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Annealing dependence of the superconductivity of $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$

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The effect of annealing conditions on the superconductivity of the Pb-based 1212 phase $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ system was studied. The weight change of the samples was measured by thermogravimetric analysis (TGA). The phases occurring in the samples were detected by X-ray diffraction (XRD) and their superconducting transitions were determined by alternating current (a.c.) susceptibility measurements. The results showed that the oxygen occupancy sites of the samples annealed under various conditions were different, and the oxygen content or oxygen occupancy site affected the phase formation of the sample. It has been found that there is an optimum value of oxygen content at which T_c is the highest, and the highest T_c can be obtained only within a very narrow range of oxygen content.

1. Introduction

Many investigations have shown that the superconductivities of the Pb-based 1212 phase compounds are unusually highly sensitive to annealing conditions [1–6]. A subtle processing technique is required to render these compounds superconducting. Ono and Uchida found that T_c was 17 K for the sample $Pb_{0.65}Sr_2Y_{0.7}Ca_{0.3}Cu_{2.35}O_y$ quenched from 860 °C to 77 K, but below 4.2 K when annealed in air at 300 °C followed by quenching [1]. For the (Pb, Cu)-1212, (Pb, Ca)-1212 and (Pb, Mg)-1212 systems, high pressure oxygen annealing was necessary for the occurrence of superconductivity [2–4]. However, post-treatment in oxygen was detrimental to the superconductivity of the (Pb, V)-1212 cuprate, and the superconductivity was only induced by annealing in a reducing atmosphere such as argon [5]. In the $(Pb_{1-x}Cd_x)Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_y$ system, the same annealing at 560 °C for 1 h, in air, which induced superconductivity in the non-superconducting "as-prepared" sample of $x = 0.1$, led to the suppression of the superconducting properties of the "superconducting as-prepared" samples of $0.2 \leqslant x \leqslant 0.6$ [6]. Tang *et al.* synthesized the 65 K superconductor $(Pb, Cu)Sr_2(Y, Ca)Cu_2O_{7-\delta}$ by precise oxygen adjustment [2]. They found that while oxidation in high pressure oxygen produced a high T_c superconductor, excess oxygen taken up during subsequent annealing at lower temperatures destroyed the superconductivity; so quenching was required for a high T_c. They also demonstrated that the oxygen content was critical and that there were both favourable and unfavourable oxygen sites for superconductivity in this compound. Maeda *et al.* [7] investigated structural changes accompanying oxygen incorporation in $(Pb, Cu)Sr_2(Ca, Y)Cu_2O_7$ using neutron powder diffraction. They found that slight structural and compositional differences between superconducting $(Pb_{0.65}Cu_{0.35})Sr_2(Y_{0.7}\ Ca_{0.3})Cu_2O_{7.0}$ and non-superconducting $(Pb_{0.65}Cu_{0.35})Sr_2(Y_{0.7}\ Ca_{0.3})Cu_2O_{7.1}$ markedly affected their electrical properties. The superconducting sample $(Pb_{0.65}Cu_{0.35})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_{7.0}$ was obtained by annealing the as-sintered non-superconducting sample $(Pb_{0.65}Cu_{0.35})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_{7.1}$ at 800 °C for 1 h, in air, and then quenching into liquid nitrogen to remove excess oxygen. The local structures of (Pb, Cu)O and SrO planes in the non-superconducting compound were more distorted than those in the superconducting one owing to the incorporation of excess oxygen, which suppressed superconductivity. The excess oxygen (0.1) was located at the interstitial site in the (Pb, Cu)O layer between the (Pb, Cu) metal ions along the *b*-axis. From the measured bond distances they also concluded that the transformation from a non-superconducting to a superconducting sample was associated with an increased charge transfer to the CuO_2 planes. So far, the effects of oxygen content and oxygen sites on T_c in this system are not clarified, and if investigated, they may lead to a better understanding

TABLE I Heat treatment conditions for $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ samples with various oxygen contents

Series	Temperature (°C)	Time (h)	Atmosphere	Cooling rate (°C min^{-1})	T_C(K)
A	930	4	Flowing oxygen	3300	50
B	930	4	Air	1800	94
C	930	4	Flowing oxygen	1	66
D	930	4	Sealed in a quartz tube	1	59

of the underlying mechanism. For this purpose, we studied the effect of annealing conditions on the superconductivity of $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$.

2. Experimental procedure

Samples with nominal composition $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ were synthesized by the solid state reaction method. Appropriate quantities of PbO, $SrCO_3$, Y_2O_3, $CaCO_3$ and CuO were mixed thoroughly by grinding in an agate mortar. The mixed powder was calcined at 900 °C for 5 h in air. The powder was then reground and pressed into pellets of 10 mm diameter and 1.5 mm thickness. Pellets with various amounts of oxygen content were obtained by four kinds of different heat treatments as illustrated in Table I:

1. they were sintered in a flowing oxygen atmosphere then quenched into liquid nitrogen (denoted as series A),
2. they were sintered in air atmosphere then quenched to room temperature (B),
3. they were also sintered in flowing oxygen but slowly cooled to room temperature (C), and
4. they were sealed in a quartz tube and sintered at 930 °C for 4 h then furnace cooled to room temperature (D).

