

Relationship between superconductivity and crystalline stability of the Y-Ba-Cu-O system

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(Received 26 May 1989; revised manuscript received 9 April 1990)

The thermal decomposition temperature and the superconductivity of nine substituted systems (Y is substituted by Gd, Dy, Pr; Ba by Sr, Ca; Cu by Sn, Al, Zn, Ni, respectively) were studied systematically. The results reveal that there is a close relationship between the T_c and the thermal decomposition temperature, and that the T_c is always suppressed as the thermal decomposition temperature is lowered. The authors consider that the thermal stability may be one of the predominant factors for the superconductivity.

INTRODUCTION

Since the $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ superconductor was identified as the orthorhombic 1:2:3 phase,^{1,2} much work has been done to reveal the origin of superconductivity from the crystalline structure. The earlier studies^{3,4} showed that, as the crystalline structure changes from orthorhombic to tetragonal, the sample loses its superconductivity. A similar phenomenon has been observed in some doped systems.^{5,6} Therefore, the orthorhombic-to-tetragonal transition was considered one of the predominant factors for superconductivity. As the structure changes from orthorhombic to tetragonal gradually, the y value changes from 0 to 0.5, and because the variation of oxygen distribution takes place in the Cu-O chain along the b direction, the oxygen content and Cu-O chain were also considered the predominant factors for the superconductivity. When the y value is less than 0.5, in order to balance the charge, Cu should appear partially Cu^{3+} oxidation state. Experiments^{3,4} showed that the higher the ratio of Cu^{3+} to Cu^{2+} is, the higher the T_c is. Based on this result, it was suggested that whether there is Cu^{3+} or not determines the superconductivity.

Much work has been done on this problem, and some workers⁷⁻¹⁰ have verified that the orthorhombic-to-tetragonal transition is not the predominant factor for superconductivity. Xiao *et al.*⁷ discovered that in the $\text{YBa}_2\text{Cu}_{3-x}\text{Ga}_x\text{O}_{7-y}$ system, the tetragonal phase sample is still superconducting. Chittipeddi *et al.*⁸ discovered that a sample of $\text{NdBa}_2\text{Cu}_3\text{O}_{7-y}$ also is a tetragonal-phase superconductor, and has zero resistance at liquid nitrogen temperature. On the other hand, the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-y}$ system studied by Goncalves *et al.*⁹ re-

veals that, although its structure is in the orthorhombic 1:2:3 phase, it is a semiconductor rather than a superconductor. Especially, Balestrino *et al.*¹⁰ obtained a single crystal of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ with a tetragonal-phase structure, and its superconductive transition temperature is as high as 92 K. All these results seem to indicate that the orthorhombic structure is not the predominant factor for superconductivity. But some people consider that these samples are only globally tetragonal and locally orthorhombic. Most experimental results have shown that a clear-cut relationship exists between the oxygen content and the superconductivity, but some researchers¹¹⁻¹³ have shown that the relationship between superconductivity and oxygen content is irregular. Zhang *et al.*¹⁴ could not find a uniform relationship between the T_c and the oxygen content in eight doped Y-Ba-Cu-O systems. So the authors think that there may be an argument on the relationship between the T_c and the oxygen content. Whether there is Cu^{3+} oxidation or not concerned many researchers; most x-ray photoemission spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) studies¹⁵⁻¹⁸ did not find the Cu^{3+} oxidation state in the Y-Ba-Cu-O system. Steiner *et al.*¹⁹ and Balzarotti *et al.*²⁰ discovered that there is a small amount of Cu^{3+} oxidation state in the XPS spectra of the system. But the relationship between Cu^{3+} and superconductivity still is not well understood. Zhang and co-workers²¹⁻²³ studied the samples of $\text{YBa}_2\text{Cu}_{2.9}\text{Al}_{0.1}\text{O}_{7.10}$ and $\text{YBa}_2\text{Cu}_{2.9}\text{Sn}_{0.1}\text{O}_{7.28}$ by XPS, and discovered that there is obviously a Cu^{3+} oxidation state, but the ratio of Cu^{3+} to Cu^{2+} does not determine the magnitude of T_c . The Cu^{3+} oxidation state only has strong correlation with the oxygen content or formal valence state of Cu. They considered that

