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High-temperature superconductivity in the Bi–Ca–Sr–Cu–O system with several variations in stoichiometry

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Abstract. We have made four-probe conductivity, AC susceptibility and x-ray diffraction measurements on the following compounds: nine compositions of $BiCa_{1-x}Sr_xCu_2O_y$ with $0.1 \leq x \leq 1$, four samples of $BiCaSrCu_2O_2$ with variations in the ambient and in heat treatment, and the samples with the starting compositions $BiCa_{1.25}Sr_{0.75}Cu_2O_p$, $Bi_2CaSrCu_2O_q$ and $Bi_2Ca_{2.25}Sr_{0.75}Cu_2O_r$. Many of these Bi-containing compounds exhibit superconductivity around 80 K. Sharp drops in resistivity near 120 K have also been observed in a few cases. The dependence of T_c on starting stoichiometry, synthesis conditions and structural parameters are discussed.

Intense activity in the field of oxide superconductors with high transition temperatures has been generated by the work of Bednorz and Müller (1986) and then by Wu *et al* (1987). Interest in rare-earth-free high-temperature superconductors is now gathering momentum. On 26 February 1988, the first paper on such systems was published by Subramanian *et al* (1988) although Maeda *et al* revealed their results on a similar system to the Japanese press on 22 January 1988. On 7 March 1988, Chu *et al* (1988) reported on $BiAl_{1-y}CaSrCuO_{7-\delta}$, $Bi_2Al_{1-y}Ca_{1-x}Sr_xCu_2O_{7-\delta}$ and $Bi_2Al_{1-y}(Ca_{1-x}Sr_x)_2Cu_2O_{8-\delta}$, where $0 \leq y \leq 0.3$ and $0.4 \leq x \leq 0.95$. Several preprints, some of which are by Takayama-Muromachi *et al* (1988) on $Bi_2(Ca, Sr)_3Cu_2O_9$, by Shaw *et al* (1988) on $BiCa_2SrCu_2O_y$ and by Zhang *et al* (1988), are also in circulation. Other recent papers include those by Xiao *et al* (1988), Hazen *et al* (1988), Meng *et al* (1988) and Torrance *et al* (1988). Studies on these systems (Bi–Ca–Sr–Cu–O) have led to a third class of high-T_c superconductors with a transition to zero resistance near 80 K in addition to an incipient superconducting transition at around 120 K. The current consensus is that the single-phase stoichiometry is close to $Bi_2CaSr_2Cu_2O_{8+\delta}$.

In this paper, we report on the systems $BiCa_{1-x}Sr_xCu_2O_y$ $(0.1 \leq x \leq 1)$, $BiCaSrCu_2O_y$, $BiCa_{1.25}Sr_{0.75}Cu_2C_y$, $Bi_2CaSrCu_2O_y$ and $Bi_2Ca_{2.25}Sr_{0.75}Cu_2O_y$. Our aim was to identify and distinguish (if possible) the phases responsible for superconductivity at 80 and 120 K. The samples were synthesised in platinum crucibles by the usual solid state reaction, using high-purity Bi_2O_3, $CaCO_3$, $SrCO_3$ and CuO as precursors. The first and second heat treatments were at 800 °C (for 12 h) and 850 °C (for 4 h). This was followed by oxygenation at 550 °C for 4 h in a quartz tube furnace using platinum sample supports. The resistivity measurements were done using the standard four-probe

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technique on 10 mm × 2 mm × 1.5 mm rectangular bars with equidistant fired-on silver spots having a separation of about 2 mm. The pairwise contact resistances were measured at room temperature before and after cooling and also at low temperatures. These were ohmic in nature and did not exceed 1–2 Ω. The temperature dependence of the AC susceptibility was measured using a standard apparatus (operating at 280 Hz) consisting of a closed-cycle refrigerator, a sapphire rod sample mount, a calibrated diode temperature sensor and copper grease for thermal homogenisation. The background susceptibility (without sample) is shown at the top in figure 2. The susceptibility signal exhibited approximately linear scaling with the sample mass (for a similar sample shape) and the probing AC magnetic field, thus allowing for normalisation to unit mass and an *approximate* measure of the relative superconducting fraction. However, we used samples of almost the same shape and mass.

