Preparation of YBCO with additives of PbO, $BaPbO_3$ and its Superconducting Properties

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Abstract – The melting temperature and critical temperature (Tc) of $YBa_2Cu_3O_x$ with deferent content impurities of PbO and $BaPbO_3$ were studied. When the PbO was used as addition in $YBa_2Cu_3O_x$, although the melting point could be reduced, the superconductivity (the transition wide, ΔTc) became poor. From the XRD pattern of the sintered mixture of $YBa_2Cu_3O_x$ and PbO it was known that there is a reaction between $YBa_2Cu_3O_x$ and PbO, and the product is $BaPbO_3$. In the process of the reaction the superconducting phase of $YBa_2Cu_3O_x$ was decreased and in the sample $BaPbO_3$ became the main phase. Therefore the superconductivity was reduced. $BaPbO_3$ was chosen as the impurity for the comparative study. The single phase $BaPbO_3$ was synthesized by the simple way from both mixtures of $BaCO_3$ and PbO, $BaCO_3$ and PbO_2. Deferent contents of $BaPbO_3$ (10%, 20%, 30%) were added in the $YBa_2Cu_3O_x$. By the phase analysis in the XRD patterns it was proved that there were not reactions between $YBa_2Cu_3O_x$ and $BaPbO_3$. When $BaPbO_3$ was used as impurity in $YBa_2Cu_3O_x$ the superconductivity was much better than PbO as impurity in $YBa_2Cu_3O_x$. But the melting point of $YBa_2Cu_3O_x$ with $BaPbO_3$ could not be found when the temperature was lower than 1000℃ in the DTA measurement.

Key words – YBCO, additives, PbO, $BaPbO_3$, superconductivity

I. INTRODUCTION

BiPbSrCaCuO system is well known developed in making superconducting tape by Powder-In-Tube (PIT) method nowadays in the world, but its critical current decreases very fast with the increasing magnetic field, that is the main drawback to be overcome difficultly. $YBa_2Cu_3O_x$ superconductor has good superconductivities under higher magnetic field, but Powder-In-Tube method can not be used for $YBa_2Cu_3O_x$ superconductor due to that its melting point is about 50 ℃ higher than that of silver. The scientists are trying to utilize the methods for preparation of $YBa_2Cu_3O_x$ superconducting films to fabricate wires or tapes [1, 2, 3, 4, 5].

Almost all the equipments are operated in vacuum and the long wire preparation is very difficult. If the meting temperature of $YBa_2Cu_3O_x$ could be reduced below the melting point of Ag the PIT technique for Bi system wires can be used for the

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preparation of $YBa_2Cu_3O_x$ wire. One way to reduce the melting temperature is to add one low melting point substance into $YBa_2Cu_3O_x$ matrix according to the thermodynamic principle. The substance must have following properties: (1) It is stable in the $YBa_2Cu_3O_x$ matrix, it does not react with $YBa_2Cu_3O_x$, (2) It can not reduce the superconductivities of $YBa_2Cu_3O_x$ when it is added into $YBa_2Cu_3O_x$. In the experiment different contents of PbO and $BaPbO_3$ were added in the $YBa_2Cu_3O_x$ matrix, the chemical reactions between the additives and $YBa_2Cu_3O_x$ as well as the transition temperatures were studied respectively.

II. EXPERIMENT

2-1 Preparation of samples of $YBa_2Cu_3O_x$ with additions and the property measurement

$YBa_2Cu_3O_x$ powder was synthesized by the sol-gel method, which was single phase, 90 K zero resistance and 0.2-1.0 μm of particle size.

In the first group samples 5 wt%, 10 wt%, 15 wt% of PbO were added in $YBa_2Cu_3O_x$. In the second group samples 10wt%, 20wt%, and 30wt% of $BaPbO_3$ were added in $YBa_2Cu_3O_x$. The mixture pellets were heated to 800℃for 10 hours. The samples were oxygenated at 400℃for 10 hours after sintering. The superconductive transition temperature was measured with standard four lines method, and the phase composition was examined with X-ray diffraction (XRD).

2-2 Sintering of $BaPbO_3$

The synthesis of $BaPbO_3$ has been presented by deferent ways [6, 7].

