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Composition and superconductivity in Bi–Sr–Ca–Cu–O and substituted systems

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The composition of the superconducting phase $Bi_4(Sr_{3\pm x}Ca_{3\mp x})_{\Sigma=6}Cu_4O_{16}$, has been determined by means of a sysmetic investigation of the relationship between composition and superconductivity, and phase analysis. The superconducting phase belongs to tetragonal system with $a = 0.3825$ nm, $c = 3.082$ nm, space group (S.G.) I4/mmm. The effect of strontium and calcium contents in the $Bi(Sr_{1\pm x}Ca_{1\mp x})_{\Sigma=2}Cu_2O_{5.5}$ system and substitution in the $Bi_{1-x}A_xSrCaCu_2O_{5.5}$ (A = V, Gd, Y) and $BiSrCa_{1-x}Pb_xCu_2O_{5.5}$ systems on superconductivity, have been investigated. In the Bi–Sr–Ca–Cu–O system, there are two superconducting phases corresponding to transition temperatures of 110 and 80 K, respectively. The difference between the two superconducting phases may be due to the stacking difference of atoms along the *c* direction in the structure and their oxygen content.

1. Introduction

Michel *et al.* [1] reported a non rare earth superconductor, $Bi_2Sr_2Cu_2O_7$, with a T_c of 7 to 22 K. Recently several groups reported that the superconductor in the Bi–Sr–Ca–Cu–O system undergoes a change in resistance at about 110 K, but that a low temperature "tail" extends to about 80 K. We then obtained a superconductor with a $T_c(0)$ higher than 120 K in the Tl–Ba–Ca–Cu–O system and investigated the structure of the superconducting phase and the relationship between composition and superconductivity [2–4].

In this paper, we report an investigation of the relationship between composition and superconductivity and the effect of the component substitution on the superconductivity.

As it is known that it is very difficult to determine the composition of the superconducting phase in one five-element system, we have tried to determine the composition of the superconducting phase by means of the relationship between T_c and composition and phase analysis.

In one sample, the greater the content of superconducting phase, the easier it is to obtain a high T_c superconductor under the same conditions. Thus, many samples were prepared with different compositions, and their superconductivities were measured; T_c of each sample was then plotted against each component content, and the optimal value range of each component was found. The content of each component in the superconducting phase must be within its optimal content range. Then, from the results of phase analysis for samples with optimal compositions and high T_c, the composition of the superconducting phase can be determined easily. This method of determining the composition of the superconducting phase is more convenient than by the means of the phase diagram of the Bi–Sr–Ca–Cu–O system.

2. Experimental procedures

2.1. Preparation of samples

Analytic reagent grade Bi_2O_3, $SrCO_3$, CaO and CuO were used as starting materials. The materials with proper compositions were weighed, mixed, ground, pressed into pellets and sintered at 820 to 850° C in air for 12 to 24 h. The samples were cooled slowly (or quickly) down to room temperature. To improve the superconductivity of the samples, the pellets were then crushed, reground, pressed into pellets again and sintered under the same conditions mentioned above. This treatment is advantageous in producing higher T_c, especially for higher J_c.

2.2. Measurement of superconductivity and phase analysis

Resistivity measurements were carried out by the standard four-probe method; magnetic susceptibility measurements were obtained by the mutual inductance method.

A Guinier–de Wolff monochromatic focus camera was used for phase analysis; Cu$K\alpha$ radiation was used.

3. Results and discussion

3.1. Composition and superconductivity

In this system, 35 samples were prepared. Plots of T_c against the content of each component in the samples are shown in Figs 1 and 2. From these figures we can see that samples over a rather wide composition range exhibit superconductivity. The optimal content ranges of each component are: $BiO_{1.5}$ 12 to 29, SrO 10 to 30, CaO 10 to 25, CuO 27 to 50 mol %. The average