Figures 1(*a*) and 2(*a*) show the plots of the resistance against temperature and the AC susceptibility against temperature respectively for the compound with an initial stoichiometry $BiCaSrCu_2O_2$ (AT2) subjected to different processing conditions. The sample codes, starting compositions and conditions of synthesis have been summarised in table 1. Sample AT2-OH was heated beyond 850 °C until it was molten; sample AT2-N was treated in pure nitrogen at 550 °C for 4 h instead of the usual oxygen treatment; sample AT2-850 was given the usual treatment—850 °C (for 4 h) followed by 550 °C (for 4 h) in oxygen; sample AT2-OX was treated at 700 °C (for 4 h) in oxygen. It is seen from the resistivity data that T_c (zero resistance) is affected strongly by the process parameters. T_c was highest (75.8 K) for sample AT2-OH while it was lowest (61.5 K) for sample AT2-OX. Nitrogen treatment (sample AT2-N) enhanced T_c to 71.0 K over the oxygen

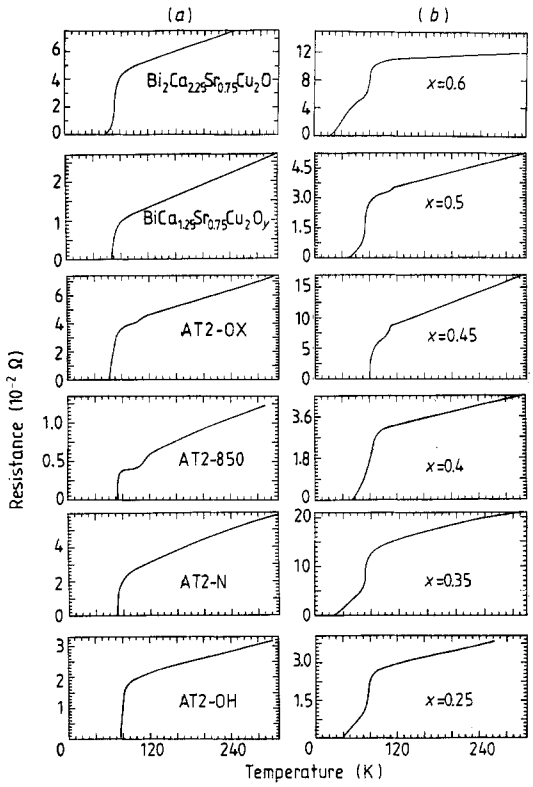

Figure 1. (*a*) Variation in resistance with temperature for the $BiCaSrCu_2O_z$ samples (AT2 series) with different processing steps as given in the text (see also table 1). $BiCa_{1.25}Sr_{0.75}Cu_2O_z$ was prepared with the same processing conditions as for sample AT2-850. (*b*) Variation in resistance with temperature for $BiCa_{1-x}Sr_xCu_2O_y$ series for different values of x. Processing conditions were the same as for sample AT2-850. Compositions with $x = 0.10$, 0.15 and 0.20 were found to be semiconducting above 96 K.

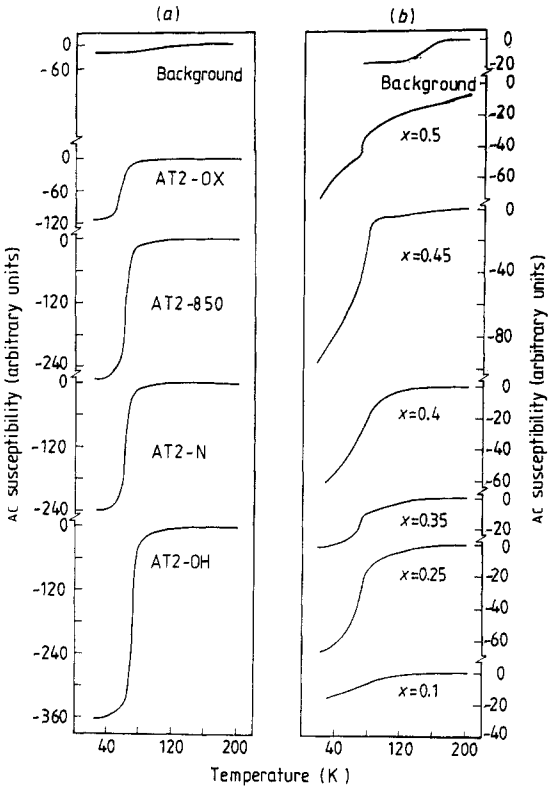

Figure 2. (*a*) Variation in AC susceptibility (280 Hz) with temperature for $BiCaSrCu_2O_z$ samples (AT2 series) with different processing steps as given in the text. (*b*) Variation in AC susceptibility (280 Hz) with temperature for the $BiCa_{1-x}Sr_xCu_2O_y$ series for different values of x. Processing conditions were the same as for sample AT2-850. Note that the $x = 0.1$ sample gives a response corresponding to the background shown at the top.

