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High-temperature superconductivity in bismuth-copper oxides of the type $Bi_mM_nCu_pO_x$ (M = Mg, Ca, Sr, Ba, Bi)†

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Abstract. Several oxides of the $Bi_mM_nCu_pO_x$ family ($m = 2, 3$; $n = 2, 3, 4$; $p = 1, 2, 3$ and M = alkaline earth or Bi), possessing structures similar to the Aurivillius family of oxides, show high T_c superconductivity.

Keywords. High-temperature superconductivity; $Bi_mM_nCu_pO_x$ (M = Mg, Ca, Sr, Ba, Bi).

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Superconductivity above liquid nitrogen temperature in the 123 oxides ($T_c \sim 90 \pm 5$ K) of the general formula $LnBa_2Cu_3O_7$ (Ln = Y or rare earth) has been the subject of much investigation in the last few months (Nelson *et al* 1987; Rao 1988a, b). In the last few weeks, an oxide system containing bismuth, alkaline earth metals (or Al) and copper has become the subject of intense activity, since there are indications that T_c s around 100 K or higher may be possible with these oxides (see High T_c update, Vol. 2, February 15, 1988). An oxide of the composition $Bi_2Sr_2Cu_2O_7$ was shown by Michel *et al* (1987) to become superconducting around 22 K. Maeda *et al* (1988) report onset of superconductivity around 105 K in $BiCaSrCu_2O_x$. Onset temperatures up to 120 K have been reported by Chu *et al* (1988) in Bi-Ca-Sr-Cu-O and Bi-Al-Ca-Sr-Cu-O systems. All these superconducting Bi-Cu oxides seem to be multiphasic and proper characterization of the phase responsible for high T_c behaviour is yet to be accomplished. In this laboratory, we have investigated a variety of bismuth oxides containing copper of the general formula, $Bi_mM_nCu_pO_x$ ($m = 2, 3$; $n = 2, 3, 4$; $p = 1, 2, 3$) where M = Mg, Ca, Sr, Ba, Bi or combinations of these elements, for superconductivity. These oxides bear resemblance to the $(Bi_2O_2)^{2+}$ $(A_{n-1}B_nO_{3n+1})^{2-}$ family of oxides described long ago by Aurivillius (1950), and investigated extensively by high resolution electron microscopy and other techniques in recent years (Hutchison *et al* 1977; Gopalakrishnan *et al* 1984; Rao 1985). In this communication, we report preliminary results of our studies on the structure and superconductivity of the $Bi_mM_nCu_pO_x$ oxides. Depending on the method of preparation, many of the oxides

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show onset of superconductivity at temperatures in the 70–100 K range or higher. Intergrowth structures formed by these bismuth oxides (Rao 1985; Rao and Thomas 1985) show exciting possibilities.

We can consider oxides of the type $Bi_2CaSrCu_3O_x$ and $Bi_2CaSr_2Cu_2O_x$ to be analogous to the Aurivillius family of oxides containing Bi_2O_2 and perovskite layers. In figure 1, we show the similarity between orthorhombic $Bi_4Ti_3O_{12}$ which is a member of the Aurivillius family and $Bi_2CaSr_2Cu_2O_x$ which is also an orthorhombic oxide (Hazen *et al* 1988). Both these have *c*-parameters in the 31–33 Å range. In figure 2, we show the electron diffraction pattern of $Bi_2CaSrCu_2O_x$ along with the lattice image. While this lattice image shows an ordered structure, we find considerable disorder in other images. The Aurivillius family of oxides is indeed known to exhibit extensive disorder and dislocations (Hutchison *et al* 1977; Subbanna *et al* 1987).

In figures 3 and 4 we show the electrical resistivity behaviour of a few members of the $Bi_mM_nCu_pO_x$ family of oxides showing superconductivity. While the onset in many of the oxides is well above 77 K, zero-resistance is attained at relatively low temperatures. All the superconducting samples showed extensive Meissner effect at 77 K. Heating in oxygen close to melting increased the T_c. Some of the oxides show steps in the resistivity curves suggesting the presence of more than one superconducting phase; such steps are found even around 200 K in certain cases. In table 1 we list all the $Bi_mM_nCu_pO_x$ compositions showing superconductivity; table 2 lists compositions which are not yet found to be superconducting.