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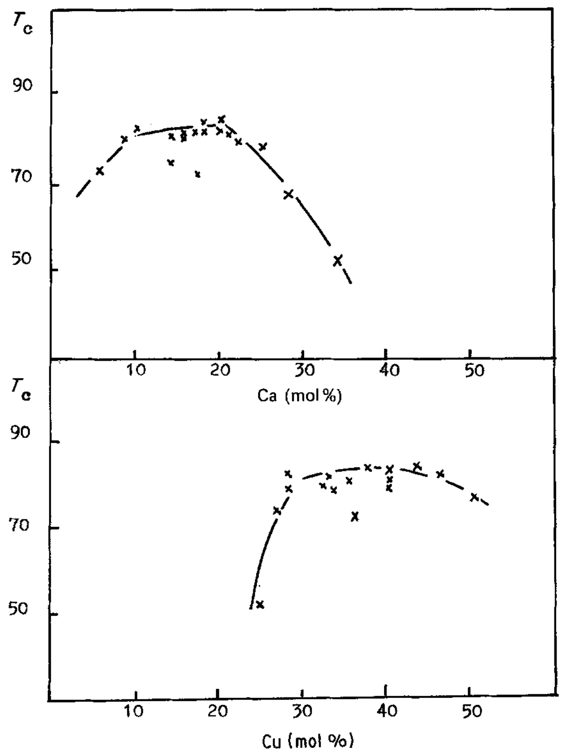

Figure 1 T_c plotted against calcium (copper) content for the superconductive samples with different compositions.

values of the optimal content of each component are: 20.5, 22, 17.5 and 40 for $BiO_{1.5}$, SrO, CaO and CuO, respectively. The composition of the superconducting phase (Bi : Sr : Ca : Cu = 1 : 1 : 1 : 2), is the same as that given by Maeda *et al.* [5]. However, the results of X-ray analysis indicate that a superconducting phase and CuO co-exist in these samples. Considering the volatilization of Bi_2O_3 and the arrangement of atoms in the structure, the composition of the superconducting phase is determined to be $Bi_4(Sr_{3\pm x}Ca_{3\mp x})_{\Sigma=6}Cu_4O_{16}$. The superconducting phase belongs to a tetragonal system with $a = 0.3825$ nm, $c = 3.082$ nm, S.G. I4/mmm. A paper about this structure has been published [6]. The resistance against temperature curves for some typical samples are shown in Figs 3a and b.

One problem which is not understood is that the superconducting samples which are close to single phase are easily obtained, when the CuO content is greater than that of the ideal formula, such as $Bi_4Sr_4Ca_2Cu_6O_{18}$ and $BiSrCaCu_2O_{5.5}$, etc.

3.2. $Bi(Sr_{1\pm x}Ca_{1\mp x})_{\Sigma=2}Cu_2O_{6.5}$ system

In this system, the effect of strontium and calcium contents on the superconductivity has been investigated. The results are shown in Table I, which shows that over a rather wide composition range, the effect of changes in strontium and calcium content on T_c is not obvious. But the coexistence of strontium and calcium is necessary to obtain high T_c superconductors. In the system containing a greater content of strontium than calcium, samples with a high T_c can be obtained easily. This can be explained from the fact that the crystal structure of the superconducting phase is similar to that of the compound whose composition is close to $Bi_2Sr_2Cu_2O_7$ and is different from $Bi_2Ca_2Cu_2O_7$.