value of 61.5 K. This is similar to what happens in $YBa_2Cu_3O_{7-\delta}$ (Matthews *et al* 1987). From the susceptibility data (figure 2(*a*)), it is seen that the strongest and sharpest diamagnetic signal as well as the highest onset again occur for sample AT2-OH. The lowest and broadest diamagnetic signal and the lowest onset are for sample AT2-OX.

Table 1. Summary of process parameters and superconducting properties for a number of different compositions (nominal) in the Bi–Ca–Sr–Cu–O family. Synthesis is in air unless otherwise specified.

Sample	Nominal composition	Synthesis conditions	Resistivity behaviour
AT1	$BiCa_{1-x}Sr_xCu_2O_y$ ($0.1 < x < 1.0$)	800 °C for 12 h + 850 °C for 4 h + 550 °C for 4 h in oxygen	See figure 4
AT2-OH	$BiCaSrCu_2O_y$	800 °C for 12 h + 890 °C for 4 h	$T_c = 75.8$ K
AT2-N	$BiCaSrCu_2O_y$	800 °C for 12 h + 850 °C for 4 h +550 °C for 4 h in nitrogen	$T_c = 71$ K
AT2-850	$BiCaSrCu_2O_y$	800 °C for 12 h + 850 °C for 4 h +550 °C for 4 h in oxygen	$T_c = 73$ K, 115 K (see text)
AT2-OX	$BiCaSrCu_2O_y$	800 °C for 12 h + 850 °C for 4 h +700 °C for 4 h in oxygen	$T_c = 61.5$ K
AT3	$Bi_2CaSrCu_2O_y$	800 °C for 12 h + 850 °C for 4 h +550 °C for 4 h in oxygen	Resistivity increases between 300 and 105 K
AT10	$BiCa_{1.25}Sr_{0.75}Cu_2O_y$	800 °C for 12 h + 850 °C for 4 h +550 °C for 4 h in oxygen	$T_c = 67.6$ K
AT12	$Bi_2Ca_{2.25}Sr_{0.75}Cu_2O_y$	800 °C for 12 h + 850 °C for 4 h +550 °C for 4 h in oxygen	$T_c = 60$ K

An interesting feature in the resistivity curve of sample AT2-850 is the resistance step (figure 1(*a*)) with an onset at about 115 K. This step is not evident in the corresponding susceptibility curve in figure 2(*a*), probably because the higher T_c fraction was too small.

In an attempt to isolate the phase responsible for the 115 K superconducting transition, we synthesised a number of compounds with different cation ratios but using the same process parameters as for sample AT2-850. Accordingly, $Bi_2Ca_{2.25}Sr_{0.75}Cu_2O_z$ and $BiCa_{1.25}Sr_{0.75}Cu_2O_z$ were prepared under identical conditions but the 115 K incipient transition was not detected for either (see figure 1(*a*), top). The compound $Bi_2Ca_{2.25}Sr_{0.75}Cu_2O_z$ exhibited zero resistance at 60 K, while the corresponding temperature for $BiCa_{1.25}Sr_{0.75}Cu_2O_z$ was 67.6 K. The former compound has the same overall stoichiometry (i.e. Bi : Ca + Sr : Cu = 2 : 3 : 2) as that studied by Takayama-Muromachi *et al* and others. Takayama-Muromachi *et al* obtained the same value of T_c for the compound with Ca : Sr = 1 : 1 as that seen by us (above) for Ca : Sr = 3 : 1. For $Bi_2CaSrCu_2O_y$, the temperature dependence of the resistivity exhibited semiconducting behaviour between 300 and 105 K.

