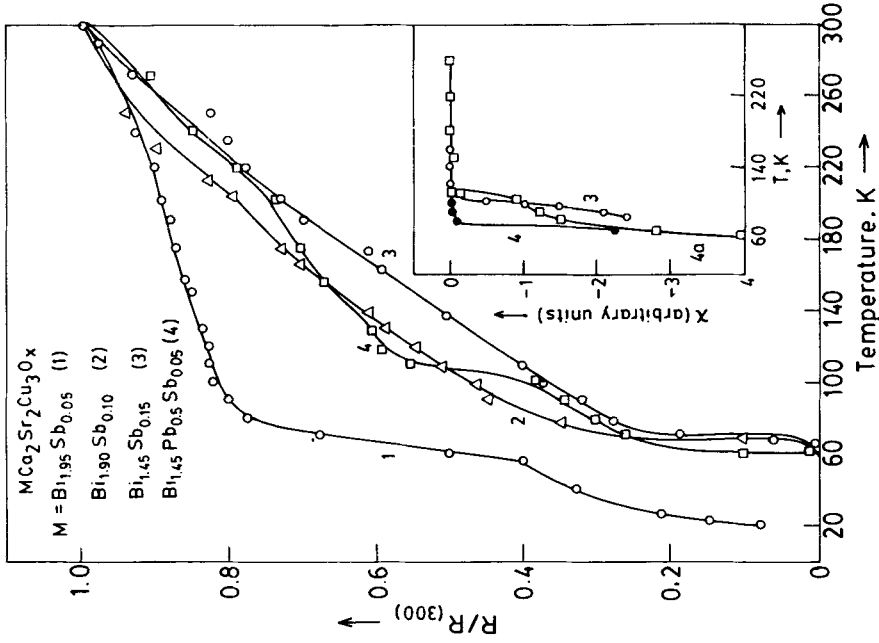


Figure 3. Temperature variation of the normalized resistance of  $MCa_2Sr_2Cu_3O_{10+\delta}$  samples. Inset: DC magnetic susceptibility variation with temperature for selected samples. Curve 4a is for the sample prepared by the matrix method.

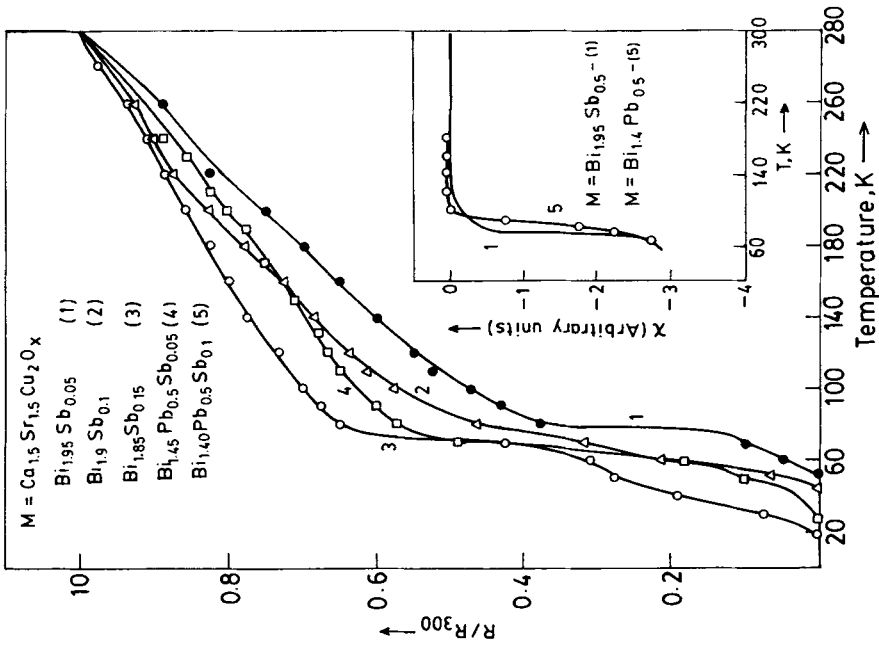


Figure 2. Temperature variation of the normalized resistance of  $MCa_{1.5}Sr_{1.5}Cu_2O_{8+\delta}$  samples. Inset: DC magnetic susceptibility variation with temperature for selected samples.