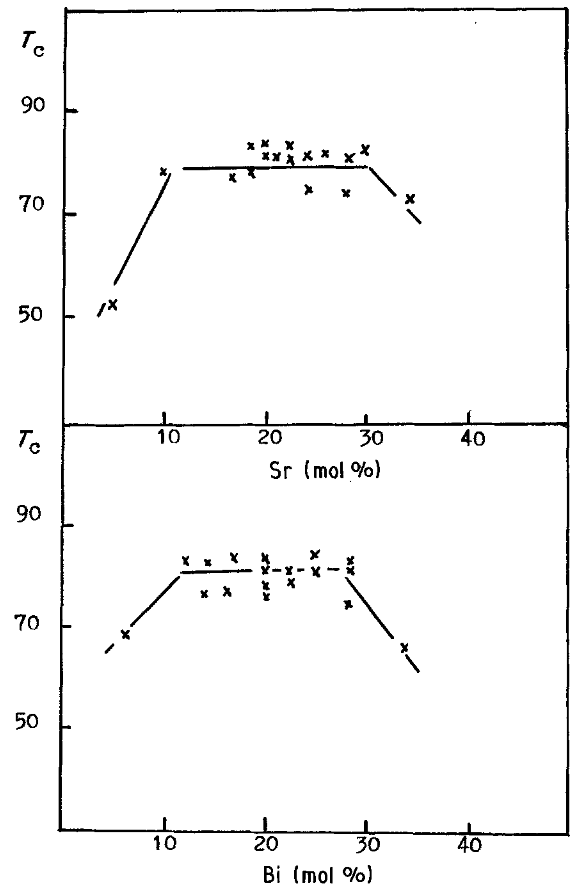

Figure 2 T_c plotted against bismuth (strontium) content for the superconductive samples with different compositions.

3.3. $Bi_{1-x}A_xSrCaCu_2O_{5.5}$ (A = V, Gd, Y) and $BiSrCa_{1-x}Pb_xO_{5.5}$ systems

We have investigated the effect of substitution on the superconductivity in these systems. The results are shown in Fig. 4. The substitution of these elements, $V(V_2O_5)$, $Gd(Gd_2O_3)$, $Y(Y_2O_3)$, $Pb(PbO_2)$ leads to a decrease in the superconducting temperature for samples of these compositions. The maximum limit of x in these systems is 0.5. When x is more than 0.5, superconducting samples cannot be obtained. The results of phase analysis indicate that the structure of the superconducting phase is not changed for these substituted systems.

From the resistivity–temperature curves of some superconducting samples, two changing points can be

TABLE I Composition and superconductivity

Number	Composition (100 mol %)				T_c (K) (R_{zero})
	Bi	Sr	Ca	Cu/(Bi + Sr + Ca + Cu)	
1	20	34	6	40	74
2	20	30	10	40	83
3	20	28	12	40	70
4	20	26	14	40	82
5	20	24	16	40	81
6	20	22	18	40	82
7	20	20	20	40	64
8	20	18	22	40	79.5, 73.8
9	20	16	24	40	80
10	20	14	26	40	79
11	20	12	28	40	79
12	20	10	30	40	70
13	20	6	34	40	< 20

