Synthesis of Superconductor $YBa_2Cu_4O_8$ by Pyrolysis of EDTA Complex

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The superconducting $YBa_2Cu_4O_8$ was synthesized in oxygen condition at 1 atm. The starting material with 1 : 2 : 4 composition was obtained by pyrolysis of EDTA complex, which was converted to 1-2-3 phase during densification, followed by the 1-2-4 phase recovery at 810℃. The phase presents were identified by XRD, TG, DTA and AC magnetic susceptibility. Our data indicated that considerable amounts of 1-2-4 phase formed but with the 1 : 2 : 3 phase or possibly 2-4-7 as visible. As the $P(O_2)$ increased with temperature, impurity peak, CuO ($2\theta = 38.8$), gradually decrease, and we conclude that the 1-2-4 phase is predominant bulk superconductor under the high oxygen pressure.

Introduction

The superconducting phase $YBa_2Cu_4O_8$ (hereafter referred to as 1-2-4) was first observed as lattice defects as partly decomposed $YBa_2Cu_3O_{7-x}$ (referred to as 1-2-3) by transmission electron microscopy[1], and was later prepared in a thin film form[2,3]. Later, Karpinski *et al*[4]. and Morris *et al*[5]. synthesized bulk 1-2-4 compounds by a high-oxygen pressure technique. The 1-2-4 phase is the $n=2$ member of the homologous series of compound with the general formula $R_2Ba_4Cu_{6+n}O_{14+n}$ where R may be the rare-earth elements. The $n=0$ and $n=1$ members correspond to the 1-2-3 phase and $Y_2Ba_4Cu_7O_{15-x}$ (2-4-7) phase. The 1-2-3 phase and 1-2-4 phase are structurally similar except that the $Cu\text{-}O_{(1)}$ chain layer in the 1-2-3 is replaced by the stoichiome tric Cu-O double layers in the 1-2-4 phase[6-8]. Therefore, the 1-2-4 phase is thermodynamically stable because of well-constrained oxygen contents. The 1-2-4 phase is expected to be a technologically useful compound and an ideal system to study the superconducting properties of Cu-O chains.

Unfortunately, the 1-2-4 phase has been difficult to prepare under ambient pressure. Lately, however, several groups reported the synthetic method of 1-2-4 phase at 1 atm by sol-gel method[9], catalytic method using alkali carbonate[10] and co-precipitation method[11]. But, the heat-treatment at low temperature caused some kinetic problems.

Since it is necessary to obtain homogeneous fine powder to overcome such problem, we carried out the pyrolysis method using EDTA (ethylenediamine tetraacetic acid), which does not have selectivity on metal ion.

The starting material with 1 : 2 : 4 nominal composition was obtained by pyrolysis of metal-EDTA complex, which was converted to 1-2-3+CuO phase during densification, followed by 1-2-4 phase recovery. Then it was investigated for the structure and the stability of the 1-2-4 phase using X-ray diffraction pattern (XRD), thermogravimetry (TG) and differential thermal analysis (DTA).

Experimental

The sample of the 1-2-4 phase has been prepared by solid state reaction. Stoichiometric amounts of high-purity powders $Y(NO_3)_3$, $Ba(NO_3)_2$ and $Cu(NO_3)_2$ in the ratio Y : Ba : Cu = 1 : 2 : 4 were dissolved in purified de-ionized water together with EDTA, and the solvent was evaporated very slowly while the solution was stirred. The stoichiometric solution was adjusted to pH = 10 using NH_4OH to obtain gel state compounds. Since the metal-EDTA complex is unstable in acidic condition, the solution should be maintained in basic condition during this process.

While this compound was heated up to 450℃ with Ar flow, the metal-EDTA complex was decomposed. After the powder was calcined at 915℃ for 3 h, pellets were formed from this powder. The pellets were then recalcined in the same condition. The calcined pellets were 1-2-3+CuO phase with 1 : 2 : 4 nominal composition. After being heated at 950 ℃ in O_2 flow for 24 h, they were sintered at 810℃ for 48 h under ambient oxygen pressure.

TG and DTA measurements were performed. The electrical resistivity-temperature relationship was measured by a conventional dc four-probe method.

