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RESEARCH ARTICLE

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Influence of the rare earth element substitution on oxygen adsorption-desorption properties of YBCO

Abstract The oxygen adsorption-desorption properties of $RBa_2Cu_3O_{7-\delta}$（R＝Gd, Er, Eu, Dy, Sm, Ho and Nd）and $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ (x＝0.1, 0.5 and 1.0) were investigated from room temperature to 950 ºC by thermogravimetry (TG). The results show that all samples will release oxygen with the increasing of temperature and the released oxygen can be absorbed back into the sample when temperature decreases. However, dependent on the rare earth element, the amount of the released oxygen is different for these samples. Moreover, in the temperature increasing and decreasing circle the repetition of oxygen adsorption-desorption is also different.

Keywords $YBa_2Cu_3O_{7-\delta}$, rare earth, substitution, oxygen adsorption-desorption, thermogravimetry

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1 Introduction

Since the discovery of high temperature superconductor $YBa_2Cu_3O_{7-\delta}$ (YBCO) in 1987, researches on its superconducting properties as well as applications have made remarkable progress. Lots of information about structure and performance of YBCO were obtained, however, the superconductivity mechanism has not yet been understood clearly now. Oxygen content of YBCO plays an important role in determining its superconductivity. The more oxygen content, the higher the superconducting transition temperature T_c is. When the oxygen content $7-\delta$ is less than 6.5, the superconductivity disappears. In order to elevate the T_c and investigate the superconducting mechanism, partial even entire substitution of elements in YBCO by other elements was investigated. Substitution Y by other rare earth (lanthanum-lutetium) results in the so-called R-123 series. The T_c of the samples in this series are almost the same [1].

Because of the importance of oxygen content to YBCO superconducting properties the oxygen diffusion and adsorption-desorption properties have been studied throughly in the past years. Basically, YBCO will release oxygen with the increasing of temperature and absorb oxygen back into the sample when temperature decreasing, which can be called as an oxygen respiration phenomenon [2－5]. It is interested to investigate whether this oxygen respiration phenomenon changes when Y is substituted by other rare earth. In this article we report the oxygen adsorption-desorption properties of $RBa_2Cu_3O_{7-\delta}$ (R = Gd, Er, Eu, Dy, Sm, Ho and Nd) and $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ (x = 0.1, 0.5 and 1.0) from room temperature to 950 °C. The results show that the amount of the released oxygen is different for sample with different rare earth element. Moreover, the repetition of oxygen adsorption-desorption in the temperature increasing and decreasing circle is also different.

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2 Experimental

Samples $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ (x = 0.1, 0.5 and 1.0) were prepared by solid state reaction method. The starting materials of Y_2O_3, La_2O_3, $BaCO_3$ and CuO weighed precisely as Y:La:Ba:Cu=(1–x):x:2:3 were thoroughly mixed and ground repeatedly. The mixture was then pressed into pellet. The sample was sintered at 950 ºC in static air. Grinding, moulding and sintering repeat 3 times. The samples of RBa_2

$Cu_3O_{7-\delta}$(R=Gd, Er, Eu, Dy, Sm, Ho and Nd) were offered by Northwest Institute of Non-ferrous Metal Research.

The oxygen absorption and desorption character of samples were measured by a thermal analyzer (SETARAM Labsys^{TM}). The experiment of the mass variation of a bulk sample with temperature was carried out in static air and repeated in two cycles between 300 ºC and 950 ºC with heating and cooling rate 10 ºC /min, respectively.

3 Results and discussion

3.1 Sample structure

The XRD patterns for $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ (x = 0.1, 0.5 and 1.0) are shown in Fig. 1. The main phase of these samples is R-123. All samples but x = 0.1 have a small amount of impurity phase of $Ba2Cu3O_{5-\delta}$ because pure La-123 phase is difficult to be prepared under static air [1]. The crystal parameters were calculated using the data of XRD and listed in Table 1. The more La, the larger crystal parameters are except b axis of the example with x = 0.1. The XRD patterns for $RBa_2Cu_3O_{7-\delta}$ (R = Gd, Er, Eu, Dy, Sm, Ho and Nd) show that the structures of all samples are very pure R-123 phase.

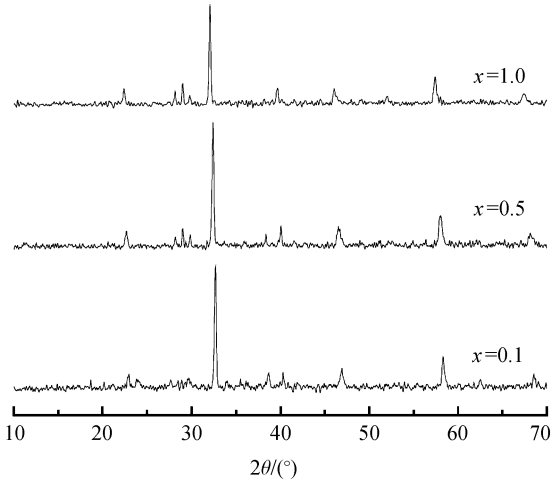

Fig. 1 XRD patterns for $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$.

Table 1 The crystal parameters of $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$.

