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Crystal growth of $Bi_2Sr_2CuO_6$ from flux system KCl–KF and its superconductivity

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Single crystals of $Bi_2Sr_2CuO_6$ (BSCO) were grown from high-temperature solution using KCl–KF as flux. Differential thermal analysis (DTA) of the starting materials enabled an appropriate temperature programme to be introduced for crystal growth by spontaneous nucleation. By means of the improved thermogravimetric (TG) method, $Bi_2Sr_2CuO_6$ crystals were grown after determination of the crystallization temperature. A single crystal in the form of a thin rectangular platelet up to 6×4 mm^2 was obtained and was identified by X-ray powder pattern and by scanning electron microscopy (SEM). Analyses were performed by using high-resolution electron probe microanalysis (EPMA), which indicated that it is the nonstoichiometric compound $Bi_{2+x}Sr_{2-x}CuO_6$. The superconducting properties are strongly dependent on the composition of Bi and Sr in the crystals and on heat treatment. The transition temperature of 7 K with 0.5 K width for as-grown crystals, has been obtained.

1. Introduction

In the recently discovered $Bi_2Sr_2Ca_{n-1}Cu_nO_{2(n+2)}$ superconductor families [1], the superconducting temperature, T_c, increases with the number of Cu–O layers which are sandwiched between the Bi–O layers. Up to now, sintered superconductors with one, two and three Cu–O layers ($n = 1,2$ or 3) have been synthesized. Much work has concentrated on the crystal growth of the two-layer compound $Bi_2Sr_2CaCu_2O_8$ with T_c about 80 K, but little was contributed on single-crystal growth of the one-layer compound $Bi_2Sr_2CuO_6$ with T_c 7–22 K. This study was undertaken to grow single-crystal $Bi_2Sr_2CuO_6$ (BSCO) using KCl–KF as flux from which the pure crystals would be easy to separate out. In the ternary system SrO–Bi_2O_3–CuO [2], there are two kinds of 2:2:1 phases. One is the real 2:2:1 phase with very small deviation from stoichiometry which exhibits superconducting properties. The other is the 2:2:1 type solid solution phase with more excess Bi which is not superconducting. The study we report here enables a better understanding of this point.

2. Experimental procedure

The chemicals were BDH Laboratory Reagent Grade 99% Bi_2O_3 and $SrCO_3$ and 99% KCl; BDH "Analar" 98% CuO and 97% KF. The flux composition was kept at 50 wt% (0.46 KCl + 0.54 KF). For all experiments, platinum containers were used and PtRh–Pt thermocouples were used to measure temperatures. Furnaces with SiC elements were regulated by a Eurotherm controller combined with a digital programmer made in the Clarendon Laboratory.

The equipment for DTA has been described previously [3]. The samples were heated and cooled at 10 °C min^{-1}. The improved TGA method [3] was used to obtain crystallization data under conditions closer to those of crystal growth and after that to enable crystals to be grown continuously. Batches consisting of 50 g mixed starting materials with Bi_2O_3: $SrCO_3$: CuO = 1:4:4 (mol) with the flux as described earlier were used for improved TGA studies, in which a platinum wire was immersed to a depth of 3 mm below the surface of the solution as the nucleation centre, and its apparent weight with temperature was recorded.

3. Results and discussion

3.1. DTA and crystal growth

Fig. 1 shows the DTA curve of the mixed starting materials, Bi_2O_3–$4SrCO_3$–4CuO–50 wt% (0.54 KF + 0.46 KCl). There are four major endothermal peaks during heating and three exothermal peaks during cooling. As with the system of Bi_2O_3–$SrCO_3$–$CaCO_3$–CuO–KF–KCl reported earlier [4], the first endothermal peak at 198 °C corresponds to the decomposition of $SrCO_3$. The second peak which started at ~ 489 °C may be caused by the eutectic reaction of KF–KCl [5]. The whole system appears to start melting slightly below 558 °C and to finish at ~ 801 °C resulting in the third and fourth endothermal peaks, respectively; corresponding exothermal effects occurred during cooling except for the decomposition peak of $SrCO_3$. From the DTA data, the liquidus to the eutectic region seems to be located at 800–500 °C which enables a suitable temperature programme to be introduced for crystal growth by spontaneous nucleation.

