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PREPARATION OF $YBa_2Cu_4O_8$ SUPERCONDUCTOR FROM OXALATE PRECURSOR UNDER AMBIENT PRESSURE

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The $YBa_2Cu_4O_8$, 124, superconductor was prepared from the coprecipitated oxalate precursor powder. Almost complete (>99.9%) precipitation of the cations as oxalates is achieved from concentrated acetic acid medium. Firing at 780°C under atmospheric oxygen pressure yielded pure phase $YBa_2Cu_4O_8$ superconducting material with $T_c \sim 81$ K. This material is quite stable upto 840°C. Further firing at 860°C it transforms to $YBa_2Cu_3O_{7-x}$.

Introduction

The $YBa_2Cu_4O_8$ (124) phase was first discovered as lattice defect in $YBa_2Cu_3O_{7-x}$ (123) phase[1] and then in inhomogeneous $YBa_2Cu_3O_{7-x}$ thin films[2]. Since then, bulk 124 samples were synthesized under high oxygen pressure[3,4] and classified to be a 80 K superconductor. The partial substitution of Y^{3+} by Ca^{2+} resulted in an increase of T_c as high as 90 K[5-7] for a 124 compound. The bulk synthesis of this compound under one atmosphere oxygen pressure was first demonstrated by the reaction of the respective nitrates in K_2CO_3 or Na_2CO_3 fluxes[8] and subsequently by the reaction of $YBa_2Cu_3O_7$ and CuO powder[9]. Recently, wet chemical synthesis techniques such as citrate-gel[10], oxalate co-precipitation[11] and sol-gel[12,13] are used for the fabrication of this compound under ambient oxygen pressure. The high stability of oxygen content in $YBa_2Cu_4O_8$ compared to $YBa_2Cu_3O_{7-x}$ for the temperatures upto 800°C offers the promise for many practical applications.

It is well known that the properties of the oxide superconductors strongly depend on the synthesis technique and the processing conditions. Therefore, the powder synthesis techniques are likely to play a crucial role in the preparation of bulk superconducting material. Microstructure can be controlled by the morphology and the particle size of the precursor powder. Conventional solid state reaction generally results in larger particle size and poor homogeneity. Co-precipitation of the respective cations as oxalates leads to homogeneous fine grained powder. However, the co-precipitation, using oxalate ion as precipitant, has been hindered by resulting undesirable stoichiometry[14-15]. Because of the differing solubility of the metal oxalate, it is necessary to optimize the experimental conditions (i.e. pH and the nature of precipitating medium) to obtain the desired stoichiometric ratio in the precursor powder. The variation in stoichiometry with pH in aqueous media have been reported[16-18]. Most recent efforts focus on the use of non-aqueous solvents to reduce the solubility of the oxalates[11,19]. In this article, we report almost complete (>99.9%) precipitation of oxalates to obtain fine, homogeneous precursor powder in the required cationic ratio by utilizing acetic acid as a solvent. After the proper heat treatment under ambient oxygen pressure this precursor powder results in $YBa_2Cu_4O_8$(124) oxide superconductor.

Experimental

The oxalate precursor powder for the fabrication of $YBa_2Cu_4O_8$ ceramic superconductor was prepared by homogeneous co-precipitation of the respective cations with oxalate ion in acetic acid. Yttrium acetate $Y(C_2H_3O_2)_3.4H_20$, barium carbonate $BaCO_3$ and copper acetate $Cu(C_2H_3O_2)$. H_2O (all high purity, 99.99%) were first dissolved in 50/50 (v/v) acetic acid /water mixture in a cationic ratio of 1:2:4. The poor solubility of barium carbonate necessitated the use of acetic acid/water mixtue. After evaporation to dryness by heating, the residue was re-dissolved in 200 ml concentrated acetic acid to give 10 mmol Y^{3+}, 20 mmol Ba^{2+} and 40 mmol Cu^{2+} (a clear blue solution). In a typical experiment, 200 ml of this solution was added dropwise into a solution of oxalic acid (a 10% excess over the required stoichiometric amount) in concentrated acetic acid. The mixture was stirred for an hour and left undisturbed overnight. The precipitate was separated by ultracentrifuge at 5000 rpm and the remaining colorless supernatant was analyzed for metal content. For inductively coupled plasma atomic emission spectroscopy (ICP/AES) analysis, the supernatant was evaporated to dryness and the residue was redissolved in dilute nitric acid. The analysis showed that more than 99.9% of each cation precipitated as oxalate. The oxalate precipitate was washed with concentrated acetic acid twice and then dried at 100°C for 12 hours.

