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Optimization of superconducting critical temperatures by control of cation and anion stoichiometry in $Bi_2Sr_2CaCu_2O_\delta$-based solid solutions

D. C. SINCLAIR, J. T. S. IRVINE*, A. R. WEST
Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB9 2UE, UK

T_c data are reported for powders of cation-stoichiometric $Bi_2Sr_2CaCu_2O_\delta$ and for non-stoichiometric samples based on the three mechanisms $Bi \rightleftharpoons Sr$, $Sr \rightleftharpoons Ca$ and Sr vacancy. For each, the T_c values depend critically on the final oxygen contents, which were varied by heating samples in either O_2 or N_2 at different temperatures. Stoichiometric $Bi_2Sr_2CaCu_2O_\delta$ has the highest T_c, 92 K, obtained after heating in O_2 at ~ 820 °C. Heating in O_2 at lower temperatures gives rise to overdoping and T_c decreases to 60 K. The other cation compositions show a smaller maximum T_c but also less reduction in T_c on overdoping. Under-doped samples, with reduced T_c values were obtained on heating in N_2. These data, together with selected literature results, lead to a unified picture of the variation of T_c with cation composition and oxygen content.

1. Introduction

Many studies have been made on the so-called 90 K 2212 phase of ideal stoichiometry $Bi_2Sr_2CaCu_2O_\delta$. Various compositions for this phase are quoted with variable Bi:Sr:Ca:Cu ratios [1–6]. Many papers state that stoichiometric $Bi_2Sr_2CaCu_2O_\delta$ cannot be made [4, 6–12], whereas others report its preparation under carefully controlled conditions [13–15]. We have recently [16] studied phase formation in the relevant region of the phase diagram Bi_2O_3–SrO–CaO–Cu–O and have shown that:

- stoichiometric $Bi_2Sr_2CaCu_2O_\delta$ can be formed as a single phase sample provided samples are heated for extended periods of time at temperatures close to melting, e.g. 860 °C for 5 days;
- an area of solid solution forms of general formula $Bi_{2+x}Sr_{2-x-y}Ca_{1+y}Cu_2O_\delta$. This is shown in Fig. 1; the approximate range of compositions is $0 < x < 0.2$ and $0 < y < 0.5$. These solid solution compositions fit within the general formula $(Bi + Sr + Ca)_5Cu_2O_\delta$.
- a general guide to obtaining reasonable reaction rates for the formation of the solid solutions is that the reaction temperature should be within 20–30° of melting. As a consequence of the variation of melting temperature with composition, different synthesis conditions are essential across the solid solution area. Thus, compositions with e.g. $y = 0.5$, $x = 0.2$ show complete reaction after 2 days at 820 °C but melt at 860 °C, the temperature required to synthesize stoichiometric ($x = y = 0$) material.

Taking into account the close interplay between formation rates and solid solution compositions, there are no major discrepancies in the literature concerning the range of compositions on the section $(Bi + Sr + Ca)_5Cu_2O_\delta$ which form single phase solid solutions.

In addition to the above solid solution area, it is also possible to prepare single phase samples with different Cu contents [6, 17, 18]. Some are regarded as Sr-deficient materials in comparison with the stoichiometric ($x = y = 0$) composition. Our own results indicate that a solid solution volume exists within the phase diagram, in which all four cation contents are variable, but the compositional extent as a function of temperature has still not been fully established. Most of the studies to date have synthesized samples in air at atmospheric pressure without particular attention to, nor knowledge of, the oxygen content of the samples. Some more detailed studies of oxygen contents have been made, both for syntheses under reduced oxygen pressures and post-reaction treatment of samples at different oxygen pressures [18–21]. It is now well-established that the critical temperature of the 2212 phase is sensitive to oxygen content and can be optimized at 92 K by appropriate treatment. An example is shown in Fig. 2 in which both resistivity mid-points and resistivity onset temperatures [22]

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* *Present address*: School of Chemistry, University of St Andrews, Purdie Building, St Andrews, Fife KY16 9ST, UK

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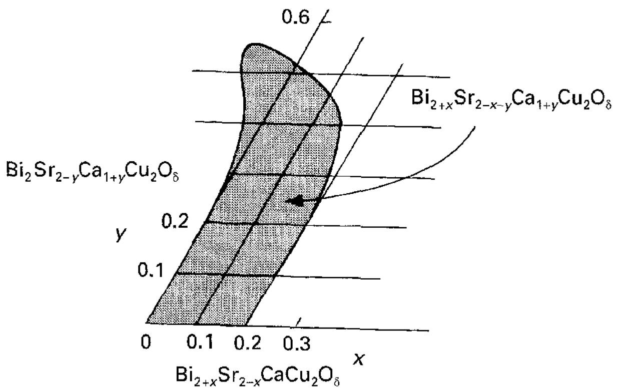

Figure 1 Area of $Bi_{2+x}Sr_{2-x-y}Ca_{1+y}Cu_2O_\delta$ solid solutions.