A total of 20 g starting mixture in a 20 cm^3 Pt crucible was used for the crystal growth. The furnace was heated at 50 °C h^{-1} to the maximum temperature

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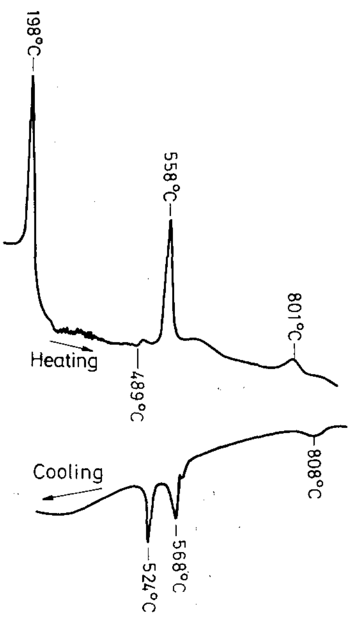

Figure 1 DTA of the flux system Bi_2O_3–$SrCO_3$–CuO–KCl–KF on heating and cooling.

between 800 and 900 °C where it was held for 2 h before starting slow cooling at 2–4 °C h^{-1} to 500–550 °C. After this, the furnace was cooled at 50 °C h^{-1} to room temperature. Two kinds of crystals appeared in the melt: black needles of CuO and black shiny flakes which could be separated from the flux by water. Fig. 2 shows a single crystal of $Bi_2Sr_2CuO_6$ 6 × 4 mm^2 in size and thickness of a few hundredths of a millimetre. The crystal was identified by its X-ray powder pattern (Table I) and the scanning electron micrograph shown in Fig. 3. The composition of the crystals has been checked by electron probe microanalysis (EPMA) [6], which also showed that residual K, F, Cl and Pt were below detection levels.

3.2. TGA and crystal growth

In Fig. 4, the TGA curve shows the crystallization of BSCO from the flux KCl–KF. Above the crystallization temperature, the whole system was completely dissolved and the TGA signal stayed at a constant level with some fluctuation caused by convection of the solution. As nucleation started on the Pt wire during cooling at 100 °C h^{-1}, surface tension at the solid–liquid interface made the curve deviate from the base line. When the crystals on the wire grew, the apparent weight increased rapidly. The crystallization temperature was clearly determined at ~ 795 °C which agreed well with the DTA result. But the open crucible which had to be used for introducing the Pt wire greatly increased the evaporation of the flux, so that the crystallization temperature rose smoothly and a thin layer always grew at the surface of the solution. We can easily lift the crystals on the wire above the surface of the solution and drain off the flux. Thin black platelets up to a few centimetres in size have been grown within a short period by the improved TGA method.

TABLE I X-ray diffraction data for a crystal of BSCO

Batch no.	D (nm)	I_{obs}	*Batch* no. (nm)	D (nm)	I_{obs}
1	0.5224	vw*	10	0.2018	w
2	0.4091	ms	11	0.1924	w
3	0.3434	s	12	0.1889	w
4	0.3074	vs	13	0.1867	vw
5	0.3001	vs	14	0.1810	vw
6	0.2683	s	15	0.1692	vw
7	0.2462	m	16	0.1660	vw
8	0.2229	vw	17	0.1600	w
9	0.2048	vw	18	0.1533	vw

*w = weak; s = strong; m = medium; vw = very weak; ms = medium strong and vs = very strong.