whether there is Cu^{3+} state or not may be just the result of charge balance. These experimental results may possibly induce a debate on the relationship between the Cu^{3+} and the superconductivity. To understand the superconductivity fully, one needs to find more factors that are closely related to the superconductivity. The experiment presented in this paper has suggested a probable candidate, the lattice energy, which represents the coupling strength between positive and negative ions in an oxide crystal. The study, based on nine doped systems, shows that as the lattice energy (determined from thermal decomposition temperature, the higher the thermal decomposition temperature is, the higher the lattice energy²⁴ is decreased, the T_c (midpoint of transition, just the same as the following description) is always suppressed, without exception. This is, we believe the most probable predominant factor superconductivity.

EXPERIMENTAL

The samples of substituted systems were prepared by the solid-state reaction method under identical conditions. Appropriate amounts of components were thoroughly mixed and ground, the mixture powder was preheated at 930 °C for 24 h flowing oxygen, followed by slow cooling within the furnace. Resistance as a function of temperature was measured on regularly shaped samples by standard dc four-probe technique; the resolution of the voltage measurement was 1×10^{-8} V. The temperature of the sample was detected by a calibrated Ge resistance thermometer. The typical resistance of the samples is $1 \times 10^3 \mu\Omega$ cm. The width of the transition is 1 to 6 K, respectively, depending on the amount of the dopant. The width of the transition increases as the amount of the dopant increases. The structure of the sample was determined with a Japan RIGAKU D/Max- γ A² rotating target x-ray diffractometer; the lattice parameters were fitted by a computer program, including intensity and angle. The goodness of the fit was about 1, that is, satisfactory. The analysis demonstrated that all of the samples are single phases. The oxygen content was determined by thermogravimetry analysis (TG) with a Japan Shimadzu DT-30 thermal analyzer. The determination of the thermal decomposition temperature of the samples was also carried out with this thermal analyzer. The weight of the sample measured was 20 mg every time, the heating rate was 10 °C/min, the range of TG was ± 10 mg, the range of different thermal analysis (DTA) was ± 100 mV, and the analysis temperature was from room temperature to 1100 °C.

RESULTS AND DISCUSSIONS

Determination of the thermal decomposition temperature

The thermal decomposition temperature was determined as follows: when decomposing, there is an endothermic peak in the DTA curve and a small amount of loss in the TG curve of the sample. The amount of loss is about 1% of the sample analyzed. Figure 1 shows the typical DTA-TG curves of the Y-Ba-Cu-Zn-O system; the curves of other doped systems are similar. The

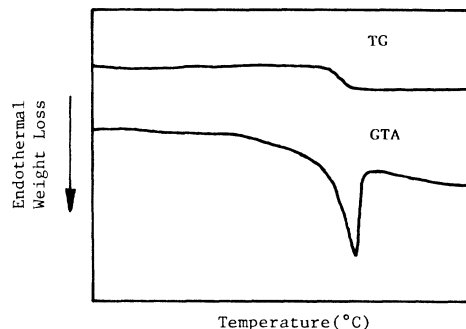


FIG. 1. The DTA-TG curves of the Y-Ba-Cu-Zn-O system.

endothermic peaks and loss of weight are very obvious when the sample begins to decompose and they disappear completely at 1100 °C. Figure 2 gives the x-ray diffraction results of the sample of the Y-Ba-Cu-Zn-O system, in which Fig. 2(a) shows the pattern of the undecomposed sample with good 1:2:3 phase, and Fig. 2(b) shows the pattern of the decomposed sample quenched from 1100 °C to room temperature. It can be seen clearly from Fig. 2(b) that the single-phase sample has decomposed completely and become a mixture of several oxides. This indicates that the temperature at the endothermic peak is certainly the decomposition temperature.

