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Superconducting Transitions of $(Pb,V)Sr_2(Ca,Er)Cu_2O_z$ Quenched from High Temperatures

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Abstract

The influence of quenching temperature and annealing time on superconducting characteristics has been investigated for a $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$ compound . From the resistivity measurements for samples annealed at 400℃ to 860℃ in oxygen and subsequently quenched, it is observed that T_c(zero) of the sample decreases with the increase of annealing temperature up to 600℃and increases again beyond 700℃. Annealings of the sample at 860℃show that T_c(zero) goes through a maximum of 62K with the increase of the annealing time. It is also found that T_c(zero) of the sample quenched from high temperature decreases when the sample is subjected to low temperature annealing below 600℃in oxygen. The experimental results indicate that the as-prepared samples contain excessive oxygen and removal of this excessive oxygen in as-prepared samples is a key factor in controlling the superconducting properties of the samples and are discussed in connection with thermal gravimetric measurements.

Keywords: (Pb,V)-1212, quenching temperature, annealing time, transition temperature

I. Introduction

Superconductors with the Pb-1212 structure are of special interest due to their structural relationship with $YBa_2Cu_3O_7$ compound. The (Pb,Cu)-1212 was first synthesized with nominal compositions of $(Pb_{0.69}Cu_{0.31})Sr_2(Ca_{0.85}Y_{0.15})Cu_2O_z$[1] $(Pb_{0.71}Cu_{0.29})Sr_2(Ca_{0.73}Y_{0.27})Cu_2O_z$[2] and was thought not to be superconducting. Later, Rouillon et al. [3] discovered a new superconducting Pb-1212 compound with nominal composition of $(Pb_{0.5}Sr_{0.5})Sr_2(Ca_{0.5}Y_{0.5})$-$Cu_2O_z$. Subsequently, Ono and Uchida[4] were able to induce superconductivity in $(Pb_{0.65}Cu_{0.35})Sr_2$-$(Ca_{0.3}Y_{0.7})Cu_2O_z$ with a critical temperature of 17 K to induce superconductivity in $(Pb_{0.65}Cu_{0.35})Sr_2$-$(Ca_{0.3}Y_{0.7})Cu_2O_z$ with a critical temperature of 17 K by annealing in air at 860℃ for 1h and then quenching into liquid nitrogen. Thereafter, considerable efforts have been devoted to the study of this kind of material and several superconducting lead-based 1212 cuprates $(Pb,M)Sr_2(Ca_{1-x}Y_x)Cu_2O_z$ (M = Sr[3],Cu[4]-[7],Ca[8],Mg[9],Cd[10]) have been found. In spite of the great flexibility of the rock-salt-type (Pb,M)O layers in the Pb-1212 cuprates, most of these compounds except M=Cd are found to be comparatively difficult to prepare and only exhibit superconductivity when synthesized in the inert atmosphere[3],[8] and either annealed in high-pressure oxygen[7],[9] or quenched to ambient temperature[4]-[6].

Recently, we have successfully synthesized new Pb-based 1212 compounds of $(Pb_{1-x}V_x)Sr_2(Ca_{1-y}R_y)$-$Cu_2O_z$ with R=Y[11] and rare-earths[12] under oxygen atmosphere which exhibited bulk superconductivity in as-prepared samples. The critical temperature of the samples could be also improved by post

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annealing at high temperatures in oxygen atmosphere and then quenching. Similar improvement of super-conducting properties by the post heat-treatments has been also reported for (Pb,Cu)-based 1212 systems[4]-[6]. However, the reason why the quenched sample after annealing at high temperatures exhibited improved super-conductivity was not systematically investigated. In this work, we have addressed the effects of heat-treatment on superconducting properties of $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$ samples in detail and report here the results.

