Journal of Thermal Analysis, Vol. 42 (1994) 957-962

THERMAL ANALYSIS OF $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$

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(Received January 6, 1993; in revised form July 27, 1993)

Abstract

TG and DTA analysis of $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ suggests that the stability of the 123 phase increases with increasing Ca contents. The O(1) in the Cu(1)–O chain is unstable but O(2) and O(3) in Cu(2)–O planes are very stable. There are hardly any oxygen vacancies in the Cu(2)–O plane. The replacement of Y by Ca does not make oxygen vacancies in Cu(2)–O planes but leads to an increase in the oxidation number of copper in Cu(2)–O planes.

Keywords: oxygen content, superconductors, thermal stability

Introduction

Since the discovery [1] of $YBa_2Cu_3O_{7-y}$ with zero-resistance about 90 K, its structure and properties have been widely studied [2, 3]. There are two Cu–O layers in the $YBa_2Cu_3O_{7-y}$ unit cell. Cu(2)–O planes neighbour with Y. The Cu(1)–O chain is separated from Y by a Cu(2)–O plane and a Ba–O layer. The structure of $YBa_2Cu_3O_{7-y}$ changes from orthorhombic to tetragonal phase and superconductivity disappears when the oxygen content decreases. When the samples are annealed in air, the oxygen content becomes higher than that of the quenched samples. It is interesting to study the process of oxygen absorption in annealing. Q. W. Zhou [4] studied the process by TG and DTA and found that O(1) in the Cu(1)–O chain in $YBa_2Cu_3O_{7-y}$ is unstable. The loss of O(1) begins above 400°C and needs little energy. O(2) and O(3) in Cu(2)–O planes are lost above 900°C. They are stable. $YBa_2Cu_3O_{7-y}$ decomposes around 950°C in N_2.

We investigated the effect of Ca on the superconductivity of Y–Ba–Cu–O [5]. $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ is a solid solution for $\chi < 0.15$ T_c decreases with increasing Ca content. The ionic oxidation state of copper increases with the increasing Ca content but the oxygen content changes only slightly. In this paper, we will discuss why the oxygen content remains nearly constant when Ca replaces Y.

0368–4466/94/ $ 4.00

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Experiment

Samples were synthesized by a solid state reaction technique as follows: the mixtures of stoichiometric proportions of Y_2O_3, CuO, $CaCO_3$ and $BaCO_3$ were ground and fired at 950°C for 6 h in air. The powders were milled and cold pressed into disc shaped pellets under a pressure of 400 MPa. The pellets were sintered at 950°C for 54 h with an intermediate grinding. The pellets were annealed at 550°C for 10 h and then at 450°C for 15 h in air.

TG and DTA curves were recorded by a Riguku Thermoflex thermal analysis system under the following conditions: N_2 (99.99%); temperature range 100–1200°C; sample size 20 mg; heating rate 10 deg·min^{-1}; sensitivity: DTA 25 μV, TG 0.01 mg. The oxygen content and copper oxidation state were determined by iodometric titration [6].

Results

Figure 1 shows the TG and DTA curves of $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$. Mass loss starts at 440°C and a corresponding endothermic peak on the DTA curve appears at about 516°C. O(1) is lost at this temperature [4]. This peak is very smooth and weak. It is not even seen in the scale of Fig. 1. This suggests that only little energy is required for O(1) to be lost, hence O(1) is unstable. The second mass loss step appears at 918°C and a corresponding strong endothermic peak appears at 929°C on the DTA curve. The peak is caused by the loss of O(2) and O(3) [4]. It is much stronger than the peak caused by the loss of O(1). This indicates that O(2) and O(3) are more stable. A strong endothermic peak on the DTA curve appears again at 942°C. It is caused by the decomposition of the 123 phase [4]. The temperature 942°C is between the start and end of the mass loss step which means that the loss of O(2) and O(3) will lead to the decomposition of the 123 phase. It can be concluded that O(2) and O(3) are very stable; the appearance of oxygen vacancy on Cu(2)–O planes is very difficult; the 123 phase will decompose if the oxygen vacancies on Cu(2)–O planes exceed a certain number. The TG and DTA curves of $Y_{0.85}Ca_{0.15}Ba_2Cu_3O_{7-y}$ are similar to those of $YBa_2Cu_3O_{7-y}$, but the intensity and position of the peak around 942°C change. Figure 2 shows the variation with x in the $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ system. The intensity of the endothermic peaks around 942°C increases with x and the peak position moves toward high temperatures. As the peaks around 942°C are caused by the decomposition of the 123 phase, the result means that the stability of the 123 phase increases when Y is partly replaced by Ca.