A second set of similar experiments were performed on the series $BiCa_{1-x}Sr_xCu_2O_y$. These were synthesised under identical conditions as for sample AT2-850, and the data are shown in figures 1(*b*) and 2(*b*). There is unmistakable evidence of an incipient superconducting transition in the resistivity data at about 115 K for the $x = 0.45$ and $x = 0.50$ samples. However, there is no clear indication of the higher-T_c fraction for these two compositions in the susceptibility data (figure 2(*b*)). Thus, it appears that further work is essential on materials with $0.45 \leqslant x \leqslant 0.50$. The AC susceptibility measurements for these two samples also show an onset of diamagnetism above the 80 K ($R = 0$) transition for $x < 0.45$ and above the 53 K ($R = 0$) transition for $x = 0.50$. It is interesting to note that the $x = 0.10$ sample was insulating. The data of resistivity against temperature for the samples with $x = 0.15$ and 0.20 showed a semiconductor-like behaviour, reaching 5.58 kΩ ($x = 0.15$) at 180 K and 2.58 kΩ ($x = 0.20$) at 96 K. This prevented measurements down to lower temperatures. Note that the $x = 1$ sample, $BiSrCu_2O_y$, did not superconduct.

X-ray diffraction measurements (with Cu Kα radiation) showed interesting results. Most of the lines in the x-ray diffraction pattern for sample AT2-850 could be fitted to a tetragonal cell (or subcell), with lattice constant values very close to those obtained for $Bi_2CaSr_2Cu_2O_{8+\delta}$ by Hazen *et al* (1988). Even though the nominal stoichiometry in the present case was $BiCa_{1-x}Sr_xCu_2O_y$, the principal phase present was always the above-mentioned Bi : Ca : Sr : Cu = 2 : 1 : 2 : 2 phase. The only additional (impurity) phases that could be definitely identified were CuO and $BaCuO_2$. Unlike Hazen *et al*, we observed no traces of $CaCu_2O_3$ or Ca_2CuO_3. These conclusions are borne out by the room-temperature spectra of the series $BiCa_{1-x}Sr_xCu_2O_y$ (for $x = 0.10, 0.25, 0.40, 0.50, 0.57$, 0.65 and 1.00) shown in figure 3. For direct comparison, a spectrum of single-phase $Bi_2CaSr_2Cu_2O_{8+\delta}$ is given at the bottom of the figure; the lines indexed by Hazen *et al* (1988) are indicated by full circles. Note that in spite of the great similarity in the line positions (and hence the lattice constants) between these two studies, there is hardly any correspondence in the line intensities, even for the single-phase 2 : 1 : 2 : 2 compound. Thus, a subtle difference in the atomic arrangements cannot be ruled out despite an overall similarity in the crystal structure.

The following additional point needs to be made regarding impurity phases. X-ray diffraction lines near $d = 4.08$, 3.44 and 2.99 Å belong to some phases(s) not identified by us. These lines are very strong in the Ca-free sample ($x = 1$). The 2 : 1 : 2 : 2 lines are