3.3. Characterization of BSCO crystal

Table II summarizes the conditions of crystal growth, the results of EPMA and superconductivity of the crystals. All the crystals obtained are nonstoichiometric in that the number of Bi atoms in the unit formula is always in excess of 2.1 [7] and the number of Sr atoms is less than 2. Fig. 5 shows the linear dependence of Bi on Sr in the crystals which suggests

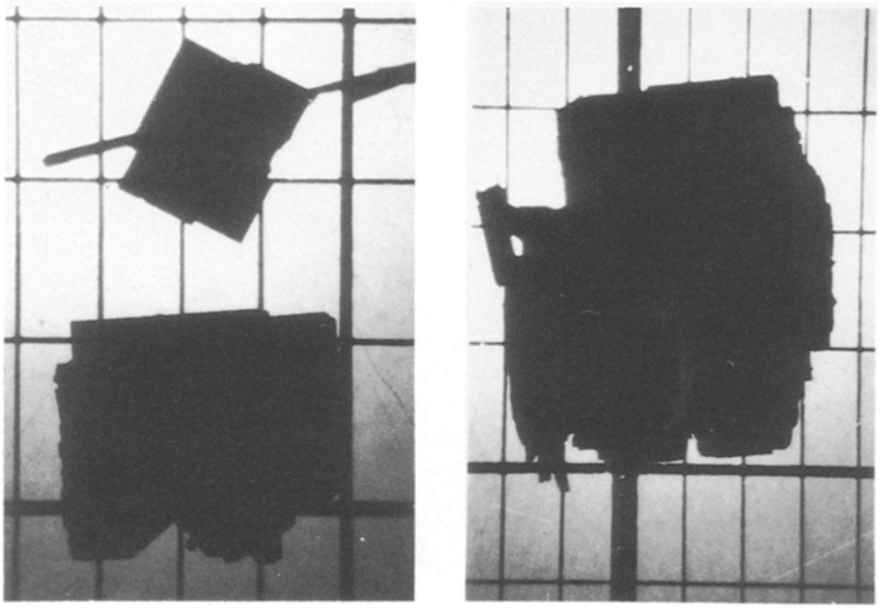

Figure 2 BSCO crystals. (Scale 2 × 1 mm^2.)