Effect of the substitution of Zn, Ni, Al, and Sn for Cu on the thermal decomposition temperature

It is generally considered that Cu and O play an important role in the Y-Ba-Cu-O system, and this opinion is also suitable for the Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O systems. Because Cu is very important to superconductivity, substitution of other elements for Cu has been performed by many workers. In the four substituted systems (Cu is substituted by Zn, Ni, Al, and Sn, respectively), T_c is always suppressed as the thermal decomposition temperature is lowered, without any exception. Figure 3

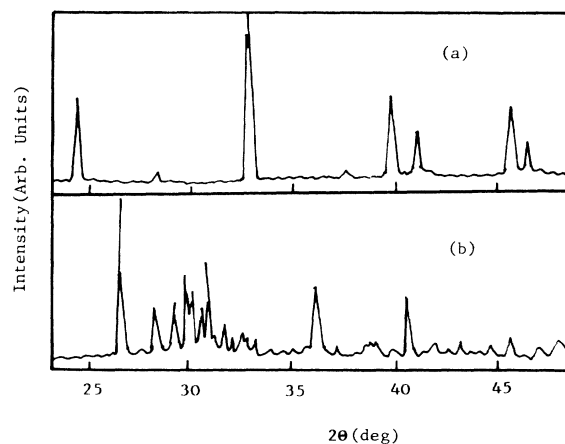


FIG. 2. X-ray diffraction patterns of (a) the undecomposed Y-Ba-Cu-Zn-O system; (b) the decomposed Y-Ba-Cu-Zn-O system.

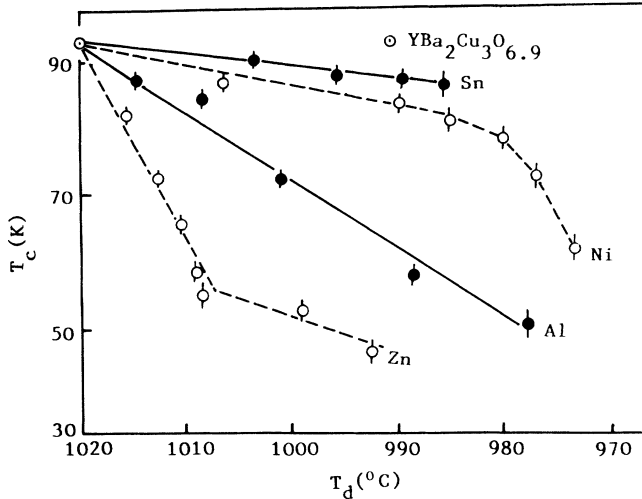


FIG. 3. The relationship between the T_c (mid) and the thermal decomposition temperature (T_d) in the $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ ($M = \text{Zn}, \text{Ni}, \text{Al}, \text{Sn}$) system. The error bar means the width of the transition.

shows these results. Table I lists the lattice parameter, oxygen content, and T_c of the four systems. It can be seen that in Zn-doped system, the oxygen content and lattice parameter are hardly changed for $x < 0.1$, but T_c is suppressed dramatically. This is a typical example in which the relationship between T_c and oxygen content or lattice parameter is irregular. Conversely, there is a strong correlation between T_c and the thermal decompo-

sition temperature. In the Ni-doped system, although there is a close relationship between T_c and the oxygen content, the relationship between the T_c and the lattice parameter is not the same as that in the pure Y-Ba-Cu-O system. As in the Zn-doped system, there is also a close relationship between T_c and the thermal decomposition temperature in the Ni-doped system.

In the $\text{YBa}_2\text{Cu}_{3-x}\text{Al}_x\text{O}_{7+y}$ and $\text{YBa}_2\text{Cu}_{3-x}\text{Sn}_x\text{O}_{7+y}$ systems, the oxygen content is increased as the x value is raised, but the structures are still good orthorhombic 1:2:3 phases, which can be seen from Table I. In the two systems, T_c is suppressed as the oxygen content is increased, which is opposite to that in the pure Y-Ba-Cu-O system. The difference is only in the T_c dropping rate: T_c drops rapidly as the oxygen content is increased in the Al-doped system, but very little in the Sn-doped system. It is obvious that among T_c , the lattice parameter, oxygen content, and the thermal decomposition temperature, there is only a good corresponding relationship between T_c and the thermal decomposition temperature. Although the suppression rate is not same, T_c is always suppressed as the thermal decomposition temperature is decreased (Fig. 3).