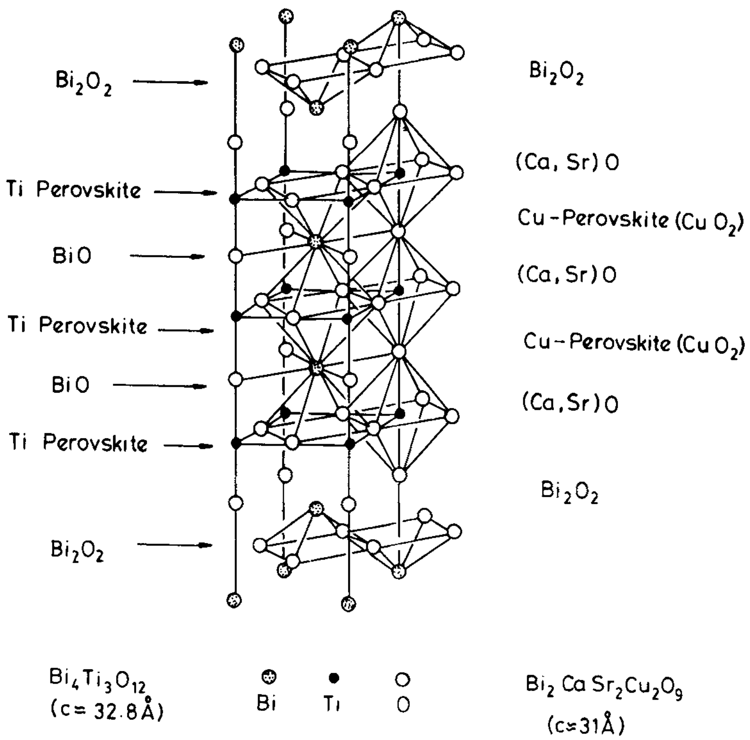

Figure 1. Structures of $Bi_4Ti_3O_{12}$ and $Bi_2CaSr_2Cu_2O_9$

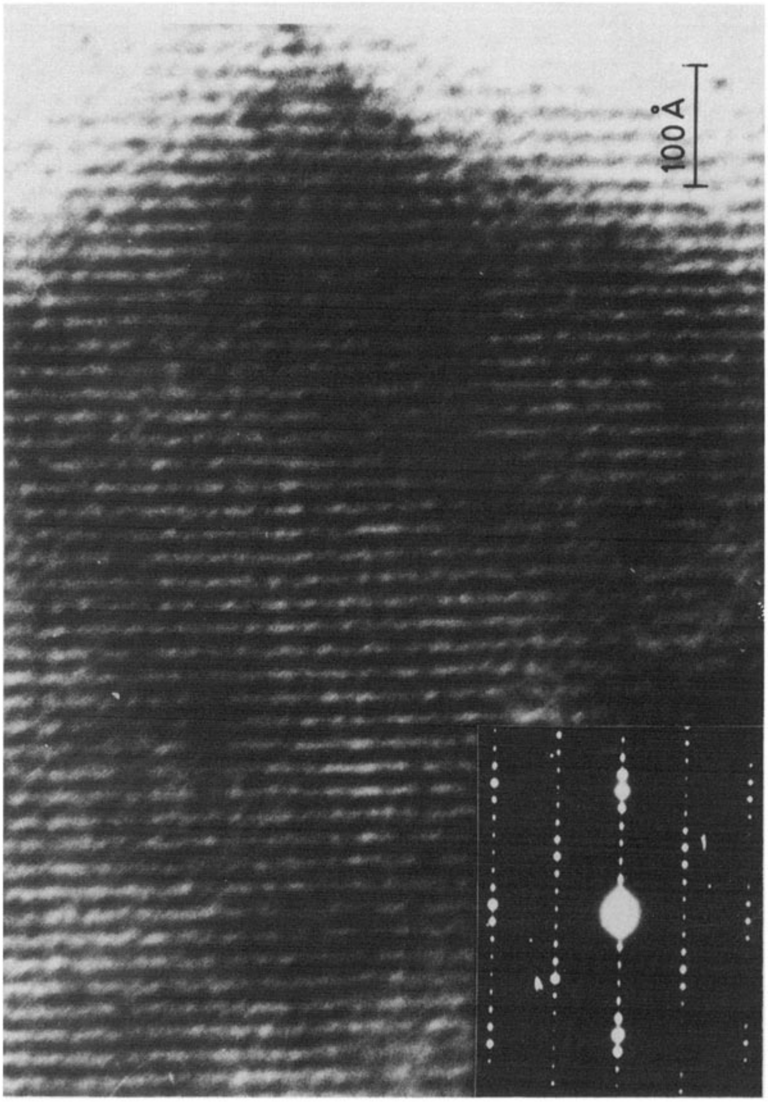

Figure 2. Electron diffraction pattern and lattice image of a sample of $Bi_2CaSrCu_2O_x$ perpendicular to the *c*-axis showing 21 Å fringes.

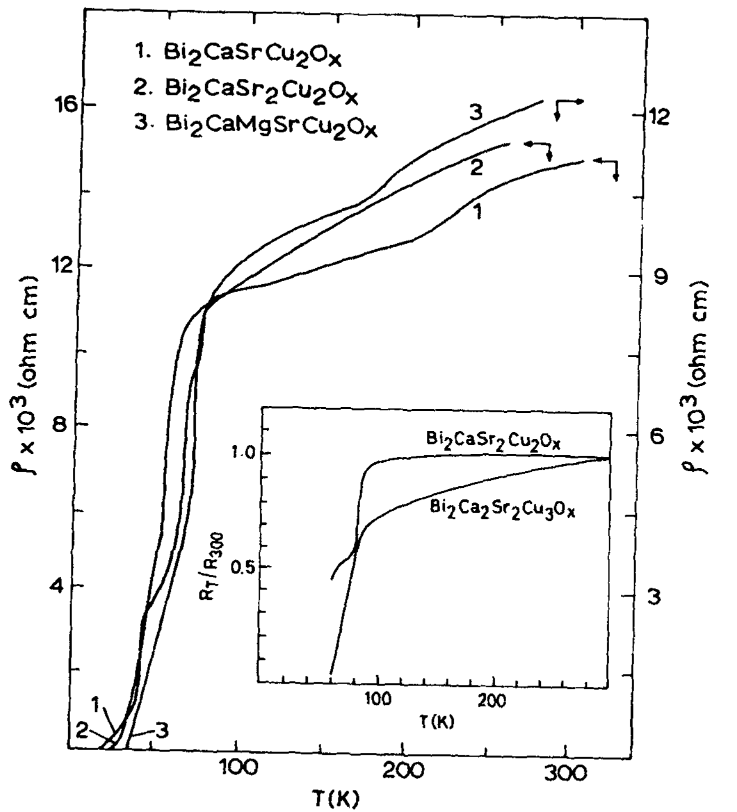

Figure 3. Resistivity behaviour of superconducting $Bi_mM_nCu_pO_x$ compositions. Behaviour of two preparations of $Bi_2CaSr_2Cu_2O_x$ is shown.

