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ScienceDirect
Journal of Crystal Growth 300 (2007) 263–266
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Ambient-condition growth of superconducting $YBa_2Cu_4O_8$ single crystals using KOH flux

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Received 21 September 2006; received in revised form 31 October 2006; accepted 5 November 2006
Communicated by M. Tischler
Available online 15 February 2007

Abstract

$YBa_2Cu_4O_8$ is a stoichiometric oxide superconductor of T_c~80 K. Unlike $YBa_2Cu_3O_{7-\delta}$, this compound is free from oxygen vacancy or twin formation and does not have any microscopic disorder in the crystal. Doping with Ca raises its T_c to 90 K. The compound is a promising superconductor for technological application. Up to now, single crystals have not been grown without using specialized apparatus with extremely high oxygen pressure up to 3000 bar and at over 1100 °C due to the limited range of reaction kinetics of the compound. This fact has delayed the progress in the study of its physical properties and potential applications. We present here a simple growth method using KOH as flux that acts effectively for obtaining high-quality single crystals in air/oxygen at the temperature as low as 550 °C. As-grown crystals can readily be separated from the flux and exhibit a perfect orthorhombic morphology with sizes up to $0.7 \times 0.4 \times 0.2\,mm^3$. Our results are reproducible and suggest that the crystals can be grown using a conventional flux method under ambient condition.

PACS: 64.75.+g; 81.10.Fq; 74.72.Bk

Keywords: A1. Crystal structures; A1. Doping; A1. Solubility; A1. Solvents; A2. Growth from melt; B2. Oxide superconducting materials

$YBa_2Cu_4O_8$ (Y-124) was observed first as a structure defect in $YBa_2Cu_3O_{7-\delta}$ (Y-123) by electron spectroscopy [1], and then was prepared as a main phase in thin films [2,3]. Karpinski et al. [4] first reported bulk synthesis of Y-124 at high oxygen pressure of 400 bar, based on the thermodynamic stability of the compound within a region of high pressure–temperature–composition phase diagram. Cava et al. [5] synthesized Y-124 powders at ambient pressure using sodium carbonate serving as a catalyst to enhance the compound reaction rate. Although the Y-124 ceramic samples can be prepared by several methods [6–9] according to the established phase diagram of Y–Ba–Cu–O, the single crystals can only be obtained in self-flux under a high oxygen pressure up to 3000 bar or minimum oxygen partial pressure $P(O_2) = 600$ bar and heating temperature over 1100 °C [9,10]. However, Y-124 is a thermodynamically stable phase at low temperature in 1 atm, and has a very high thermal stability up to 850 °C [5]. Thus, we may expect to grow Y-124 single crystals under ambient pressure at a reduced temperature if a proper solvent can be found. We selected potassium hydroxide, KOH, as a flux to grow Y-124 crystals. This alkaline compound is a classical flux which can dissolve rare-earth and alkaline-earth metals and yields both peroxides and superoxides [11,12], being able to stabilize the high oxidation state of copper, namely Cu^{3+}, in favor of the formation of the Y-124 phase. In addition, the ionic radius of K^+ ~2.03 Å is rather large, compared to those of Y, Ba and Cu. Therefore, the potassium hardly incorporates into Y-124 when using as a flux.

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doi:10.1016/j.jcrysgro.2006.11.076

In this paper, we report the details of the newly developed crystal growth technique and the results obtained from several characterization methods as applied to as-grown and Ca-doped Y-124 single crystals. The crystals grown by this method have no contaminations and show a sharp superconducting transition temperature T_c.

Y-124 powder samples were synthesized using $Y(NO_3)_3 \cdot 6H_2O$ (99.9%), $Ba(NO_3)_2$ (99.95%), $Cu(NO_3)_2 \cdot 2.5H_2O$ (99.99%) in a molar ratio of 1:2:4. The mixtures were ground and loaded in an Al_2O_3 crucible, sintered at 800 °C for 100 h with several intermediate grindings. Y-123 polycrystalline powders were prepared by calcining the mixtures of $1YO_{1.5}$:$2BaCO_3$:3CuO (>99.9% purity) at 880 °C for 2 days for the decomposition of CO_2. The calcined mixtures were then sintered at 920 °C in flowing oxygen for 2 days with several intermediate grindings. All the sintered powders were then identified by XRD to confirm the pure phases of Y-124 and Y-123 obtained.

