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Preparation of single crystals of $YBa_2Cu_3O_{7-x}$ from nonstoichiometric melts

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Abstract. Studies on the single crystal growth of $YBa_2Cu_3O_{7-x}$ show that the growth conditions have not been optimised yet and they vary in many ways. Here we report the growth of single crystals of YBCO in the size range 0·5–1·2 mm from nonstoichiometric melts. We have made systematic variations in the flux composition (constituting CuO and $BaCO_3$) in order to arrive at an optimum composition for consistently getting single crystals of size 0·5–1·2 mm. The tetragonal phase was confirmed by X-ray diffraction and single crystallinity by the Laue technique. Superconductivity was confirmed in oxygen-annealed crystals.

Keywords. Yttrium barium copper oxide; flux technique; crystal growth; high T_c superconducting oxide.

1. Introduction

A thorough understanding of the basic properties of high temperature superconductors, possible only through measurements on single crystals, aid the unravelling of interesting features such as the anisotropy in the electric and magnetic properties. Many attempts to prepare single crystals of these compounds are reported in the literature and the crystal sizes so far grown are still in the millimetre size (Cook *et al* 1987; Kaiser *et al* 1987; Damento *et al* 1987; Haneda *et al* 1987; Scheel and Licci 1987; Takekawa and Iyi 1987; Schneemeyer *et al* 1987). It is interesting to note that even with single crystals of millimetre size it is possible to attach a number of electrical leads and perform meaningful measurements (Iye *et al* 1988). We have developed a method in which certain nonstoichiometric compositions are heated and subsequently slowly cooled to yield several platelet-single crystals of YBCO, and we report the details in this paper.

2. Phase diagram considerations

From the phase diagram of the system Y_2O_3–BaO–CuO (Laudise *et al* 1987; Hinks *et al* 1987) it is clear that YBCO single crystals cannot be grown by the melt method as no stoichiometric melt is available and hence the task requires trying out alternative routes such as high temperature solution or flux. It appears that BaO–CuO based solvents are the most appropriate. In the present work, a $BaCO_3$ (starting material for BaO) and CuO mixture was choosen for the flux and after the optimum composition of the flux was identified, it was possible repeatedly to grow single crystals up to a size of 1·2 mm.

3. Experimental procedure

The starting materials used were Y_2O_3 (purity 99·9%, Sigma Chemical Company, USA), $BaCO_3$ (purity 99·5%, Sarabhai Chemicals, Baroda) and CuO (purity 99%, Sarabhai Chemicals, Baroda). Crucibles of platinum and mullite were tried but were found to react with the melt. It was found that to a large extent alumina served the purpose although a slight amount of reaction with the melt material was observed during prolonged heating at temperatures higher than 1000°C.

The following starting compositions were found to yield satisfactory results. Composition A: 25 parts by weight of YBCO (stoichiometric mixture) and 75 parts of flux containing 25 mol% of $BaCO_3$ and 75 mol% of CuO. Composition B: (ratio of YBCO to flux wt.% remaining the same) 35 mol% of $BaCO_3$ and 65 mol% of CuO. Composition C: (ratio of YBCO to flux wt.% remaining the same) 30 mol% of $BaCO_3$ and 70 mol% of CuO.

Around 25 g of YBCO and flux were thoroughly mixed and loaded in a 20 ml alumina crucible which was placed in a vertical tubular furnace. The temperature was slowly increased until melting was observed which for the above composition was around 1020°C. The crucible was held at this temperature for at least 15 hr, after which a slow cooling at the rate of 5–7°C hr^{-1} was started. When the temperature fell to 880°C the crucible was quickly removed from the furnace.

4. Results

The first composition (A) yielded many needle-like crystals of size 5 mm × 1 mm. The colour of the crystals was greenish. The Laue and XRD showed that the crystals were mostly CuO. The CuO single crystals appeared to be less in number in the case of composition B and many tiny crystals of morphology different from that of CuO crystals were found sticking on the surface of the solidified mass. Composition C was most successful in yielding several crystals of YBCO. Inspection of the crucible top under a microscope showed shining platelets. No