Thermogravimetric studies were performed in air at a heating rate of 5°C/min. The TGA thermogram indicated the loss of water at a temperature below 200°C, followed by the decomposition of CuC_2O_4 to CuO between 200 and 300°C. The two step decomposition of yttrium oxalate toY_2O_3 via $Y_2(CO_3)_3$ occured between 300 and 550°C, overlapped by the transformation of barium oxalate to barium carbonate. These decompositions agree with the weight change observed for the individual oxalates and are in correspondence with the exothermic peaks in the DTA curve. Thermogravimetric analysis were also performed on $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_{7-x}$samples to study the thermal stability of these materials. Synthesis of $YBa_2Cu_3O_{7-x}$ from oxalate precursor powders have been recently reported recently by our group[20].

The oxalate precursor powder was calcined at 700°C for 12 hours in air and then slowly cooled (~ 1 °C/min.) to room temperature. The calcined powder was pressed into pellet of 6 mm in diameter under a static pressure of 120 MPa and the pellet was sintered at 780°C for 24 hours in flowing oxygen under ambient pressure. To determine the decomposition of 124 phase to 123, pellet sintered at 780°C were heated again at various temperatures in the flowing oxygen atmosphere. The chemical composition of the calcined powder was determined by energy dispersive X-ray analysis (EDAX). The structure and the phase composition was determined by Phillips powder X-ray diffractrometer using Cu Kα radiation at 40 KV, 100 mA. The instrument was

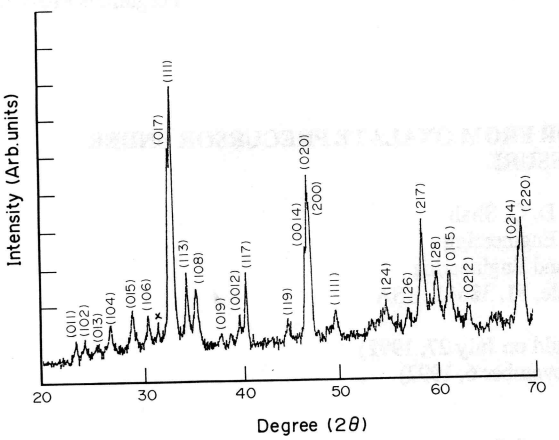

Figure 1: X-ray diffraction pattern of the sample sintered at 780°C in oxygen atmosphere. 124 peaks are indexed and impurity peak is marked by cross (x).

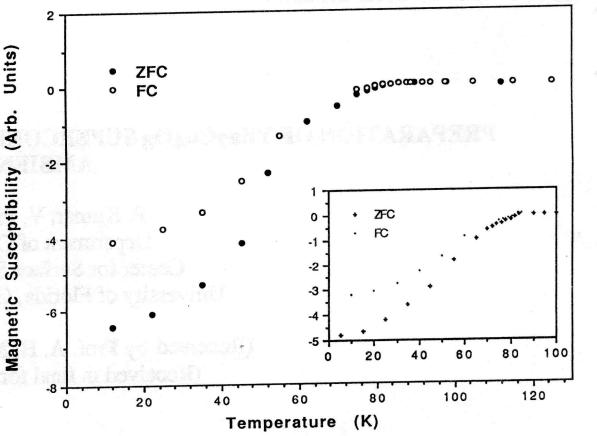

Figure 2: DC magnetic susceptibility as a function of temperature for the sample sintered at 780°C. Inset: DC magnetic susceptibility for the sample further sintered at 840°C.

calibrated with Si. The D.C. magnetic susceptibility measurements were performed using a commercial Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design). The surface morphology of the sintered specimen was examined by Scanning Electron Microscopy.

Results and Discussion

The chemical composition of the calcined powder, as determined by EDAX is in the required cationic ratio. No variation in the composition was observed in the chemical analysis at the several spots, confirming the homogeneity of the calcined material. The X-ray diffraction pattern of the sample sintered at 780°C in flowing oxygen is shown in figure1.