The oxygen pressure in the sealed tube was 0.1 Mpa pressure at room temperature. The purpose of using the sealed quartz tube in point 4 was to give a high oxygen pressure at elevated temperatures. The estimated pressure in the sealed tube at 900 °C was 3.5 Mpa.

The phases presented in the samples were detected by XRD. Superconducting transitions were determined by a.c. susceptibility measurements. The weight change of the samples was measured using a Shimadzu DT-50 thermal analyser.

3. Results and discussion

Fig. 1 shows the TGA traces for the $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ samples annealed under various conditions. It is found that the shapes of the TGA curves are different for the four series, depending on the annealing histories of the samples. All the TGA curves can be divided into three stages; although the temperature ranges of the three stages are different for the various series. For series A, which was sintered in flowing oxygen, then quenched into liquid nitrogen, the weight was constant in the temperature range 20–180 °C (stage I). Then the unique weight loss of series A occurred in the temperature range 180–210 °C (stage II); the weight loss was 0.11%. Finally, the weight was constant again in the temperature range 210–900 °C (stage III). For series B and C, which were sintered in air or flowing oxygen, followed either by quenching to room temperature in air (B) or by slowly cooling to room temperature in flowing oxygen (C), the shapes of the TGA curves were quite similar. The weight was constant in the temperature range 20–180 °C (stage I). Then initial weight losses of 0.35% (B) and 0.37% (C) occurred in the range 180–760 °C (stage II). Finally, there were further losses of 0.36% (B) and 0.93% (C), in the range 760–900 °C (stage III). For series D, which was sealed in a quartz tube and sintered at 930 °C for 4 h, then furnace cooled to room temperature, the TGA curve was very different from those of the series A, B and C. It did not lose any weight in the range 20–460 °C (stage I). Then in the range 460–680 °C (stage II) there was a relatively rapid weight loss of 1.25%. Finally, 0.5% weight loss occurred in the range 680–900 °C (stage III).

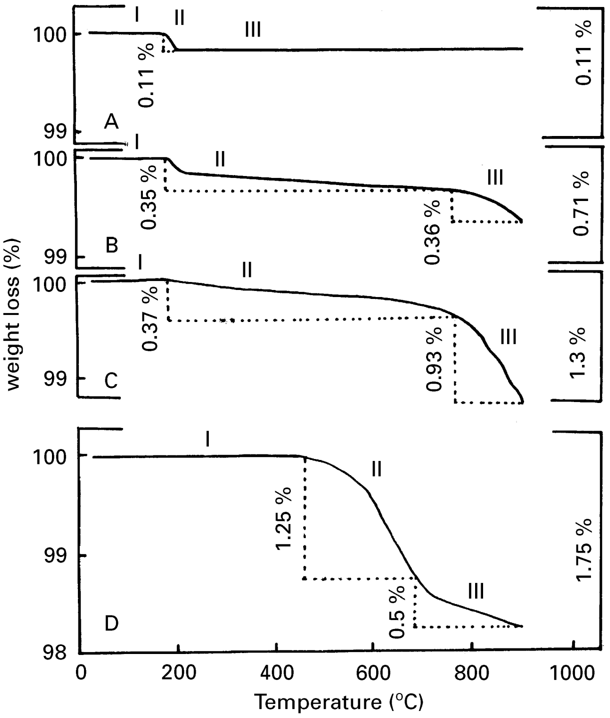

Figure 1 TGA traces for the series A, B, C and D conducted in nitrogen atmosphere. The heating rate is 10 °C min^{-1}.

The three stages of oxygen loss seen in the TGA curves suggest that the structure has three different oxygen sites. Hence, the occupancies of oxygen of the samples annealed under various conditions are different. The exact positions of the three oxygen sites have not yet been clearly determined. The total weight losses of the series A, B, C and D are 0.11, 0.71, 1.3 and 1.75%, respectively. It is reasonable to assume that the oxygen content can be determined by TGA, especially for the purpose of relative comparison. Therefore, from Fig. 1 we can conclude that the sequence of oxygen contents in these samples is as follows: oxygen content is highest in series D followed by series C,