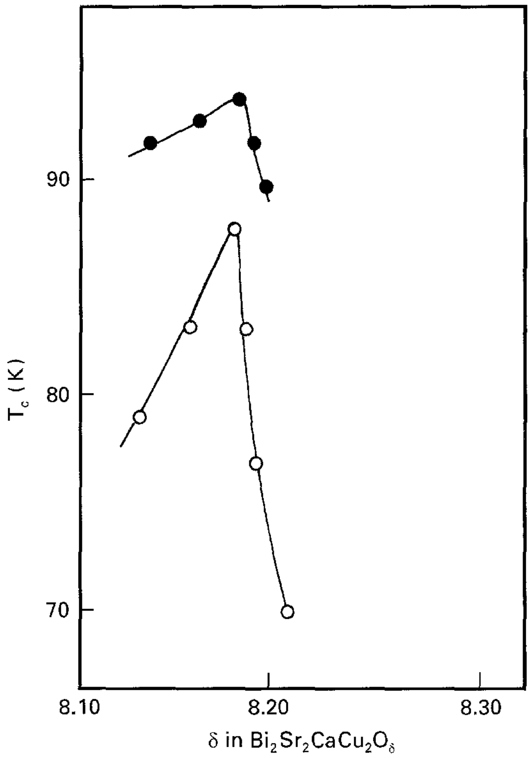

Figure 2 d.c. resistivity mid-point and onset temperatures as a function of oxygen content δ for stoichiometric $Bi_2Sr_2CaCu_2O_\delta$. ● T_c (onset); ○ T_c (mid point).

pass through a maximum at an oxygen content δ of 8.175. Although variations of T_c with the Sr/Ca ratio in single crystals [23] and in "almost" single phase powders [18] have been investigated, systematic studies into the variation of T_c with cation content for monophasic ceramic samples appear not to have been made, particularly for mechanisms other than $Sr \rightleftharpoons Ca$, and form the basis of the present work.

Four compositions were selected for a detailed study. These are:

A. Stoichiometric $Bi_2Sr_2CaCu_2O_\delta$ (i.e. $x = y = 0$)
B. $Bi_{2.1}Sr_{1.9}CaCu_2O_\delta$ (i.e. $x = 0.1$, $y = 0$)
C. $Bi_2Sr_{1.7}Ca_{1.3}Cu_2O_\delta$ (i.e. $x = 0$, $y = 0.3$)
D. $Bi_2Sr_{1.7}CaCu_2O_\delta$ (i.e. 0.3 Sr vacancies).

Samples B–D are members of the three principal solid solution mechanisms which are often quoted and widely accepted for the 2212 phase.

2. Experimental procedure

Details of reagents and synthesis conditions are as in [10]. Briefly, pelleted samples were reacted in Au foil boats in air at 800–860 °C, depending on composition and analysed for phase purity by X-ray powder diffraction. This included the indexing of supercell reflections and recognition of a significant reduction in the *c* lattice parameter with both increasing *x* and *y* in the general formula for the 2212 solid solutions.

Each of the compositions was pressed into 3-mm diameter pellets of weight 15–20 mg, which were wrapped in Au foil and heated for 24 h before quenching in liquid N_2. Heat treatment conditions included flowing O_2 at isothermal temperatures in the range 300–850 °C and flowing N_2 at 400–675 °C. Magnetic susceptibilities (a.c.) were measured with a Lake Shore AC7000 susceptometer employing 1G at 333 Hz applied magnetic field.

3. Results and discussion

Susceptibility data for sample A, $Bi_2Sr_2CaCu_2O_\delta$, after annealing in O_2 at three temperatures are shown in Fig. 3. The data show sharp diamagnetic onset temperatures, T_c. The diamagnetic volume fractions were estimated to be at least 25%, indicating that a bulk response was measured. T_c values clearly vary with oxygen content over the range ~ 60–90 K and are in excellent agreement with the results of Triscone et al. [19].