Figure 3 shows the positions of Y and Cu(2)–O layers in the 123 phase. Y^{3+} tries to draw oxygen ions out of the Cu(2)–O plane. This makes the lattice of $YBa_2Cu_3O_{7-y}$ collapse when the temperature rises and the ionic vibration is violent. As the attraction of Ca^{2+} to O^{2-} is weaker than the attraction of Y^{3+}, the action which makes Cu(2)–O plane collapse decreases when Y^{3+} is partly replaced by Ca^{2+} and the stability of the 123 phase increases. The energy that is required when the lattice disintegrates increases, hence the peaks caused by the lattice disintegration move towards high temperatures and the intensity of the

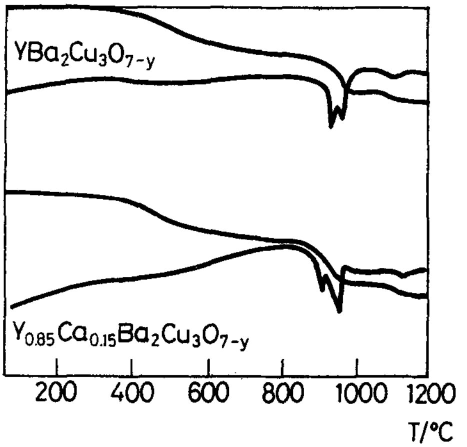

Fig. 1 TG and DTA curves for $Y_{1-x}Ca_xBa_2Cu_3O_{6.86}$ (x = 0 and 0.15)

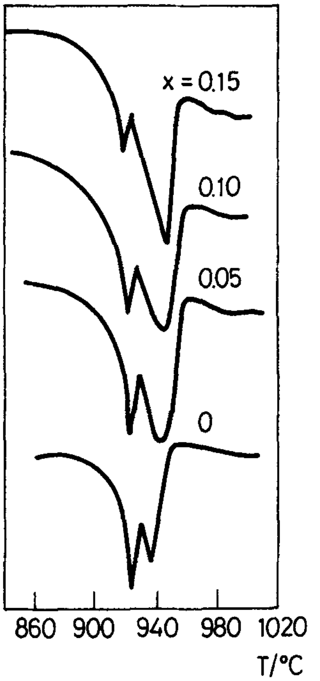

Fig. 2 Variation of peaks around 942°C with x for $Y_{1-x}Ca_xBa_2Cu_3O_{6.86}$

peaks increases. The positions of the endothermic peaks corresponding to the stability of O(2) and O(3) hardly change hence O(2) and O(3) are still stable when Y is partly replaced by Ca. When $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ forms, the positions of O(2) and O(3), which have high stability, will first be filled by absorbed oxygen, then the positions of O(1) are filled. When samples have been annealed in air and oxygen has been sufficiently absorbed, mostly positions of O(1) are occupied. Since the stability of O(2) and O(3) is much higher than that of O(1), the positions of O(2) and O(3) should be fully filled. This means that there are no oxygen vacancies in the Cu(2)–O layers.

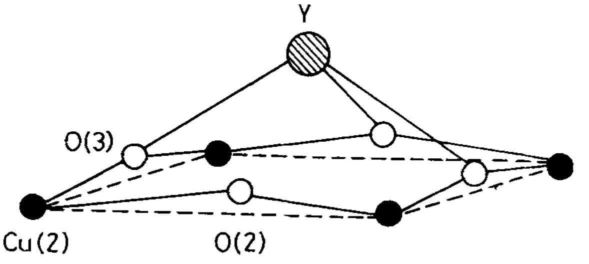

Fig. 3 Y and Cu(2)–O planes in the lattice of 123 phase

Table 1 shows the relations between the oxygen content, copper oxidation state and Ca content in the system $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$. For $\chi < 0.15$, the oxidation number increases with increasing Ca content, however, the oxygen content hardly changes.