II. Experiments

Samples with nominal composition of $(Pb_{0.6}V_{0.4})$-$Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$ were prepared by solid state reaction . The starting materials with the appropriate ratios of PbO, V_2O_3, $SrCO_3$, $CaCO_3$, Er_2O_3 and CuO (all $\geq$ 99.9% pure) were mixed and heated at 790 ℃ for 10 h in air. The products were well ground, then pressed into pellets and sintered at 997℃ for 4 h in flowing O_2 followed by slow cooling to room temperature. The pellet samples were cut into rectangular specimen with dimension of about 0.1cm × 0.2cm × 1.0cm for measuring resistivity. The sliced specimen was subjected to a high temperature annealing in oxygen atmosphere and subsequently quenched into liquid nitrogen except noted otherwise. The resistivity was measured in the range of 8~300 K by the four-probe method. The measuring current was 5 mA. X-ray diffraction (XRD) analysis was carried out on a Rigaku diffractometer with Cu Kα radiation. Thermo-gravimetric analysis was carried out using a TA Inst. SDT-2960. The weight of the sample for analysis was about 20mg and the heating rate was 10℃/min in O_2 flow.

III. Results and Discussions

Figure 1 shows the powder XRD pattern of the as-prepared sample. The main phase could be indexed with tetragonal 1212 structure[4,5]. The impurity phases are marked by * and the main impurity phase is identified as $Sr_5Pb_3CuO_{12}$. Lattice constants of this sample are a=3.818Å and c=11.856Å. After the

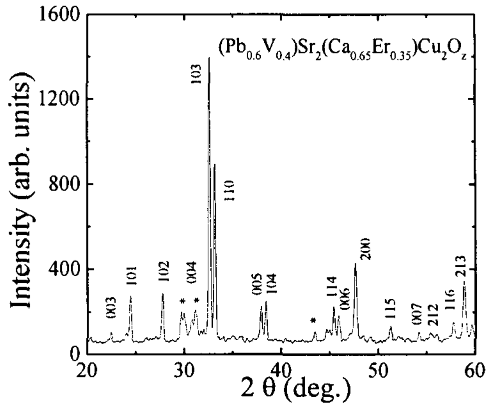

Fig. 1. The powder XRD pattern for the as-prepared sample with nominal composition $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$. Peaks due to impurity phase are also marked.

various heat treatments, the overall crystalline structure was unchanged.

Figure 2 shows the temperature dependence of electrical resistivity for $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})$-$Cu_2O_z$ samples annealed at various temperatures for 3 h in oxygen and subsequently quenched into liquid nitrogen. The as-prepared sample exhibits the onset transition temperature, T_c(onset)=34 K and zero-resistivity temperature, T_c(zero)=17 K and it can be seen that the T_c(zero) of the sample decreases with the increase of the annealing temperature up to 600℃ and increases again beyond 700℃ and reaches at a maximum value of 62K at annealing temperature of

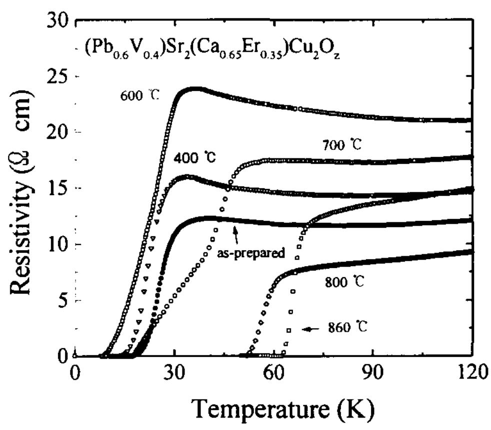

Fig. 2. Temperature dependence of electrical resistivity for $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$ samples annealed at various temperatures for 3h in oxygen and subsequently quenched.

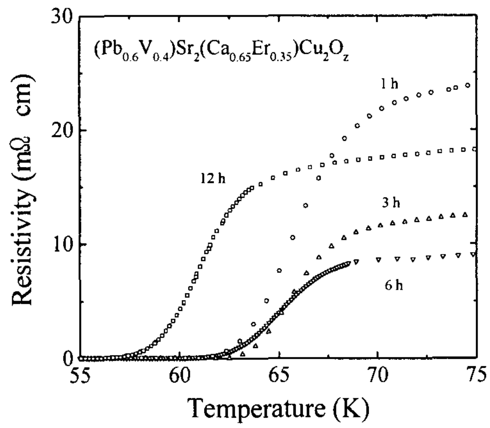

Fig. 3. Temperature dependence of electrical resistivity for ($Pb_{0.6}V_{0.4}$)Sr_2($Ca_{0.65}Er_{0.35}$)Cu_2O_z samples annealed at 860℃ for different annealing times.