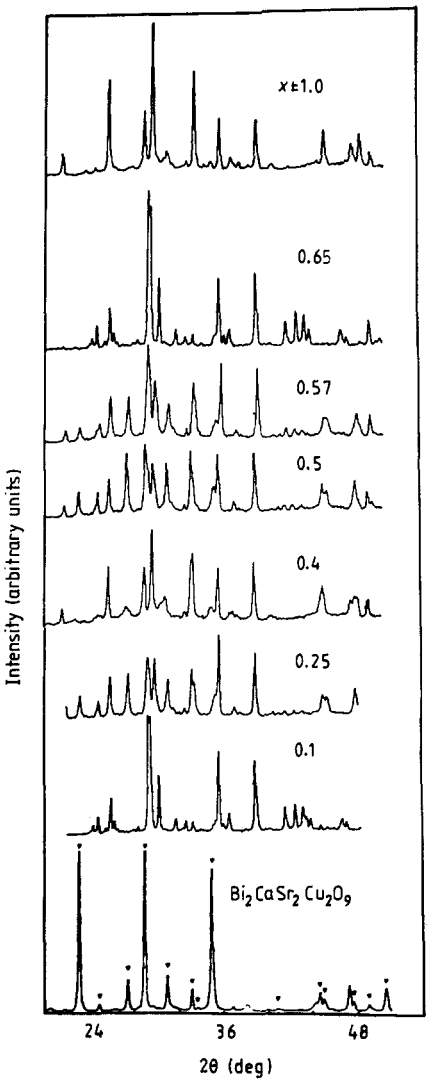

Figure 3. X-ray diffraction spectra (with Cu Kα radiation) for the series $BiCa_{1-x}Sr_xCu_2O_y$ (x = 0.10, 0.25, 0.40, 0.50, 0.57, 0.65 and 1.00). A spectrum of $Bi_2CaSr_2Cu_2O_{8+\delta}$ (single phase) is shown at the bottom as a reference standard: ●, the lines indexed by Hazen *et al* (1988).

correspondingly weak in this sample; not surprisingly, it does not exhibit superconductivity.

For the series with the starting composition $BiCa_{1-x}Sr_xCu_2O_y$, the lattice constants of the major phase (with a structure similar to that of the 2:1:2:2 phase) change in a systematic way with x (shown in figure 4). It is interesting to note that the unit-cell parameters a and c peak at around the x value of 0.45. The T_c ($R = 0$) against x interpolation has a similar peak at $x = 0.45$, as shown in figure 4. Such data appear to imply that superconductivity is highly sensitive to small variations in the crystal structure. It is clear from the figure that the zero-resistance temperatures corresponding to x = 0.25 and 0.35 lie away from the smooth hand-drawn curve. We point out that if, however, T_c is determined from an extrapolation of the sharpest part of the R–T curve (rather than from $R = 0$) a monotonic variation with x is obtained. The non-monotonicity in the $R = 0$ temperatures arises from the presence of the 'shoe' at the low-temperature end

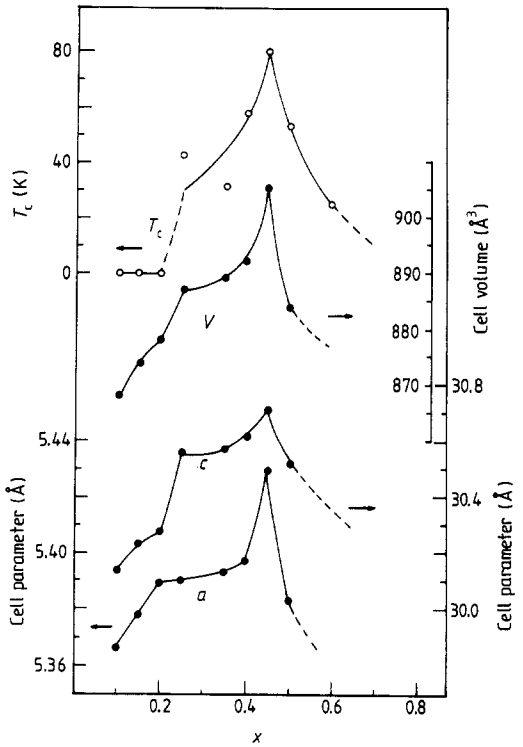

Figure 4. Dependence of the lattice parameters a and c, the unit-cell volume V (assuming a tetragonal cell without superstructure) and the zero-resistance temperature T_c on the Sr fraction x in the series $BiCa_{1-x}Sr_xCu_2O_y$: ——, for visual guidance.

of the R–T curves. This feature can be ascribed to sample inhomogeneities. We are investigating further the correlation between T_c and the lattice dimensions.

In conclusion, we have verified that a third class of high-T_c superconductors is indicated in the almost single-phase systems (AT2 series) studied here. These results agree with the earlier work. In addition, the presence of a higher-T_c phase (in the vicinity of 115–120 K) is also indicated. We observe a strong correlation between the unit-cell dimension and the superconducting T_c. An observation worth noting is that the presence of copper yet again in this third class of superconductors points to the importance of polaronic behaviour in the strong electron–phonon interaction. As is well known, the Bardeen–Cooper–Schrieffer expression $T_c = 1.14\theta_D \exp(-1/\gamma_{eff})$ has been obtained in the weak-coupling approximation. The presence of a new class of superconductors with T_c ranging from 60 to 115 K is a strong indication that the expression derived for an arbitrary strength of the electron–phonon coupling (see, e.g., Kresin 1987) is more relevant.

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