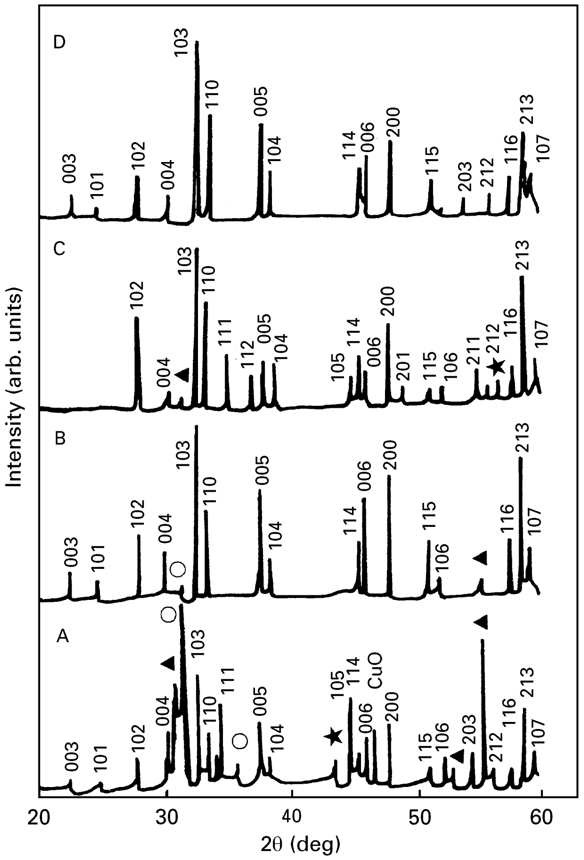

Figure 2 XRD patterns of the $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ samples annealed under various conditions: (★) Ca_2PbO_4, (▲) CaY_2O_4, (○) unknown phases. The Pb-1 2 1 2 phase is labelled as the *hkl* peaks.

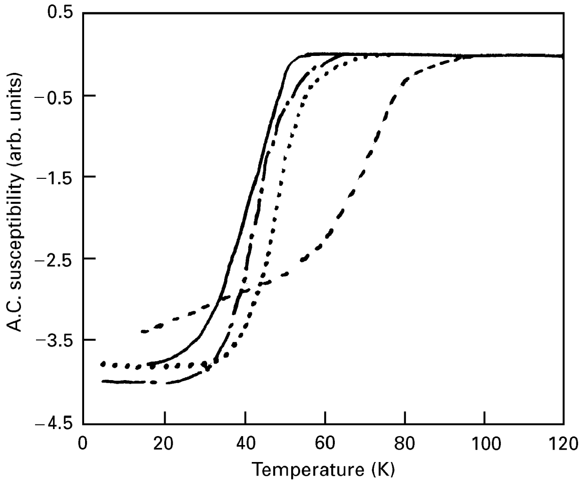

Figure 3 The temperature dependence of the a.c. susceptibility for the series A (-), B (– – –), C (· · ·) and D (—-—).

B then A. This is in agreement with what we would expect from the sample preparation conditions. From the view point of the annealing atmosphere and cooling rate, we expected that the oxygen content in series D would be the highest because the high oxygen pressure would lead to higher incorporation of oxygen in the sample. The oxygen content in series A was expected to be the lowest because its cooling rate was the fastest, thus the sample retained the lower oxidation state corresponding to the higher temperature annealing.

Fig. 2 shows the XRD patterns for the samples. Sample A is multiphase, consisting of Pb-1 2 1 2, Ca_2PbO_4, CaY_2O_4 and other unknown phases, in which the Pb-1 2 1 2 phase is only minor. Although sample A is multiphase, its TGA result is still meaningful for the purpose of relative comparison of the oxygen content of the Pb-1 2 1 2 phase among these samples. The weight loss of the Pb-1 2 1 2 phase in sample A must be less than 0.11% because it is multiphase. Samples B and C are nearly single phase Pb-1 2 1 2, but both include two weak peaks of impurity phases. Sample D shows a completely pure Pb-1 2 1 2 single phase. Therefore, the oxygen content or oxygen occupancy site can affect the phase formation of a sample. A single phase Pb-1 2 1 2 cannot be successfully synthesized if the oxygen content in a sample is too small. The temperature dependence of the a.c. susceptibility for the samples is shown in Fig. 3. The T_c values for the series A, B, C and D are 50, 94, 66 and 59 K, respectively. Combining with Fig. 1, it can be found that with increasing oxygen content from Series A to B, T_c value increases from 50 K to a maximum value of 94 K for series B, then it decreases to 59 K for series D with a further increase of oxygen content. Thus, it can be concluded that there is an optimum value of oxygen content at which T_c is the highest. It is worth noting that the only difference between series B and C in their TGA curves is the amount of weight loss at stage III; this is 0.36 and 0.93%, (respectively for samples B and C). However, this minor difference has resulted in a marked distinction in T_c values, one is 94 K and the other is 66 K. Hence, it is believed that the highest T_c can be obtained only within a very narrow range of oxygen content. The exact effect of the oxygen content on the superconductivity of the Pb-1 2 1 2 materials needs further investigation.

4. Conclusions

The shapes of TGA curves are different for $Pb_{0.65}Sr_{2.35}Y_{0.5}Ca_{0.5}Cu_2O_y$ samples annealed under various conditions, suggesting different oxygen sites of the samples under various annealings. However, phase purity complicates the analyses. The oxygen content or the oxygen occupancy site can affect the phase formation of a sample. A single phase Pb-1 2 1 2 cannot be successfully synthesized if the oxygen content in a sample is too small. There is an optimum value of oxygen content at which T_c is the highest and the highest T_c can be obtained only within a very narrow range of oxygen.

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