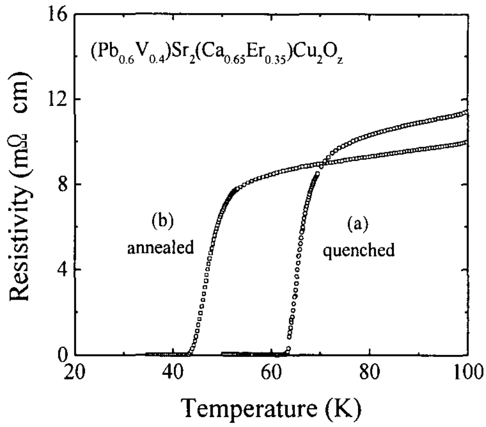

Fig. 4. Temperature dependence of electrical resistivity for ($Pb_{0.6}V_{0.4}$)Sr_2($Ca_{0.65}Er_{0.35}$)Cu_2O_z samples. Curve (a) refers to the quenched sample after annealing at 800℃ for 12h in oxygen and curve (b) refers to the same sample after a further heating up to 600℃ followed by cooling at a rate of about 10℃/min to room temperature in oxygen atmosphere (annealed sample).

860℃. Fig. 3 shows the temperature dependence of electrical resistivity for the ($Pb_{0.6}V_{0.4}$)Sr_2($Ca_{0.65}Er_{0.35}$)-Cu_2O_z samples annealed at 860℃ for different annealing times. One observes that T_c increases at first up to 3h and then decreases beyond this time. This fact suggests that the annealing time as well as the annealing temperature is also an important synthetic parameter for optimization of superconductivity of the 1212 sample. The fact that T_c goes through a maximum with the increase of the annealing time may imply that there is an optimum value of oxygen content which plays an important role in the superconductivity of cuprates.

From the results of Fig. 2 and Fig. 3, there is no doubt that annealing above 700℃ for the proper time in oxygen followed by quenching is a key factor for optimization of the superconductivity. Since the high temperature annealing followed by quenching is expected to leave less oxygen in as-prepared samples, the improvement of superconducting properties by quenching implies that there is excessive oxygen in the as-prepared samples. In order to evaluate the effect of quenching, the sample obtained by quenching after annealing at 800℃ for 12h (quenched sample) was further subjected to heating in flowing oxygen up to 600℃ followed by cooling down to room temperature at a rate of about 10℃/min (annealed sample). The resistivity measurements performed before and after this additional treatment are shown in Fig. 4. The T_c(zero) of the quenched sample (curve (a)) is 62.5K and nearly the same as that of the sample annealed at 860℃ for 3h and then quenched. We find that the annealed sample (curve (b)) exhibits a significant degradation of superconductivity compared to that of the quenched sample (curve (a)). This result demonstrates why the quenching is required for high temperature superconductivity in the (Pb,V)-1212 system. The lattice constants are a=3.812Å and c=11.851Å for the quenched sample, and they are a=3.814Å and c=11.852Å for the annealed sample. Thus, we can notice that the improvement of the superconductivity for the quenched sample is related to the decrease of the lattice constants. The decrease of the lattice constants of quenched samples caused by the quenching procedure has been also reported for the (Pb,Cu)-1212 compound[4].