In order to compare the properties of the four samples, susceptibility data are shown in Fig. 4 for samples heated in O_2 at 800 °C. All samples show bulk superconductivity with a similar diamagnetic response. Sample A shows the highest T_c. Samples B and C are similar with a somewhat lower T_c. Sample D has the lowest T_c and also a poorly defined T_c onset. A similar pattern of behaviour was seen for samples heated in O_2 over the range 700–850 °C (Fig. 5) with A having the highest T_c and D the lowest. The results for samples A, B and C where (Bi + Sr + Ca) = 5 are in agreement with those on polycrystalline powders and single crystals in which the highest T_c values obtained are for compositions where the Sr/Ca ratio approaches a value of 2 [18, 23]. At lower annealing temperatures a complete reversal of T_c behaviour was seen. For instance, after annealing in O_2 at 300 °C, sample A had the lowest T_c, 60 K. The same samples were subjected to a further 24 h at 300 °C in O_2, but the results were unchanged; this indicated that 24 h were sufficient to achieve a steady state for all temperatures used in this study. By using high oxygen pressures and low temperatures (e.g. 100 bar at 300 °C) T_c in the stoichiometric composition can be supressed to as low as 51.5 K [19].

The results in Fig. 5 show that, for compositions A, B and C, annealing in O_2 at temperatures below ~ 825 °C leads to a reduction in T_c associated with overdoping and an excess of *p*-type carriers. In order to examine the possibility of under-doping, two methods were considered, either to heat samples in O_2 at temperatures close to melting, or to heat in an inert

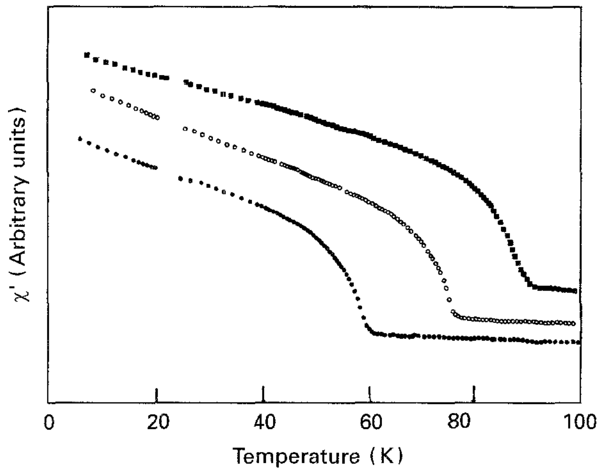

Figure 3 a.c. susceptibility data for $Bi_2Sr_2CaCu_2O_\delta$ after heating in O_2 at three different temperatures. Frequency 333/Hz; field 1/Oe; ● 300 °C; ○ 500 °C; ■ 850 °C.

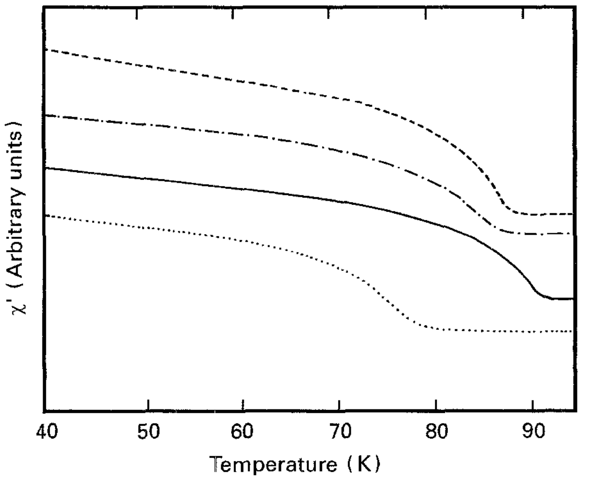

Figure 4 a.c. susceptibility data as a function of cation composition for samples heated in O_2 at 800 °C. Frequency 333/Hz; field 1/Oe; — A; —.— B; --- C; .... D.