Table 1 Oxidation state of copper ions and oxygen contents dependence on Ca contents

Ca contents	Cu oxidation state	Oxygen contents
0.00	2.24	6.86
0.05	2.26	6.87
0.10	2.27	6.86
0.15	2.29	6.86

Figure 4 shows the structure of $YBa_2Cu_3O_{7-y}$ [7]. The positions of Y ions are near the Cu(2)–O layers mainly in that Ca substitutes for Y. The Cu(1)–O layers are hardly affected by substituting Ca for Y, hence the oxygen content of Cu(1)–O layers does not change. The stability of O(2) and O(3) should be affected when Y is replaced by Ca. However, from the thermoanalytical experiment, we know that O(2) and O(3) are very stable. Substituting Ca for Y does not reduce their stability severely, so the positions of O(2) and O(3) are still filled fully in

$Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ and the oxygen content in Cu(2)–O layers does not change either. As the oxygen contents of the Cu(1)–O and Cu(2)–O layers hardly change the oxygen content of the whole unit cell hardly changes, either when Y is partly replaced by Ca.

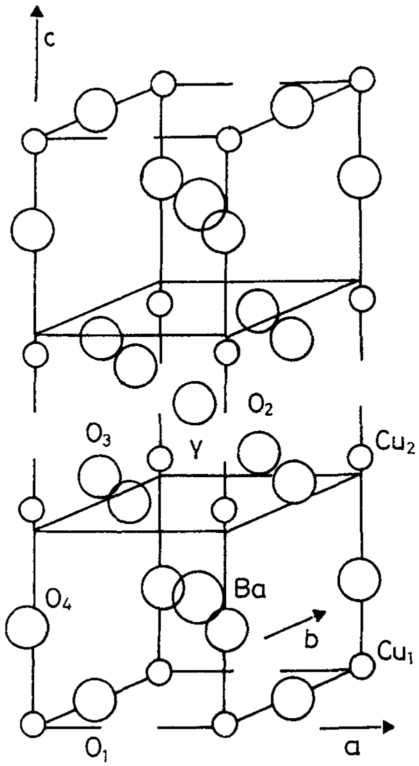

Fig. 4 Structure of $YBa_2Cu_3O_{7-y}$

The number of oxygen ions around Ca^{2+} does not change but substituting divalent Ca for trivalent Y makes the positive charge numbers decrease, hence a local excess of negative charge should appear. According to the controlled valence principle [8], the oxidation number of copper in Cu(2)–O planes must increase for compensating for the decrement of positive charge numbers caused by substituting Ca^{2+} for Y^{3+}.

Conclusion

The replacement of Y by Ca makes the stability of the 123 phase increase. O(2) and O(3) on Cu(2)–O planes are very stable. The lattice of the 123 phase will collapses if O(2) and O(3) are lost. The replacement of Y by Ca does not produce oxygen vacancies on Cu(2)–O planes but leads to an increase in the oxidation number of copper ions on Cu(2)–O planes.

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This work is supported by National Nature Science Fund of China and Laboratory of Rare Earth Chemistry and Physics.

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Zusammenfassung — Die TG- und DTA-Analyse von $Y_{1-x}Ca_xBa_2Cu_3O_{7-y}$ läßt darauf schließen, daß die Stabilität der 123 Phase mit zunehmenden Ca-Gehalt ansteigt. O(1) in der Cu(1)-O Kette ist instabil, sehr stabil sind jedoch O(2) und O(3) in den Cu(2)-O Ebenen. In der Cu(2)-O Ebene gibt es kaum Sauerstoffleerstellen. Der Austausch von Y durch Ca verursacht keine Sauerstoffleerstellen in der Cu(2)-O Ebene, führt aber zu einer höheren Oxidationszahl von Kupfer in der Cu(2)-O Ebene.