Effects of Additives on the Properties of $YBa_2Cu_3O_X$

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Abstract

The superconducting properties of $YBa_2Cu_3O_x$ with different content impurities of PbO and $BaPbO_3$ were studied. When the PbO was used as an additive in $YBa_2Cu_3O_x$, although the melting point could be reduced, the superconductivity 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 $BaPbO_3$ would be the main phase in the sample. Therefore, $BaPbO_3$ was chosen as the impurity additive for the comparative study. The single phase of $BaPbO_3$ was synthesized by the simple way from both mixtures of $BaCO_3$ and PbO, $BaCO_3$ and PbO_2. Different 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 was no reaction 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 an impurity additive in $YBa_2Cu_3O_x$.

Key Words : impurities, additive, melting point, superconducting phase, single phase

1. Introduction

$YBa_2Cu_3O_x$ superconductor has good superconductivities under higher magnetic field, but Powder In Tube method (PIT) 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 [1-5]. Almost all the equipments are operated in vacuum and the long wire preparation is very difficult. If the melting temperature of YBa2Cu3Oxcould be reduced below the melting point of Ag the PIT technique for Bi system wires can be used for the 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 as well as the superconducting properties of $YBa_2Cu_3O_x$ were studied respectively.

2. 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 [6], which was single phase, 90 K zero resistance and 0.2~1.0 μm of particle size. In the first group samples 5, 10, 15 wt% of PbO were added in $YBa_2Cu_3O_x$. In the second group samples 10, 20, and 30 wt% of $BaPbO_3$ were added in $YBa_2Cu_3O_x$. The mixture pellets were heated to 880 ℃ for 10 hours. The samples were oxygenated at 400 ℃ for 10 hours after sintering. The superconductive transition temperature and electric properties were measured with standard four probe method, and the phase composition was examined with X-ray diffraction (XRD) and EDX.

2.2 Sintering of $BaPbO_3$

The synthesis of $BaPbO_3$ has been presented by deferent ways [7,8]. In the experiment $BaPbO_3$ was synthesized from the mixture of $BaCO_3$ and PbO or PbO_2. The reactions in the synthesis processing respectively are:

$$BaCO_3 + PbO + 1/2O_2 = BaPbO_3 + CO_2 \quad (1)$$

$$BaCO_3 + PbO_2 = BaPbO_3 + CO_2 \quad (2)$$

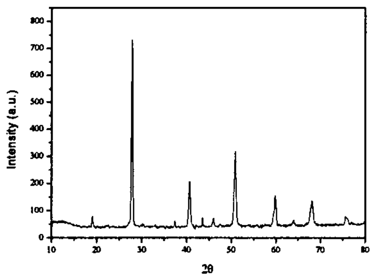


Fig. 1. XRD pattern of $BaPbO_3$ sintered from $BaCO_3$ and PbO or PbO_2

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 Fig. 1. Comparing the XRD data with the standard one [9], it is proved that the products are single phase $BaPbO_3$, which could be sintered using either PbO or PbO_2 in air.

3. Results and Discussions

3.1 The effects of PbO on the melting temperature and the superconductivies of $YBa_2Cu_3O_x$

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

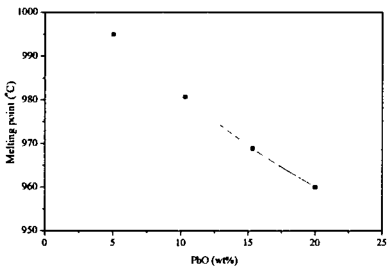


Fig. 2. The melting points of $YBa_2Cu_3O_x$ with different PbO contents

The melting temperature of $YBa_2Cu_3O_x$ is decreased with the increasing PbO contents. When the PbO content reaches 20 wt% the melting temperature reduces to about 960 ℃. From the results the melting temperature was reduced remarkably with the increasing PbO contents.