The formation constant, K_f, of a metal-EDTA complex is the eqilibrium constant for the reaction

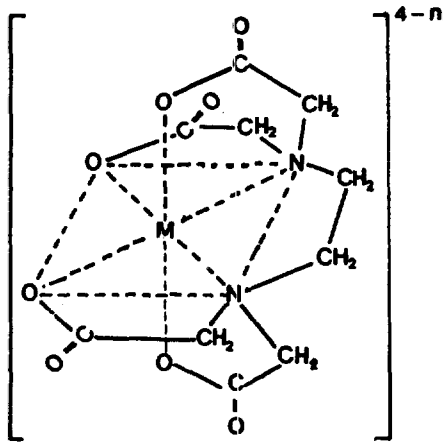
$$M^{n+} + Y^{4-} \rightarrow MY^{n-4}$$

$$K_f = [MY^{n-4}]/([M^{n+}][Y^{4-}])$$

Note that K_f is defined for the reaction of the species Y^{4-} with the metal ion. In gerneal, four different forms of free EDTA are present in the basic solution. Figure 1 shows the structure of the metal-EDTA complex and the formation constants for the Ba^{2+}, Cu^{2+}, Y^{3+} ions, which form the six coordinate species. Although each metal has a different formation constant, these values are so large EDTA does not have selectivity on the metal ions. Thus homogeneeous metal-EDTA complex is maintained during the solvent evaporation process.

Results and Discussion

The electrical resistivity versus temperature (R-T) of our 1-2-4 sample is shown in Figure 2, with T_c^{onset} and T_c^{offset} 90



Cation	log K
Ba^2	7.76
Cu^2	18.80
Y^3	18.09

Figure 1. The structure of metal-EDTA complex and formation constant for metal ions.

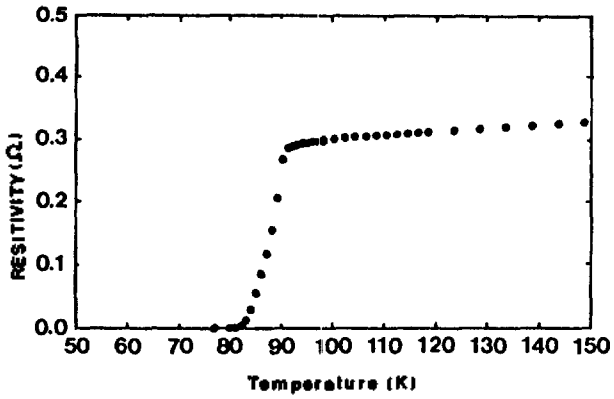


Figure 2. Plot of resistivity of the 1-2-4 as a function of temperature.

K and 82 K, respectively. In order to clarify the origin of the higher T_c than the known values for the 1-2-4. The AC magnetic susceptibility owing to the superconducing transit ions are observed in Figure 3 at about 82 K and 92 K. The transition at 92 K is attributed to the 1-2-3 phase and the 82 K transition to the 1-2-4 phase.

Figure 4 shows the results of TG and DTA curve for our sample under air atomosphere. As shown clearly in the figure, on heating, the 1-2-4 sample exhibited decomposition into 2-4-7 at 820℃ and 1-2-3 at 860℃. The 1-2-3 then decomposed at 900℃, and the CuO phase melted at 925℃. We notice that the decomposition temperature is different from that of the 1-2-3 synthesis because of the different composition. This result is compatible with the Shoji Tanaka report.[12,13]

From the DTA and AC magnetic susceptibility data, we can identify a considerable amount of the 1-2-4 phase in our sample. The X-ray powder diffraction pattern using Cu K-α radiation is shown in Figure 5. The corresponding 1-2-4 reflection peaks are shown along with the (*hkl*) indices,

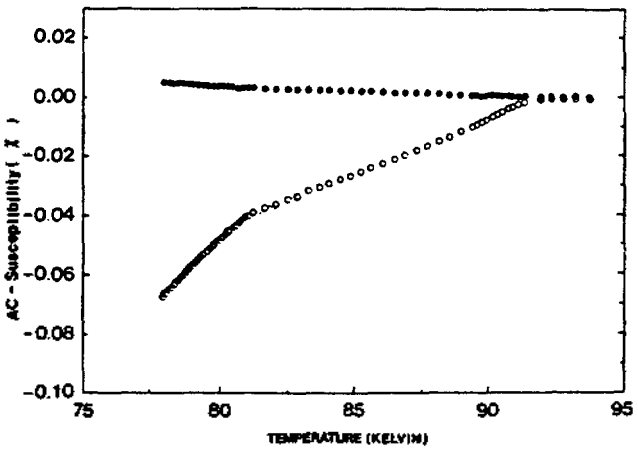


Figure 3. Plot of Ac magnetic susceptibility of the 1-2-4 as a function of temperature (The effect of separated line is deduced to mixed phase; 1-2-3 phase and 1-2-4 phase. Open circle is 1-2-4 phase, closed circle is 1-2-3 phase).