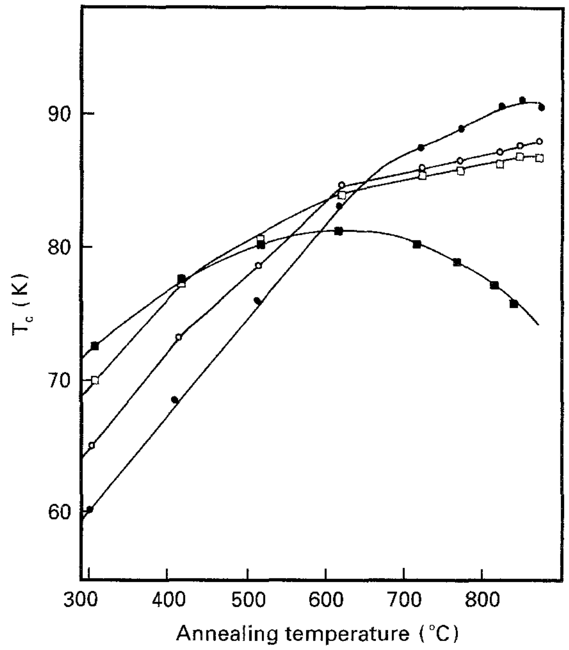

Figure 5 T_c (onset) data for samples heated in O_2 at different temperatures. ● sample A; □ sample B; ○ sample C; ■ sample D.

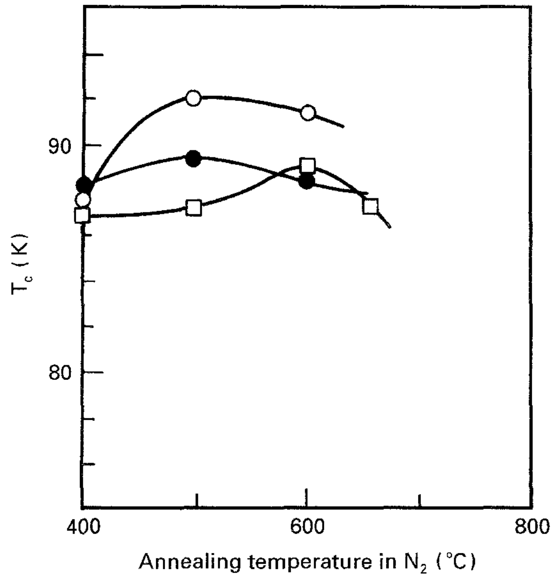

Figure 6 T_c (onset) data for samples heated in N_2 at different temperatures. ○sample A; □ sample B; ● sample C.

atmosphere at various temperatures. The latter course was chosen. Results are shown in Fig. 6 for samples A, B and C heated in flowing N_2 in the range 400–675 °C; the T_c values for sample D heated under these conditions was always below 77 K. Oxygen partial pressure was maintained constant throughout the series of experiments, but no checks were made either to control or determine the O_2 content of the atmosphere used in this experiment. The results for all three compositions show a maximum in T_c. A reduction in T_c occurs where samples were heated at the higher temperatures and entered the under-doped region. The range of accessible T_c values in this underdoped region appears to be significantly less than in the overdoped region.

The behaviour of sample D where (Bi + Sr + Ca) < 5 appears to be rather different; the optimum T_c occurs in samples heated at ~ 600 °C in O_2, (Fig. 5) and a significant region of underdoping is seen in samples heated in O_2 at higher temperature.

We have no information on the oxygen contents of samples B, C and D. Previous studies on A (Fig. 2) showed that the range of oxygen contents corresponding to the behaviour shown in Fig. 5 is very narrow, ranging from $\delta = 8.14$ to 8.21 with a T_c maximum at $\delta = 8.175$ [22, 24]

4. Conclusions

We have investigated for the first time, the variation of T_c with cation content of monophasic ceramic samples, under controlled atmospheric conditions, when (Bi + Sr + Ca) = 5. The stoichiometric composition (sample A) is found to have both the highest T_c value and the largest range of T_c suppression in the overdoped regime. The non-stoichiometric samples based on the substitution mechanisms $Bi \rightleftharpoons Sr$ and $Sr \rightleftharpoons Ca$ (samples B and C) have similar T_c values when annealed above 600 °C in oxygen but differ significantly when annealed at lower temperatures. For a vacancy substitutional mechanism where $(\mathrm{Bi}+\mathrm{Sr}+\mathrm{Ca})<5$ (sample D) the variation in T_c appears to be quite different; the optimum T_c is significantly lower, ~ 82 K, and demonstrates only a weak dependence on annealing temperature.

Acknowledgement

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