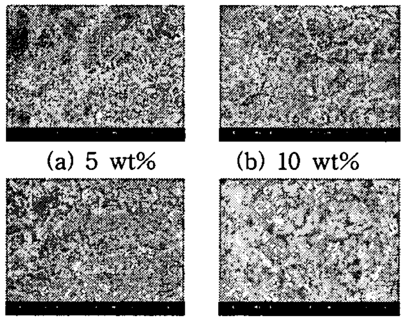


Fig. 3. SEM photographs(×2000) of $YBa_2Cu_3O_x$ sample prepared with sol-gel synthesized powder and 20 wt% PbO.

Table 1. PbO content and its effect on the critical temperature

No.	PbO (wt %)	$T_{c,onset}$, K	ΔT_c, K	T_{c0}, 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	-

Figure 3 showed the surface state of samples with PbO additives of 5~20 wt%. After the measurements of superconductivities of the PbO doped $YBa_2Cu_3O_x$ are shown as in table 1.

Although the PbO doped $YBa_2Cu_3O_x$ samples are 90 K zero resistance superconductors, their transition width are about 11 K, for comparison, ΔT_c of pure $YBa_2Cu_3O_x$ sample is only 3 K.

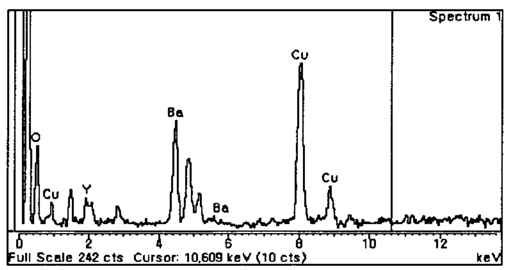


Fig. 4. EDS analysis of $YBa_2Cu_3O_x$ sample prepared with sol-gel powder and 15 wt% PbO.

Table 2. The critical current density of $YBa_2Cu_3O_x$ samples with different PbO content

No.	Contents of PbO (wt%)	J_c, (A/㎠)
1	0	272
2	5	415
3	10	293
4	15	349
5	20	283

From the EDX analysis (Fig. 4) and measurement of critical current density (Table 2) it is reasonable to think that there is a reaction between PbO and $YBa_2Cu_3O_x$ and PbO is not an 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 Fig. 5. 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.

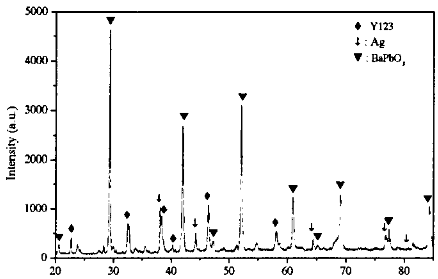


Fig. 5. XRD of Sintered mixture of $YBa_2Cu_3O_x$, PbO and Ag

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:

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

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 width (ΔT_c).

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 a conductive additive in $YBa_2Cu_3O_x$ by several authors [10,11], 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 into the $YBa_2Cu_3O_x$ matrix. 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.

The XRD patterns of $YBa_2Cu_3O_x$ with different $BaPbO_3$ contents are shown in Fig. 6. In each XRD pattern in Fig. 6 there are not any other impurity phases except the origin 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 $BaPbO_3$.

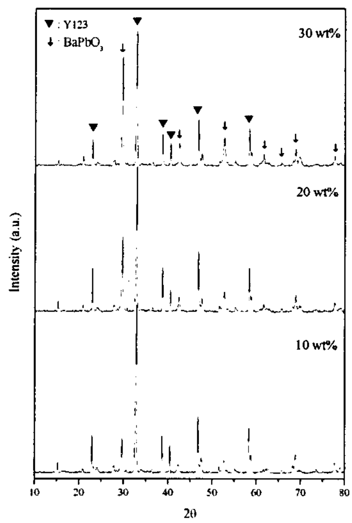
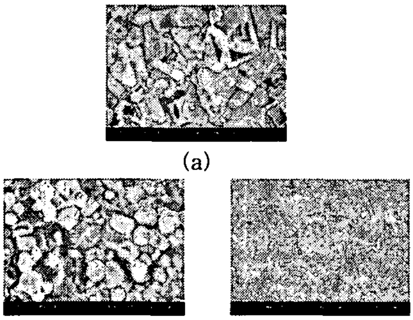


Fig. 6. XRD patterns of $YBa_2Cu_3O_x$ with 10%, 20%, and 30% of $BaPbO_3$.