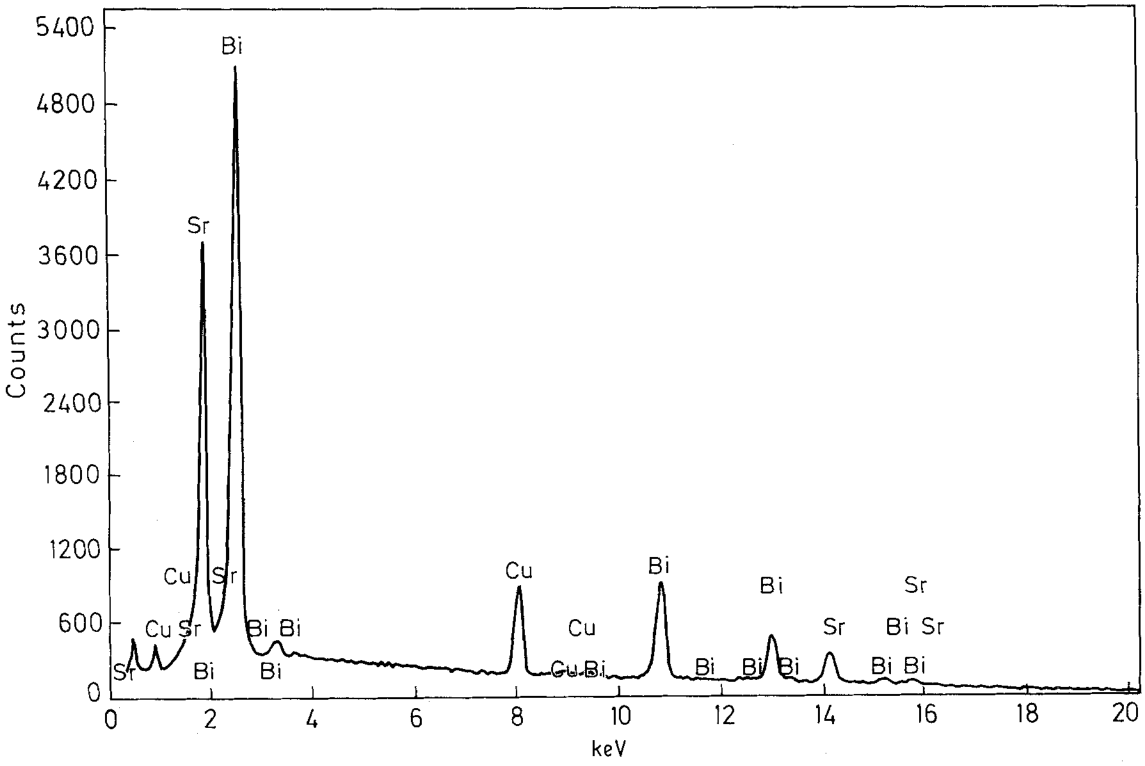

Figure 3 Scanning electron spectra of BSCO crystal.

TABLE II Crystal growth and characterization of BSCO

Batch no.	Composition of solute (mol)			Cooling range (°C)	Cooling rate (°C h^{-1})	Loss (wt %)	Av. composition of crystals (at.)		SC[a]
	Bi_2O_3	$SrCO_3$	CuO				Bi	Sr	
1	1	4	4	860–500	5	5.0	2.13	1.96	yes
2	1	6	4	900–550	2–4	7.2	2.26	1.79	no
3	1	4	4	886–500	5	13.3	2.34	1.6	no
4	1	4	4	850–500	5	12.8	2.23	1.66	no

[a]SC Superconducting

Figure 4 TGA curve of BSCO growth system.

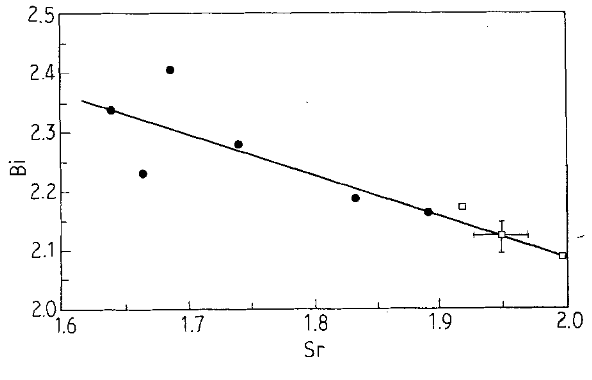

Figure 5 The Bi and Sr composition of the as-grown crystals of BSCO. (□) Superconductive, (●) non-superconductive.

that some excess Bi substitutes for Sr. In the crystal structure of BSCO, the Sr atom is closer to the Cu–O layer. The replacement of Sr by Bi, with larger radius and higher charge than Sr, will greatly affect the superconducting properties. So only the crystals with high content of Sr exhibit superconductivity. Fig. 6 shows the result of the resistivity measurement for one of the as-grown crystals. The transition temperature is ~ 7 K with 0.5 K width.

Fig. 7 shows the location of the average composition of our four batches of crystals (Table II) in the

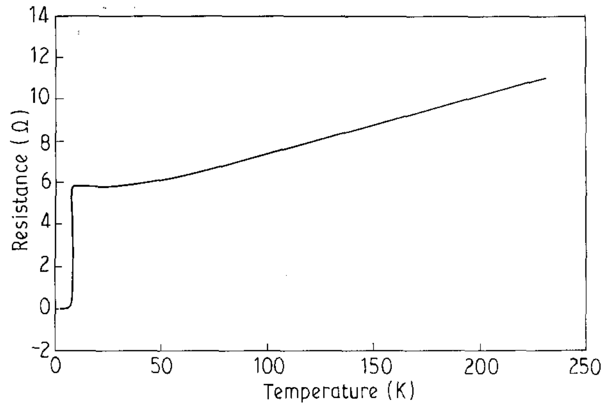

Figure 6 The dependence of electrical resistivity in the a–b plane on temperature for an as-grown BSCO crystal.