The variation of the critical temperature after various thermal treatments may be related to the change in oxygen content of the (Pb,V)-1212 phase. To find some information on change of the oxygen content, thermogravimetric analysis (TGA) was carried out on an as-prepared sample (curve a), a quenched sample

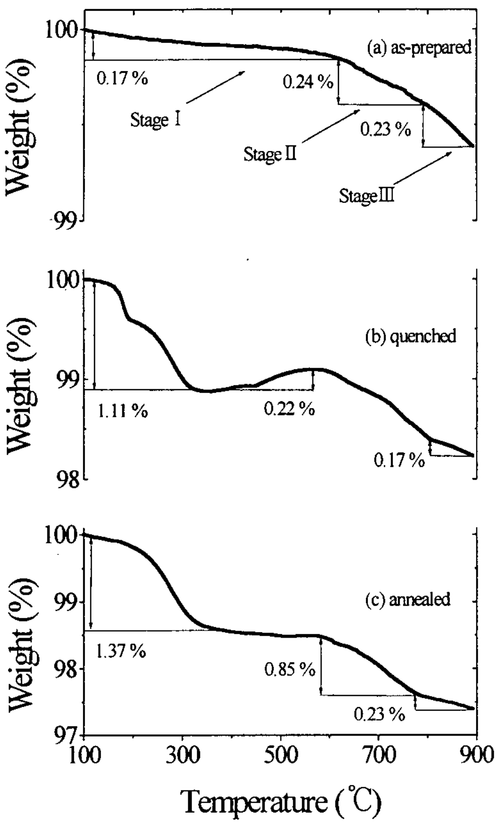

Fig. 5 The results of thermogravimetric analysis for $(Pb_{0.6}V_{0.4})Sr_2(Ca_{0.65}Er_{0.35})Cu_2O_z$ samples. The heating rate was 10℃/min in O_2 flow. Curve(a) refers the as-prepared sample. Curve (b) refers to the quenched sample after annealing at 800℃ for 12h in oxygen and curve (b) refers to the same sample after a further heating up to 600℃ followed by cooling at a rate of about 10℃/min to room temperature in oxygen atmosphere (annealed sample).

(curve b), and an annealed sample (curve c) and the results are shown in Fig. 5. It can be seen from Fig. 5(a) that the weight loss of the as-prepared sample takes place in three stages. The stage-I loss of the sample occurs in the temperature range 100~620℃. But the weight loss in the temperature between 350~620℃ is very small. Then, in the temperature range 620~800℃, there is a stage-II loss. Finally, there is a third weight loss from 800~900℃. Comparing Fig. 5(a) with Fig.2, we can infer that stage-II and stage-III losses cause a significant improvement of the super-conducting properties of the sample. The TGA curve for the quenched sample shows a large decrease of weight in the range 100~350℃ and a slight increase of weight at around 580℃. This increase of weight was not observed for the annealed sample. The increase of weight at around 580℃ means that the quenched sample absorbs oxygen at the corresponding temperature and reveals that the quenched sample has less oxygen than the as-prepared sample, as expected. In stage-I, the weight loss of the annealed sample was relatively higher, 1.37% versus 1.11% for the quenched sample. It should be noted that TGA curves for both quenched and annealed samples were obtained using the same specimen subjected to consecutive heat treatments. Consequently, both the degradation of the superconductivity and the increase of the lattice constants observed in the annealed sample compared to those of the quenched sample (Fig. 4) can be attributed to uptake of oxygen during the annealing process.

IV. Summary

The effects of annealing on superconducting properties of a 1212 lead cuprate, $(Pb_{0.6}V_{0.4})Sr_2$-$(Ca_{0.65}Er_{0.35})Cu_2O_z$ have been studied by characterizing samples annealed at 400℃ to 860℃ in oxygen and subsequently quenched by XRD, resistivity and TGA measurements. It was observed that annealing under oxygen atmosphere below 600℃ degrades the superconducting properties of the sample, while annealing at temperature between 700~860℃ improves significantly the critical temperature of the sample. The annealing time as well as the annealing temperature is also found to be an important synthetic parameter for optimization of superconductivity of the 1212 sample. We also found that Tc of the (Pb.V)-1212 sample quenched from 800℃ decreases when the sample is subjected to low temperature annealing below 600℃ in oxygen due to uptake of oxygen during the annealing process. This uptake of oxygen has also brought about an increase of lattice constants. The improvement in T_c observed for samples annealed at high temperatures could be associated with the weight loss in the temperature range 620℃~900℃ observed in TGA curves. From these results, it is concluded that the removal of excessive oxygen in as-prepared samples is a key factor for optimization of the superconductivity.

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