The critical temperature and critical current density of above 3 samples were measured by four probe method after calcination and oxygenation process. Figure 7 is the SEM photographs of samples with addition of BaPbO3. The superconductivities of samples are shown as in table 3.



(a) (b) (c)

Fig. 7. SEM photographs (×2000) of $YBa_2Cu_3O_x$ samples with different content of $BaPbO_3$.

From table 3 it can be seen that the critical temperature and the critical current density of YBa2Cu3Ox with an addition of BaPbO3were improved compared with that of YBa2Cu3Ox with PbO in table 1.

Table 3 Superconductivity of $YBa_2Cu_3O_x$ with $BaPbO_3$

No.	Contents of BPO (wt%)	T_c, (K)	ΔT_c, (K)	J_c, (A/㎠)
1	10	91.2	6.0	443
2	20	91.9	3.7	474
3	30	90.5	6.7	282

4. 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 width, 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 $BaCO_3$ and PbO, $BaCO_3$ and PbO_2. Deferent contents of $BaPbO_3$ (10%, 20%, 30%) were added in the $YBa_2Cu_3O_x$. There are not reactions between $YBa_2Cu_3O_x$ and $BaPbO_3$. When BaPbO3 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.

References

[1] K. Hasegawa, K. Fujimo, H. Mukai, M. Konishi, K. Hayashi, K. Sato, S. Honjo, Y. Sato, H. Ishi, and Y. Iwata: Appl. Supercond., 1998, 4, 487.

[2] M. Fukutomi, S. Aoki, K. Komori, R. Chatterjee, and H. Maeda: Physica C, 1994, 219, 333.

[3] A. Goyal, D.P. Norton, D. Kroeger, D. K. Christen, M. Paranthaman, E. D. Specht, J. D. Budai, Q. He, B. Saffian, F. A. List, D. F. Lee, E. Hatfield, C. E. Klabunde, P. M. Martin, J. Mathis, and C. Park: J. Mater. Res., 1997, 12, 2924.

[4] Z. Aslanoglu, Y. Akin, M. I. El-Kawni, L. Arda, W. Sigmund, and Y. S. Hascicek: IEEE Trans. Appl. Supercond., 2003, 13, 2755.

[5] T. Yamashita, A. Y. Ilyushechkin, J. A. Alarco, J. Riches, P. Talbot, and I. D. R. Mackinnon: Physica C, 2000, 341-348, 2485.

[6] F. H. Li, J. Wang, D. W. Soh, Z. G. Fan: J. of the Chinese Rare Earth Soc., 2002, 20, 501.

[7] S. L. Zhang, S. M. Wang, Z. X. Chen, L. Zhao, and Z. X. Xu: Journal of Hubei University (Natural Science Edition), 2001, 23(4), 335 (in Chinese)

[8] X. Y. Liu, M. Y. Zhan, and M. Zhou: Rare Metals and Hard alloys, 1999, 138, 11 (in Chinese)

[9] 1995 JCPDS-International Centre for Diffraction Data, 12-0664, BaPbO3

[10] A. G. Mamalis, S. G. Ovchinnikov, M. I.Petrov, D. A. Balaev, K. A. Shaihutdinov, D. M. Gohfeld, S. A. Kharlamova, and I. N. Vottea: Physica C, 2001, 364-365, 174.

[11] J. Y. Kim, S. Y. Lee, I. S. Yang, T. G. Lee, S. S. Yom, K. B. Kim, and J. H. Kim: Physica C, 1998, 308, 60.