La content x	a /Å	b /Å	c /Å
0.0	3.819	3.885	11.633
0.1	3.862	3.874	11.637
0.5	3.869	3.921	11.691
1.0	3.924	3.966	11.710

3.2 Adsorption-desorption property of the samples

The mass changes of $RBa_2Cu_3O_{7-\delta}$ except for Nd-123 show a very unshapely repetition in the thermogravimetric experiments. The weight losses of samples are obvious in the preliminary stage of the temperature increasing. The result shows that the samples are intensively hydrophilic in room temperature. The mass curve of the Dy-123 is shown in Fig. 2. It's repetition is more better than that of the samples R-123 (R = Gd, Er, Eu, Sm and Ho). The increase of mass in decreasing temperature can not cancel out the mass decrease in increasing temperature at every circle, which shows that oxygen desorption speed of the sample is greater than oxygen adsorption. The mass of all the samples $RBa_2Cu_3O_{7-\delta}$ but Nd-123 can not recover. The mass curve of the Nd-123 is shown in Fig. 3. We can see that the repetition of Nd-123 is good. But in comparison with the mass curve of YBCO not only repetition is bad, but also the ratio of oxygen content variation is small.

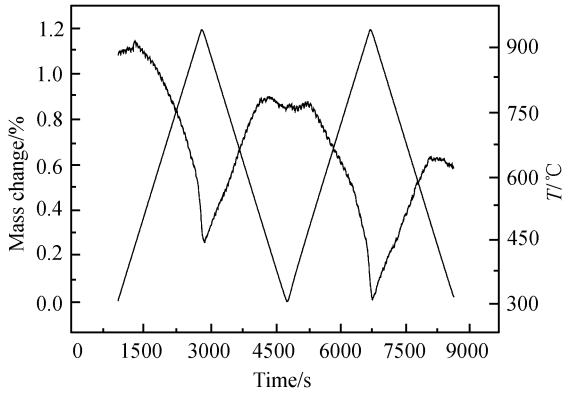

Fig. 2 The TG curve of Nd-123.

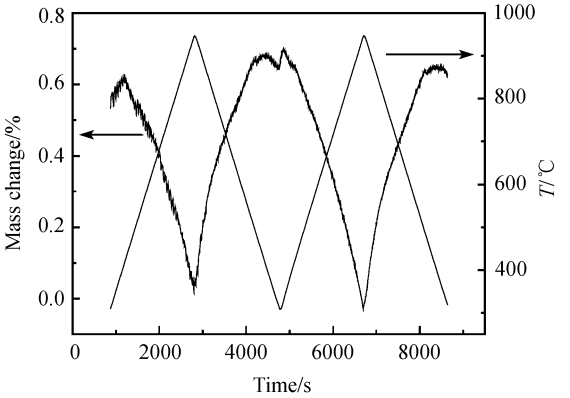

Fig. 3 The TG curve of Nd-123.

The mass variation rates are shown in the Table 2, which are calculated on the assumption that mass variations correspond oxygen content changes from the experiment data in the second increasing temperature. Gd, Er, Eu, Dy, Sm, Ho and Nd are listed in Table 2 by atomic radius, but the orderliness of the oxygen absorption contents is not visible. Re-

ports about $RBa_2Cu_3O_{7-\delta}$ at present indicated that the superconducting transition temperature is not change or decreasing with the atom radium decreasing of lanthanide series when Y is substituted by lanthanide series elements. We conclude that there is not correlation between oxygen absorption property of $RBa_2Cu_3O_{7-\delta}$ and superconducting transition temperature T_c.

Table 2 The mass varieties percent of R-123 samples in TG experiments.

Sample	Mass/mg	Mass varieties percent /%
Nd123	71.75	0.721
Sm123	105.78	1.143
Eu123	147.30	0.974
Gd123	97.57	1.189
Dy123	167.80	0.833
Ho123	101.40	1.10
Er123	128.20	1.275

The thermogravimetric experiment plots of $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x = 0.1$, 0.5 and 1.0) are similar. As a representation, the experiment curve of $LaBa_2Cu_3O_{7-\delta}$ is given in Fig. 4. From Fig. 4 we can conclude that the repetition of oxygen adsorption-desorption is comparatively good with the temperature changing. But comparing with YBCO the repetition is not fine and mass variation rate is small. The mass variation rates of $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x = 0.1$, 0.5 and 1.0) are 1.3 %, 0.9 % and 0.8 %, respectively. The rates decreasing with La content increasing may be possibly due to the impurity phase increase with La.

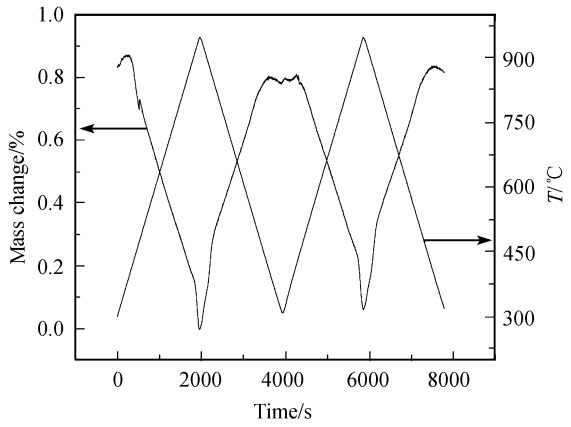

Fig. 4 The TG curve of La-123.

4 Conclusion

There is no oxygen adsorption-desorption repetition of $RBa_2Cu_3O_{7-\delta}$ (R = Gd, Er, Eu, Dy, Sm, Ho and Nd) with temperature variation except $NdBa_2Cu_3O_{7-\delta}$. The oxygen adsorption-desorption repetition of $Y_{1-x}La_xBa_2Cu_3O_{7-\delta}$ ($x = 0.1$, 0.5 and 1.0) is good and the mass rates variation decreases with La content increasing. The oxygen adsorption-desorption repetition of R-123 studied in this thesis is not good as YBCO. Besides, there is not correlation between oxygen adsorption-desorption property of $RBa_2Cu_3O_{7-\delta}$ and atom radium of R. We couldn't find obviously relation between T_c and oxygen adsorption-desorption property.

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