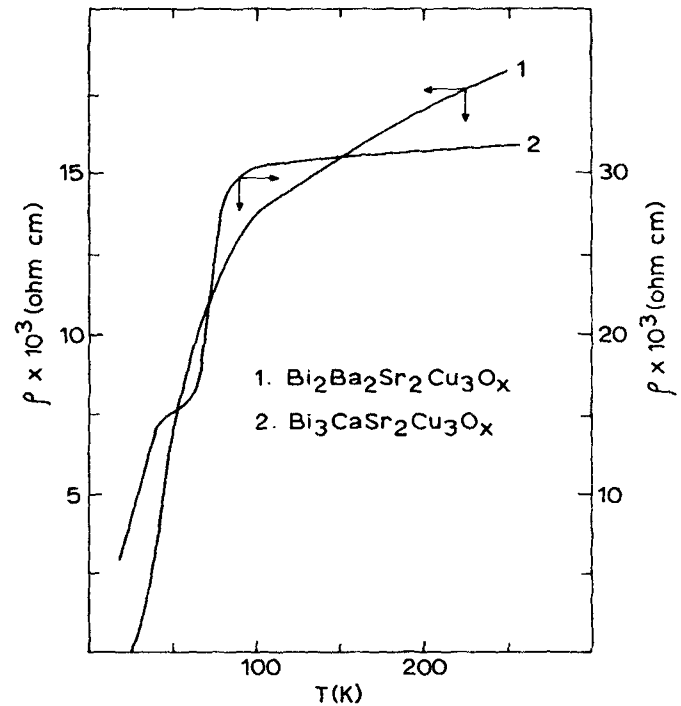

Figure 4. Resistivity behaviour of superconducting $Bi_mM_nCu_3O_x$ compositions.

Table 1. Superconducting properties of $Bu_mM_nCu_pO_x$.

Composition	Preparative conditions (temperature in K)	Onset temperature (K)	Zero resistance temperature (K)
$Bi_2CaSrCu_2O_x$	1100–32 h/air	77	20
	+ 1100–18 h/oxygen annealed	80 (steps at 220 and 60)	25
$Bi_2CaSr_2Cu_2O_x$	(a) 1100–32 h/air	70	28
	+ 1100–18 h/oxygen annealed	(step at 55)	
	(b) 1100–48 h/air	100	—
	+ 1160–12 h/oxygen quenched		
$Bi_2CaMgSrCu_2O_x$	1100–32 h/air	100 (steps at 200 and 65)	34
$Bi_2Ca_2SrCu_2O_x$	1100–48 h/air	90	—
	+ 1160–12 h/oxygen quenched		
$Bi_2CaMgSr_2Cu_2O_x$	1100–32 h/air	80	—
$Bi_2Ca_2Sr_2Cu_3O_x$	1100–48 h/air		
	+ 1160–6 h/oxygen quenched	95	~ 60
$Bi_2Ba_2Sr_2Cu_3O_x$	1100–32 h/air	65	28
	+ 1100–18 h/oxygen annealed	94	30
$Bi_3CaSr_2Cu_3O_x$	1100–32 h/air	70	—
	+ 1100–18 h/oxygen annealed	100 (step at 70)	—
$Bi_3Ca_2SrCu_3O_x$	1100–48 h/air quenched	73	—

Table 2. $Bi_mM_nCu_pO_x$ compositions not yet found to be superconducting.

Composition	Preparative conditions (temperature in K)	Resistivity behaviour
$Bi_2BaSrCu_2O_x$	1110–36 h/air + 1110–18 h/oxygen	Insulating
$Bi_2BaSr_2Cu_2O_x$	1110–36 h/air + 1110–13 h/oxygen	Semiconducting
$Bi_2Ba_2SrCu_2O_x$	1145–36 h/air + 1145–12 h/oxygen	Semiconducting
$Bi_3CaSrCu_2O_x$	1110–36 h/air + 1110–18 h/oxygen	Semiconducting
$Bi_3Sr_2Cu_2O_x$	1110–36 h/air + 1110–18 h/oxygen	Semiconducting
$Bi_3BaSrCu_2O_x$	1110–36 h/air + 1110–18 h/oxygen	Insulating
$Bi_2Ba_2SrCu_3O_x$	1110–36 h/air + 1110–18 h/oxygen	Semiconducting