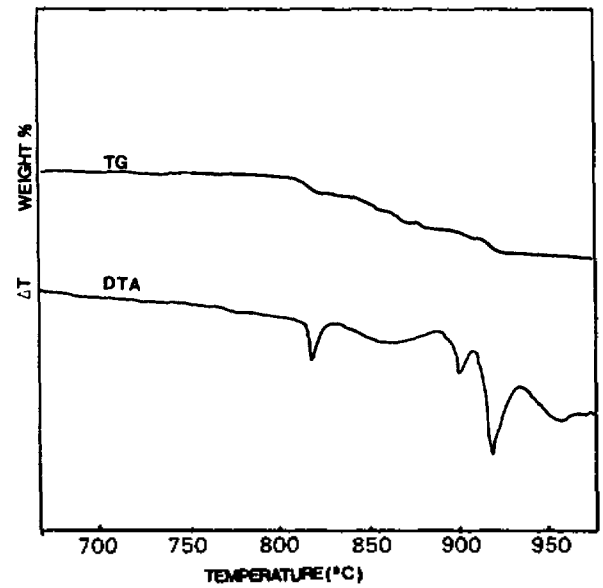


Figure 4. TG and DTA patterns for the 1-2-4 phase under air condition.

and some impurity peaks were detected. Although the sample is not a pure 1-2-4 phase, we estimate that roughly half of it is the 1-2-4 phase, and since it is possible to obtain homogeneous fine powder. The 1-2-4 phase's grain size is larger.

But 1-2-4 compound is thermodynamically stable under the high oxygen pressure bounded by the stable regions of the 1-2-4 and 1-2-3 phases; the required $P(O_2)$ with temperature. Figure 6 shows the result of XRD data for 1-2-4 sample after sintering under the high oxygen pressure (50 atm, 80 atm). As $P(O_2)$ increases with temperature at 80℃, impurity peak, CuO ($2\theta=38.8$), is gradually decreases and we conclude that the 1-2-4 phase is the predominant bulk superconductor under the high oxygen pressure. Also, inspite of phase transition is difficult under low temperature, Figure 7 shows that at 500℃, the 1-2-4 phase is stable in $P(O_2)=50$ atm.

Summary. We have succeeded in synthesizing the YBa_2

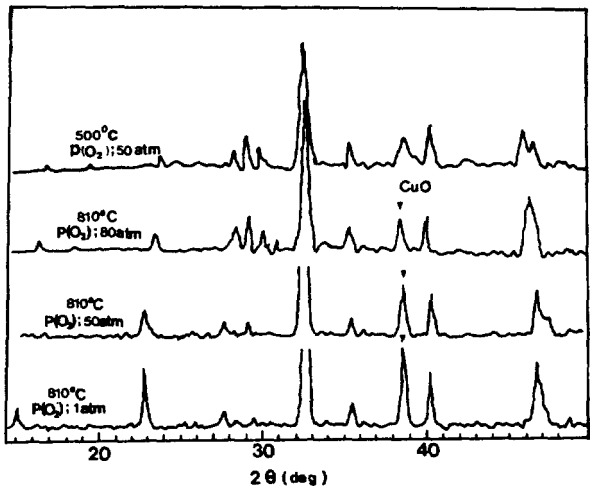


Figure 5. X-ray diffraction patterns of the 1-2-4 samples after sintering under the high oxygen pressure.

Cu_4O_8 superconductor by the EDTA complex pyrolysis method under 1 atm oxygen pressure. This method can overcome kinetic problems, since homogeneous fine powder is obtained. The starting material with 1-2-4 nominal composition was converted to the 1-2-3+CuO phase during densification, followed by the recovery of the 1-2-4 phase and the resultant samples were studied by the XRD, TG, DTA and AC magnetic susceptibility measurements. In conclusion, we have developed a new 1-2-4 synthesis requiring no special technique such as particularly high temperature and 1-2-4 phase is predominant as the $P(O_2)$ is increased.

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Average Walk Length in One-Dimensional Lattice Systems

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We consider the problem of a random walker on a one-dimensional lattice (N sites) confronting a centrally-located deep trap (trapping probability, $T=1$) and $N-1$ adjacent sites at each of which there is a nonzero probability s ($0<s<1$) of the walker being trapped. Exact analytic expressions for $<n>$ and the average number of steps required for trapping for arbitrary s are obtained for two types of finite boundary conditions (confining and reflecting) and for the infinite periodic chain. For the latter case of boundary condition, Montroll's exact result is recovered when s is set to zero.

Introduction

The theories of random walks on a space lattice have been dealt for a couple of decades since the turn of the century[1-4]. There are numerous examples which can be explained by a random walk on a space lattice. To name some of them, diffusion of electrons, excitons, energy transfer[3,5,6], etc.

In this paper for a particular class of one-dimensional lattice problem, we have shown an analytic expression for the average walk length on a chain with a centrally-disposed

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