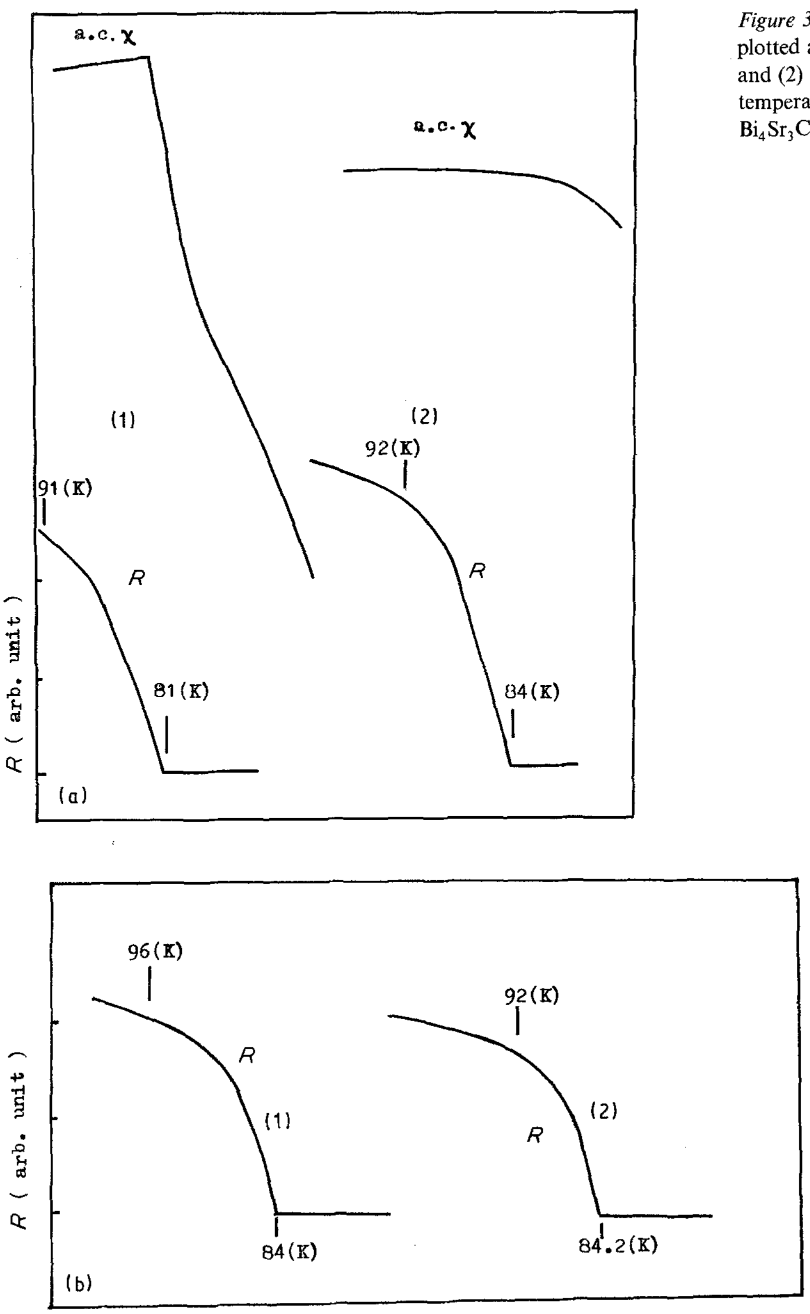

Figure 3 (a) Resistivity and a.c. magnetic susceptibility plotted against temperature for (1) $Bi_{6.5}Sr_{6.5}Ca_{5.5}Cu_{10.5}O_{32.2}$ and (2) $BiSr_{1.5}Ca_{1.5}Cu_2O_{6.5}$. (b) Resistivity plotted against temperature for (1) $Bi_{17}Sr_{20}Ca_{20}Cu_{43}O_{108.5}$ and (2) $Bi_4Sr_3Ca_3Cu_6O_{18}$.

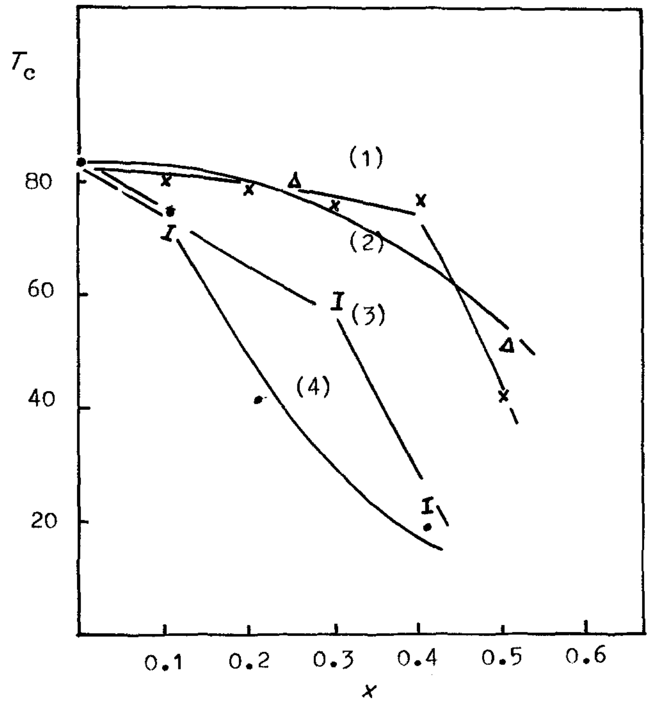

Figure 4 T_c plotted against x in $Bi_{1-x}A_xSrCaCu_2O_y$ (A = V, Gd, Y) and $BiSrCa_{1-x}Pb_xCu_2O_y$ systems: (1) V, (2) Gd, (3) Y, (4) Pb.

observed; one is $T_c > 110$ K, the other is T_c about 80 K. This shows that two superconducting phases exist in the system. The 110 K phase is dominant in samples subjected to repeated sintering at 850 to 880° C, the 80 K phase is dominant in samples first sintered at 820° C; sometimes the two phases coexist. The strong X-ray diffraction lines of the two superconducting phases are not obviously different. The difference between the two phases may result from the stack of atoms along the *c* direction in the structure or the difference in oxygen content.

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