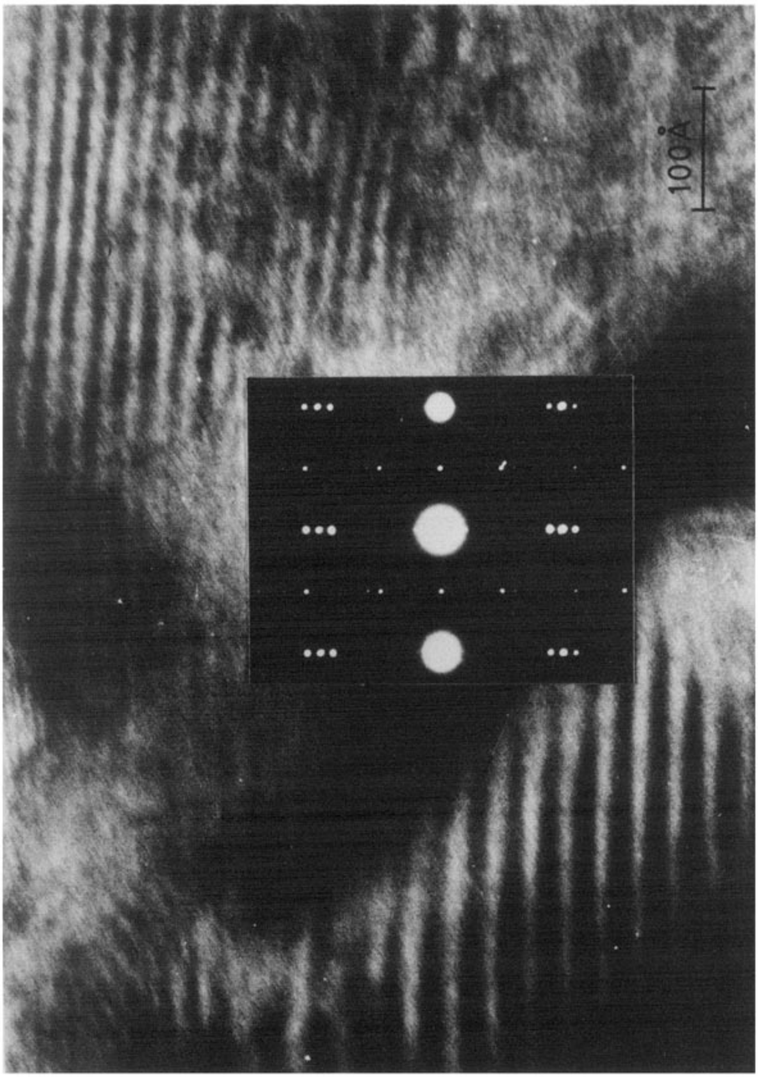

Figure 5. Lattice image showing intergrowth of two $Bi_mM_nCu_pO_x$ phases. Notice two regions with different *c*-parameters (~ 23 and 31 Å).

While there is little doubt that many of the $Bi_mM_nCu_pO_x$ compositions have at least one high T_c phase, it has not yet been possible to exactly pin down the compositions and structures of the superconducting phases. Many of the multiphasic compositions contain CuO or Bi_2O_3 as impurity. Proper heat treatment of the samples seems to be crucial. We are now examining many samples by closely varying the composition (e.g. Ca/Sa ratio) and the composition $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_x$ seems nearly ideal.

It is well known that the Aurivillius family of oxides form intergrowths of the type $Bi_4A_{m+n-2}B_{m+n}O_{3(m+n)+6}$. We have examined intergrowths of the general formula $Bi_{m_1+m_2}M_{n_1+n_2}Cu_{p_1+p_2}O_{x_1+x_2}$. In figure 5 we show the lattice image of an intergrowth structure. We are now attempting to synthesize and characterize more ordered intergrowths. Present indications are that the intergrowths have better superconducting properties, some with high T_cs. We shall shortly make a report on these studies.

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Note added in proof

The optimal composition of the high T_c(110 K) phase in the Bi-Ca-Sr-Cu-O system is close to $Bi_2Ca_{1.5}Sr_{1.5}Cu_2O_{8+\delta}$ ($c \approx 31$ Å) with a δ value depending on heat treatment. TGA gave $\delta \approx 0{\cdot}4$ for a sample which on extended heating at 880 K gave $\delta \approx 0{\cdot}1$. The X-ray pattern shows no significant change on such heating although T_c increases. $Bi_2CaSrCuO_{6{\cdot}2}$ with $c \approx 24$ Å shows onset of superconductivity at 85 K.