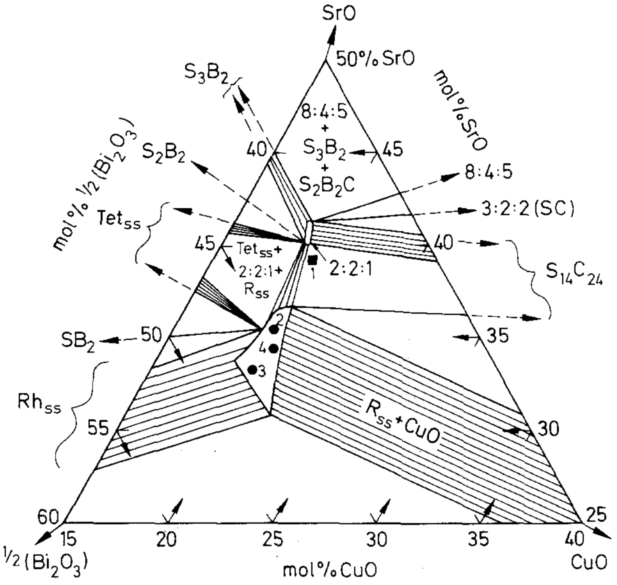

Figure 7 The location of the as-grown crystals from four batches in the ternary composition diagram [2] of Bi_2O_3–SrO–CuO. (■) Superconductive, (●) non-superconductive.

ternary composition diagram SrO–Bi_2O_3–CuO [2]. The sample from Batch 1 which was superconducting is located near the real 2:2:1 phase region. But the samples from Batches 2–4, which were not superconducting, are located in the region of the solid solution phase. For our system, increasing the Sr content in the starting materials did not increase the proportion of Sr in the crystals. It is said that during heat treatment of the sinter the solid solution phase always forms first and then gradually changes to the real 2:2:1 phase. Its formation seems to be quite complex, because we observe that different samples from the same batch have different contents of Bi and Sr. The process of this change may be very sensitive to evaporation of the flux, the holding temperature and the annealing atmosphere: O_2 probably slows down the kinetics of formation of the real 2:2:1 phase and deficiencies of O_2 perhaps speed up this reaction [2]. Therefore, for one of our as-grown crystals, T_c was observed to decrease from 5.5 K to below 4.2 K after annealing in air at 400 °C for 15 h, and then to increase to 12.5 K after annealing in vacuum at 400 °C for 8 h, in agreement with the above speculation.

4. Conclusions

1. DTA data were useful for determining an appropriate temperature programme for crystal growth by spontaneous nucleation.
2. TGA was a more practical method for the study of crystallization and could be directly used for top-seeding.
3. Using the DTA and TGA information, crystals of $Bi_2Sr_2CuO_6$ have been successfully grown from the flux system KCl–KF.
4. In this system only those crystals with high content of Sr are superconducting. We deduce that excess Bi inhibits the superconducting behaviour.

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References

1. H. MAEDA, Y. TANAKA, M. FUKUTONI and T. ASANO, *Jpn. J. Appl. Phys.* **27** (1988) L309.
2. R. S. ROTH, C. J. RAWN and L. A. BENDERSKY, *J. Mater. Res.* **5** (1990) 46.
3. CHEN CHANGKANG, B. E. WATTS, B. M. WANKLYN, P. A. THOMAS and P. W. HAYCOCK, *J. Crystal Growth* **91** (1988) 659.
4. CHEN CHANGKANG and B. M. WANKLYN, *ibid.* **96** (1989) 547.
5. W. PLATO, *Z. Physik. Chem.* **58** (1907) 364.
6. A. MACKENZIE, E. MARSEGLIA, I. MARSDEN, G. LONZARICH, CHEN CHANGKANG and B. WANKLYN, *Physica* **C162–164** (1989) 1029.
7. J. L. TALLON, R. G. BUCKLEY, P. W. GILBERD, M. R. PRESLAND, I. W. M. BROWN, M. E. BOWDEN, L. A. CHRISTIAN and R. GOGUEL, *Nature* **333** (1988) 43.

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