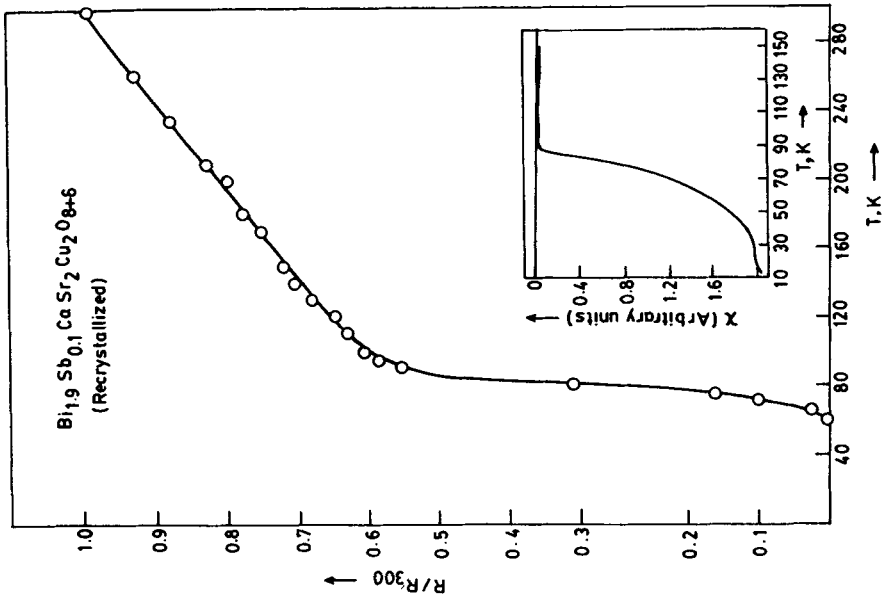


Figure 4. Temperature variation of the normalized resistance of Bi<sub>1.9</sub>Sb<sub>0.1</sub>CaSr<sub>2</sub>Cu<sub>2</sub>O<sub>8+δ</sub> glass recrystallized sample. Inset: DC magnetic susceptibility variation with temperature.

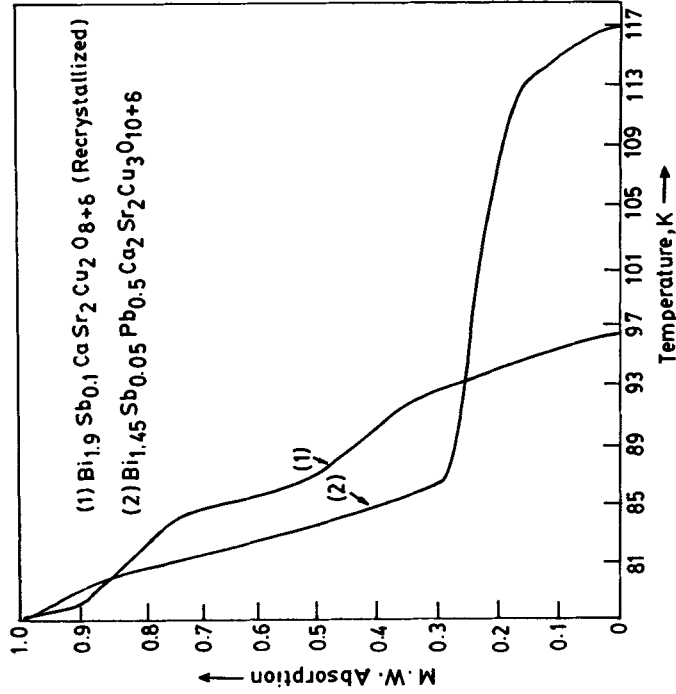


Figure 5. Relative intensity variation of microwave absorption with temperature in selected samples.

From all these studies we conclude that the substitution of Sb in Bi–Ca–Sr–Cu–O system does not occur under attempted preparative conditions and hence cannot enhance the  $T_{c(0)}$  as observed by some groups.

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### **References**

- Bhat S V, Ganguli P, Ramakrishnan T V and Rao C N R 1987 *J. Phys.* **C20** L559  
Chandrachood M R, Mulla I S and Sinha A P B 1989 *Appl. Phys. Lett.* **55** 1472  
Ganapathy L, Krishna S, Murthy K, Vijayaraghavan R and Rao C N R 1988 *Solid State Commun.* **67** 967  
Hongbao L, Liezmao C, Ling Z, Zhiqiang M, Oxian L X, Zhidong Y, Bai X, Xianglei M, Guien Z, Yaozhong R, Zhaojia C and Yuheng Z 1989 *Solid State Commun.* **69** 867  
Hongbao L, Xiaonong Z, Zaoin C, Guien Z, Yaozhong R, Zhaojia C and Yuheng Z 1988 *Physica* **C156** 804  
Luo J S, Michel D and Chevarkar J P 1989 *Appl. Phys. Lett.* **55** 1448  
Maeda H, Tanaka Y, Fukutomi T and Asami T 1988 *Jpn J. Appl. Phys.* **27** L209  
Maeda T, Sakuyama K, Yamuchi H and Tanaka S 1989 *Physica* **C159** 784  
Pissas M and Niarchos D 1989 *Physica* **C159** 643  
Rao C N R and Raveau B 1989 *Acc. Chem. Res.* **22** 107  
Takano M, Takada J, Oda K, Kitaguchi H, Miyura Y, Ikeda Y, Tomii Y and Mazaki H 1988 *Jpn J. Appl. Phys.* **27** L1041  
Varma K B R, Rao K J and Rao C N R 1989 *Appl. Phys. Lett.* **54** 69