Table I: Observed X-ray difraction pattern of $YBa_2Cu_4O_8$

2θ (degree)	Intensity	d-spacing (Å)	h	k	l
23.35	7	3.806	0	1	1
24.19	8	3.675	1	0	2
25.47	5	3.494	0	1	3
26.77	12	3.326	1	0	4
29.01	15	3.075	0	1	5
30.61	13	2.917	1	0	6
32.75	75	2.732	0	1	7
33.13	100	2.701	1	1	1
34.43	27	2.602	1	1	3
35.33	22	2.538	1	0	8
37.87	4	2.373	0	1	9
39.81	10	2.262	0	0	12
40.52	25	2.224	1	1	7
44.87	9	2.018	1	1	9
46.76	34	1.940	0	0	14
47.11	63	1.927	0	2	0
47.34	52	1.918	2	0	0
49.82	11	1.828	1	1	11
54.89	12	1.671	1	2	4
57.11	8	1.611	1	2	6
58.68	40	1.572	2	1	7
60.13	23	1.537	1	2	8
61.38	24	1.509	1	2	28
63.24	10	1.469	0	2	12
68.44	26	1.369	0	2	14
68.88	39	1.362	2	2	0

The diffraction peaks are indexed based on the results reported in the literature[9,12,21]. As observed X-ray diffraction pattern is tabulated in table I. All the peaks corresponding to 124 phase are identified in the diffraction spectrum. No impurity peaks corresponding to $BaCO_3$ and CuO were identified in the diffraction pattern. There exist one unidentified peak at 2θ=31.57. This is due to the fact that all the species were present in the perfect cationic ratio. However, it is difficult to make the assesment of the phase purity from these data. The quantitative determination of contamination by 123 is difficult because the strong diffraction peaks of 123 almost overlap the strong 124 peaks. The 123 peaks which differs from 124 appear at 2θ values approximately 7.5, 15.2, 22.8 and 38.5. These lines were not detected in X-ray diffraction spectrum.

The temperature dependence of the DC magnetic susceptibility of the sintered pellet was measured by cooling the sample in zero field (diamagnetic shielding) and warming it up in a field of 20 G (flux expulsion). A T_c of 81 K was observed (figure 2). The surface microstructure of the sintered sample was observed under a scanning electron microscope. Monophasic grains as large as 5 μm were observed (figure 3). As depicted in SEM micrograph, sintering at 780°C in oxygen atmosphere results in a dense 124 superconducting oxide ceramic material. The SEM micrograph showed no second phase.

Further sintering of this material at a temperature of 840°C for 12 hours in the flowing oxygen did not have any effect on T_c (~81 K). The

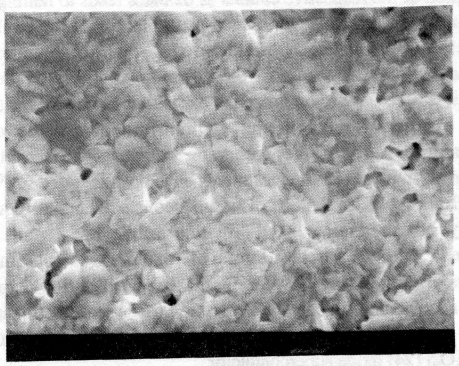

Figure 3: SEM micrograph of the pellet sintered at 780°C in oxygen atmosphere.

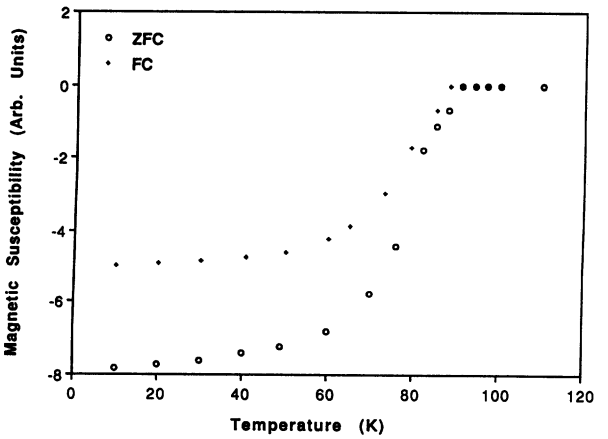

Figure 4: DC magnetic susceptibility as a function of temperature for the sample re-sintered at 860°C.