In the experiment $BaPbO_3$ was synthesized from the mixture of $BaPbO_3$ and PbO or PbO_2. The reactions in the synthesis processing respectively are:

$$BaPbO_3 + PbO + 1/2O_2 = BaPbO_3 + CO_2 \quad (1)$$

$$BaPbO_3 + PbO_2 = BaPbO_3 + CO_2 \quad (2)$$

The mixture samples were sintered at 800℃in air for 10 hours. The phase composition of the product was examined by XRD. The XRD patterns of samples sintered from equation (1) and (2) are shown in figure 1. Comparing the XRD data with the standard one [8], it is proved that the products are single phase $BaPbO_3$, which could be sintered using either PbO or PbO_2 in air.

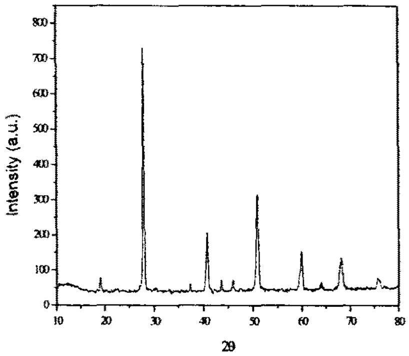

Fig. 1. XRD pattern of $BaPbO_3$ sintered from $BaCO_3$ and PbO or PbO_2

III. RESULTS AND DISCUSSION

3-1. The effects of PbO on the melting temperature and critical temperatures of $YBa_2Cu_3O_x$

The relation of $YBa_2Cu_3O_x$ and the PbO contents are shown in figure 2.

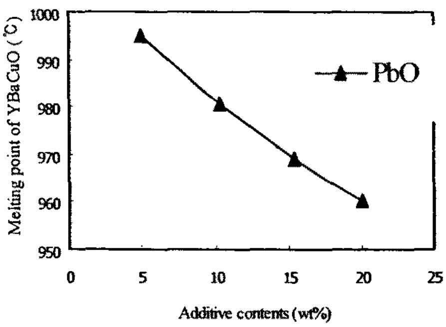

Fig.2. The melting points of $YBa_2Cu_3O_y$ with different PbO contents

The melting temperature of $YBa_2Cu_3O_x$ is decreased with the increasing PbO contents. When the PbO content reaches 20wt% the melting temperature reduces to about 960℃. From the results the melting temperature was reduced remarkably with the increasing PbO contents. After the measurements of critical temperature(Tc) of the PbO doped $YBa_2Cu_3O_x$ and the transition wide (△Tc) are shown as in table 1.

Table 1 PbO content and its effect on the critical temperature

Sample	PbO (wt %)	Tc,onset, K	△Tc, K	Tc0, K
1	0	92.0	3.0	89
2	5	90.3	11.2	81.1
3	10	92.6	11.5	81.1
4	15	91.0	11.2	80.8
5	20	88.2	11.6	

Although the PbO doped $YBa_2Cu_3O_x$ samples are 90 K zero resistance superconductor, their transition width is about 11 K, for comparison, △Tc of pure $YBa_2Cu_3O_x$ sample is only 3 K. It is reasonable to think that there is a reaction between PbO and $YBa_2Cu_3O_x$ and PbO is not a independent phase in $YBa_2Cu_3O_x$ matrix. The reaction and the result may have effect on the superconductivities of $YBa_2Cu_3O_x$.

3-2 The chemical reactions between PbO and $YBa_2Cu_3O_x$

A sample with components of $YBa_2Cu_3O_x$ (70%), PbO (20%), Ag (10%) was heated at 850℃ for 5 hours. The sample was examined by X-ray diffraction (XRD). The XRD pattern is shown in figure 3. In the XRD pattern the main phase is $BaPbO_3$, and other two phases are $YBa_2Cu_3O_x$ and Ag. The PbO phase disappeared and $YBa_2Cu_3O_x$ phase reduced obviously.

It can be deduced that there is a reaction between $YBa_2Cu_3O_x$ and PbO, the product of the reaction is $BaPbO_3$, that is:

$$2PbO+YBa_2Cu_3O_{6.5}+O_2=2BaPbO_3+1/2Y_2O_3+3CuO \quad (3)$$

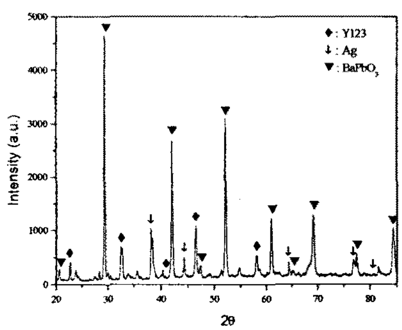

Fig.3. XRD of Sintered mixture of $YBa_2Cu_3O_x$, PbO and Ag

The mole ratio should be 42.4 mol% of PbO and 57.6 mol% of $YBa_2Cu_3O_{6.5}$, if the addition of PbO is 20 wt% in $YBa_2Cu_3O_{6.5}$. According to reaction (1), 21.2 mol% $YBa_2Cu_3O_{6.5}$ would be consumed, and remained $YBa_2Cu_3O_{6.5}$ is 57.6-21.2=36.4 mol%, which has the mole ratio of 23.8 mol% in products after sintering. That small superconductive phase (23.8 mol%) may be the reason of large transition wide (ΔTc).