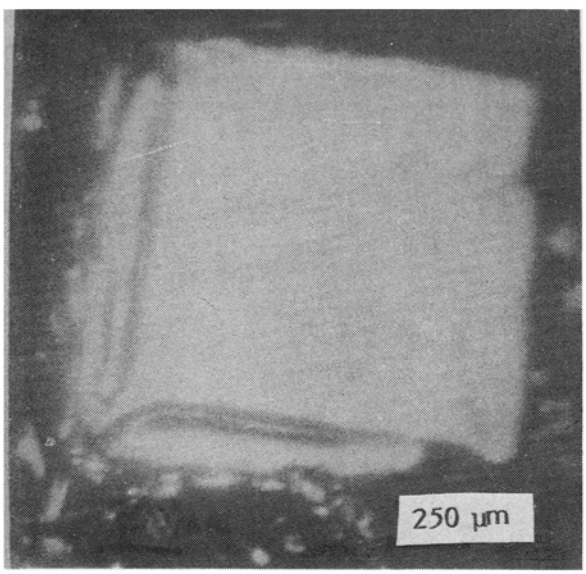

Figure 1. A typical photograph of a YBCO single crystal.

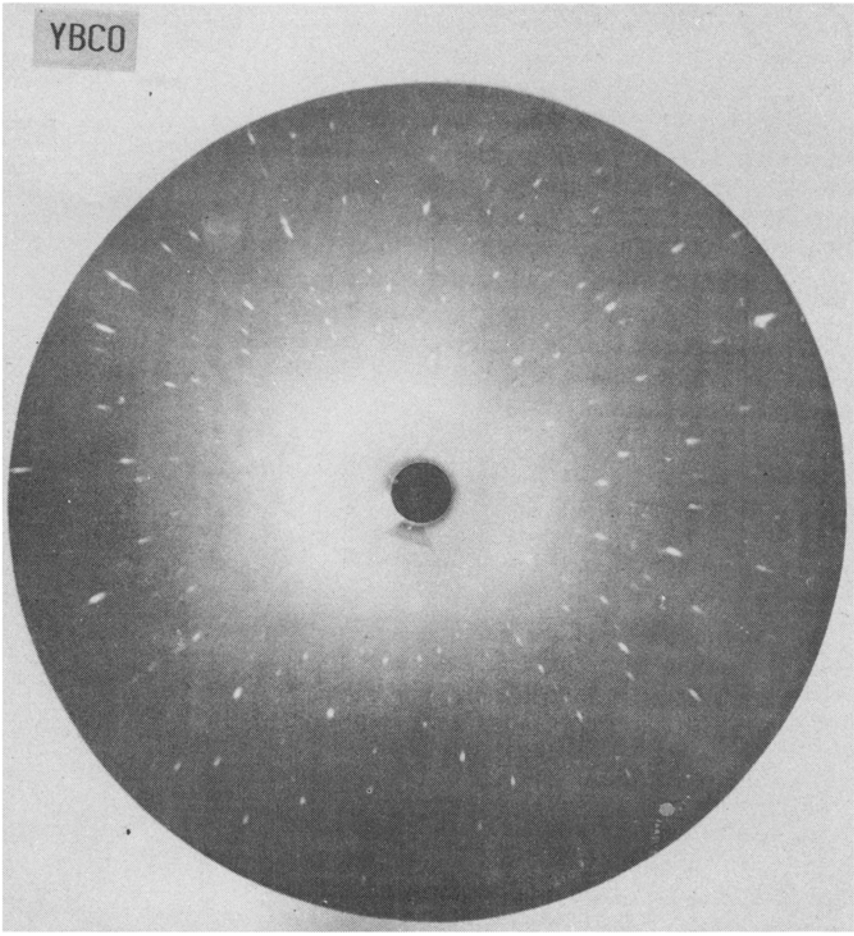

Figure 2. A Laue picture of a single crystal of YBCO.

simple method could be identified for separating the crystals from the frozen mass. However, by sectioning the crucible into smaller bits a sufficiently large collection of YBCO single crystals were obtained in the range 0·5–1·2 mm. A photograph of a typical crystal appears in figure 1.

The Laue pattern obtained using one of these crystals is shown in figure 2. The *d* values calculated from powder X-ray diffraction results were found to match with *d* values reported in the literature for tetragonal phase YBCO (Gallagher *et al* 1987). The single crystals were subjected to the usual oxygen-annealing and superconductivity was confirmed by observing Meissner effect at liquid nitrogen temperature.

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