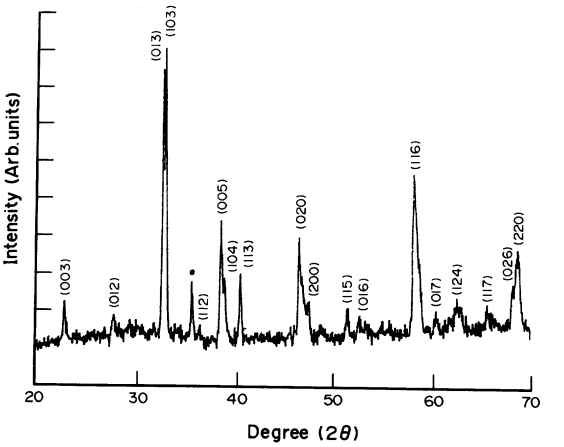

Figure 6: X-ray diffraction pattern of the sample sintered at 860°C in oxygen atmosphere. 123 peaks are indexed and CuO impurity peak is marked by the solid circle (o).

DC magnetic susceptibility data as function of temperature are shown in the inset of figure 2. A clear transition in the magnetization curve was observed at 81 K. From these results it can be argued that sintering in the temperature range from 780 to 840°C in oxygen atmosphere would result in 124 superconducting phase.

To explore further the effect of sintering temperature, the pellet sintered at 780°C was further sintered at 860°C for 12 hours in flowing oxygen. Figure 4 shows the DC magnetic susceptibility data as a function of temperature. A clear transition at 92 K in the magnetization curve was observed. This confirms the transformation of 124 to 123 phase and is in agreement with the thermogravimetric results[3], which indicated that 124 phase decomposes rapidly above 850°C. Shown in figure 5a, is the thermogravimetric curve of 124 sample by heating at 5°C/min. to 950°C followed by cooling at the same rate. The 124 phase has very high thermal stability upto the temperature about 800°C and decomposes rapidly at the higher temperature ~850°C and after slow cooling the decomposition products are 123 + CuO. By comparison 123 began losing oxygen above ~400°C as shown by TGA curve, figure 5b. The decomposition behavior shown in figure 5 is almost identical to those reported previously[12,22-23]. The X-ray diffraction pattern of this sample (124 sample further sintered at 860°C) is shown in figure 6. All the peaks pertaining to 123 phase were identified along with the characteristic peak for CuO. This result further confirms that by heating at 850°C, 124 phase rapidly transforms to 123 and CuO.

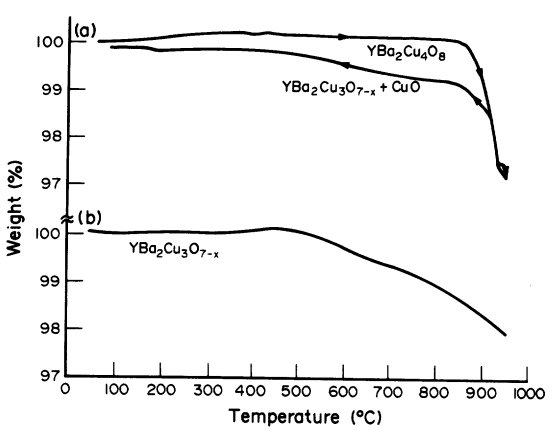

Figure 5: (a) Thermogravimetric curve for 124 powder. Heating and cooling rates were 5°C/min. 124 oxygen content remain constant upto ~800°C and decomposes to 123 and CuO above ~850°C. (b) Thermogravimetric curve of 123 powder at a heating rate of 5°C/min.

Conclusions

In conclusion, we have successfully achieved the complete precipitation of all the cationic species as oxalates from acetic acid medium. The precursor oxalate powder when sintered at 780°C in oxygen atmosphere results in phase pure $YBa_2Cu_4O_8$(124) oxide superconductor which is quite stable upto the temperature as high as 840°C. Further sintering at 860°C transforms 124 to 123 phase.

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