Thermogravimetric and differential thermal analysis (TG-DTA) measurements were performed with NETZSCH STA449C equipment. The ground Y-124 single-crystal powders mixed with 60 wt% KOH were loaded in a lid-covered Al_2O_3 crucible and then heated in the TG-DTA apparatus at 10 °C/min up to 850 °C and then cooled to room temperature at 10 °C/min in flowing oxygen.

The structural parameters were identified by X-ray diffraction (XRD) powder utilizing Cu Kα radiation on the ground Y-124 crystal powders, a scanning rate of 0.02°/min was employed to perform the θ–2θ scans from 0° to 70°. The lattice constants were determined by the powder diffraction patterns using the Dicvol 91 program. The chemical composition of crystals was determined by energy dispersive X-ray spectrometry (EDX) at an accelerating voltage of 20 kV. The magnetic susceptibility measurements were performed by ac susceptibility using a superconducting quantum interference device magnetometer (SQUID) with the field of 10 G for the Meissner effect and flux screening measurements.

The growth of Y-124 single crystals was performed in a box furnace in either air or flowing oxygen. The source material was used either from Y-124 ceramic powders synthesized at ambient condition [5] or from conventionally prepared polycrystalline Y-123 mixed with CuO in a molar ratio of 1:1. Usually, 8 g of source materials mixed with KOH flux were loaded in an alumina crucible. A lid was used to cover the crucible for preventing the evaporation loss of flux during heating. The sample was then kept at a maximum temperature between 550 and 790 °C for 4 h, then slowly cooled to 450 °C and finally fast cooled to room temperature.

In order to estimate the optimal ratio of flux to Y-124, we examined mixtures with various weight ratios, ranging from 30 to 90 wt%. No crystals were obtained from 30 wt% charges. Small crystals could be grown from flux ratios of 40 or 50 wt%. The majority phase of CuO was crystallized at 80–90 wt%. The best crystals of Y-124 were obtained from 55 to 70 wt%. Table 1 summarizes the results obtained from our experiments with various growth conditions. We also tried to estimate the optimal cooling rate. Among various rates investigated at 55–70 wt% flux ratio the best result is found for ~5 °C/h. Any lower cooling rates lead to a long growth period and thus cause more flux loss from evaporation. This leads to small Y-124 crystals and vice versa for the cooling rate of >5 °C/h. To optimize growth condition, however, soaking temperature, flux ratio and cooling rate, all must be taken into account together.

The melting behavior of the mixtures of Y-124 and KOH was investigated by TG-DTA measurements and observed in a ventilated system. As shown in Fig. 1, an endothermic peak with onset temperature $T = 136$ °C on the DTA curve corresponds to the KOH dehydration, indicating a 1% loss by TG. The weight loss from 200 to 400 °C is assumed to be the thermal reaction of $KOH \rightarrow K_2O + H_2O\uparrow$. During the reaction process, the endothermic peaks at 237 and 386 °C correspond repectively to the KOH partial and complete melting. The peak at 494 °C is attributed to the starting melt of Y-124 in KOH. The broad exothermic peak between 550 and 800 °C corresponds to the formation of Y-124, as confirmed by the XRD patterns and in agreement with our solubility measurement. This reveals

Table 1
The conditions and results of $YBa_2Cu_4O_8$ (Y-124) single-crystal growth in KOH flux

Sample no.	Source material (synthesized powders)	KOH (wt%)	Maximum temperature (°C)	Ambient condition	Cooling rate (°C/h)	Results
A	Y-124	30	750	O_2 flowing	8	No crystals
B	Y-124	40	750	O_2 flowing	8	Small crystals
C	Y-124	45–65	750	O_2 flowing	8	Good crystals
D	Y-123:CuO (1:1)	50	550–650	Air	5–8	Small crystals, $Y_2Cu_2O_5$
E	Y-123:CuO (1:1)	55–70	700–750	Air	5-8	Best crystals
F	Y-123:CuO (1:1)	60–70	790	Air	1–2	Small crystals, CuO
G	Y-123:CuO (1:1)	80–90	750	Air	2–5	CuO