The chemical reaction is an oxidized process. If the reaction was controlled in low oxygen partial pressure or in inert gas the oxidation process may be suppressed.

3-3. Study of properties of $YBa_2Cu_3O_x$ added with $BaPbO_3$

$BaPbO_3$ was studied as additive in $YBa_2Cu_3O_x$ by several authors [9, 10], and it is a promising inter-granular material for synthesis of $YBa_2Cu_3O_x$ composites. In the experiment 10%, 20% and 30% of $BaPbO_3$ were added in the $YBa_2Cu_3O_x$ matrix. The XRD patterns of $YBa_2Cu_3O_x$ with different BaPbO contents are shown in figure 4.

Table 2 Superconductivity of $YBa_2Cu_3O_x$ with $BaPbO_3$

Sample	$T_{c,\ onset}$, K	ΔT_c, K	T_{c0}, K
Y123	91.2	0.75	90.45
Y123 + 10% BPO	91.2	6.0	85.2
Y123 + 20% BPO	91.9	3.7	88.2
Y123 + 30% BPO	90.5	6.7	83.8

In each XRD pattern in figure 4 there are not any other impurity phases except the original two phases, $YBa_2Cu_3O_x$ and $BaPbO_3$, and the diffraction intensities of $BaPbO_3$ increase proportionally with increasing its content in $YBa_2Cu_3O_x$ matrix. It can be concluded that there are not any chemical reactions between $YBa_2Cu_3O_x$ and $BaPbO_3$.

The critical temperature of above 3 samples was measured by 4 probe method. The results are shown as in table 2.

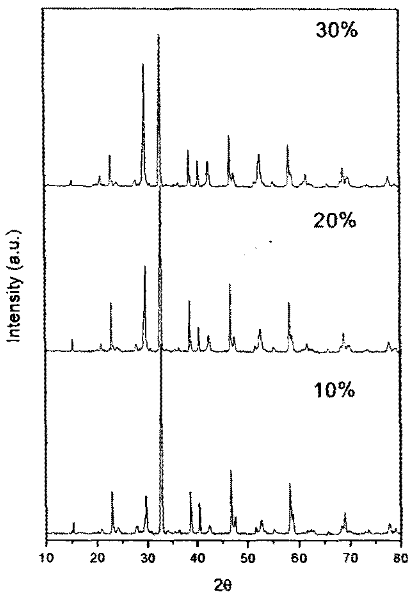

Fig. 4. XRD patterns of $YBa_2Cu_3O_x$ with 10%, 20%, and 30% of $BaPbO_3$

From table 2 it can be seen that ΔT_c and T_{c0} of $YBa_2Cu_3O_x$ with $BaPbO_3$ were improved compared with that of $YBa_2Cu_3O_x$ with PbO in table 1. Unfortunately, the melting temperature of $YBa_2Cu_3O_x$ doped with $BaPbO_3$ could not be found when the temperature was lower than 1000℃ in the DTA measurement.

IV. CONCLUSIONS

When the PbO was used as addition for reducing the melting point of $YBa_2Cu_3O_x$, although the melting point could be reduced, the superconductivity (the transition wide, ΔT_c) became pure. There is a reaction between $YBa_2Cu_3O_x$ and PbO, and the product is $BaPbO_3$, which was studied from XRD phase analysis. In the process of the reaction the superconducting phase of $YBa_2Cu_3O_x$ was decreased and in the sample $BaPbO_3$ became the main phase. Therefore the superconductivity was reduced. The single phase $BaPbO_3$ was synthesized by the simple way from both mixtures of $BaPbO_3$ and PbO, $BaPbO_3$ and PbO. Deferent contents of $BaPbO_3$ (10%, 20%, 30%) were added in the $YBa_2Cu_3O_x$. There are not reactions between $YBa_2Cu_3O_x$ and $BaPbO_3$. When $BaPbO_3$ was used as impurity in $YBa_2Cu_3O_x$ the superconductivity was much better than PbO as impurity in $YBa_2Cu_3O_x$. But the melting point of $YBa_2Cu_3O_x$ with $BaPbO_3$

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