According to the preceding results, it is doubtless that there is a close relationship between T_c and the thermal decomposition temperature in the four doped systems. We think that substitution of other elements for Cu influences the coupling strength between the positive and negative ions, lowers the lattice energy of the crystal, and then suppresses T_c .

TABLE I. Some parameters of the $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-y}$ ($M = \text{Zn}, \text{Ni}, \text{Al}, \text{Sn}$) system.

M	X	a (Å)	b (Å)	c (Å)	Oxygen content	T_c (mid) (K)
Zn	0.025	3.809	3.882	11.653	6.94	82.0
	0.05	3.850	3.876	11.626	6.94	73.0
	0.075	3.815	3.888	11.663	6.94	65.0
	0.10	3.816	3.884	11.644	6.94	57.0
	0.15	3.816	3.887	11.666	6.90	55.0
	0.20	3.818	3.885	11.651	6.83	54.0
	0.30	3.825	3.885	11.644	6.94	47.0
Ni	0.025	3.813	3.882	11.656	6.86	87.0
	0.05	3.804	3.871	11.629	6.84	85.0
	0.075	3.807	3.878	11.641	6.83	82.0
	0.10	3.813	3.879	11.646	6.82	80.0
	0.25	3.808	3.888	11.648	6.80	74.0
	0.50	3.818	3.880	11.633	6.80	63.0
Al	0.05	3.839	3.882	11.656	6.95	88.0
	0.10	3.834	3.886	11.629	7.10	85.0
	0.15	3.832	3.884	11.639	7.13	72.0
	0.20	3.840	3.891	11.655	7.15	71.6
	0.25	3.836	3.886	11.637	7.18	58.0
	0.50	3.841	3.880	11.630	7.29	51.0
Sn	0.05	3.824	3.875	11.651	7.15	90.1
	0.10	3.821	3.873	11.642	7.28	90.0
	0.20	3.832	3.881	11.661	7.34	89.5
	0.30	3.826	3.872	11.630	7.34	89.0

Effect of Ca and Sr for Ba on the thermal stability

Table II lists the lattice parameter, oxygen content, and T_c of $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-y}$ and $\text{YBa}_{2-x}\text{Ca}_x\text{Cu}_3\text{O}_{7-y}$ systems. It can be seen from the table that the relationship between the T_c and lattice parameter is the same as that in the pure Y-Ba-Cu-O system. As the x value is increased, the crystalline structure changes from orthorhombic to tetragonal gradually, and the T_c is dropped systematically, while the oxygen content is hardly changed. This result is possible because of the disorder of oxygen in the Cu-O chain along the b and a directions. Zhang *et al.*²² studied these two systems by XPS and discovered that the oxidation state of Cu is between Cu^{2+} and Cu^{3+} in both systems. This result is considered because of the difference of the electronegativity among Ca, Sr, and Ba. The electronegativities of them are 1.00, 0.95, and 0.89, respectively. The element with the higher electronegativity does not readily give the electron. The substitution of Ca and Sr for Ba makes the oxygen getting the electron from the Ba site more difficult. In order to be consistent with the O^{2-} state, oxygen has to get more electrons from the Cu sites. Therefore, although the oxygen content is hardly changed by the substitution, the Cu appears in the oxidation state between Cu^{2+} and Cu^{3+} . It is also for this reason that oxygen in the Cu-O chain along the a and b directions disorders, which makes the tetragonal degree increase. Meanwhile, the substitution of Ca and Sr for Ba influences the coupling strength between the positive and the negative ions in the crystal, and makes the lattice energy decrease. Figure 4 shows the relationship between T_c and the thermal decomposition temperature, and it is evident that, as the thermal decomposition temperature is dropped, T_c is suppressed.

Effect of substitution of Gd, Dy, and Pr for Y on the thermal stability

The changes in the oxygen content, thermal decomposition temperature, and T_c caused by the substitution of Gd and Dy for Y are very little. Conversely, when Y is

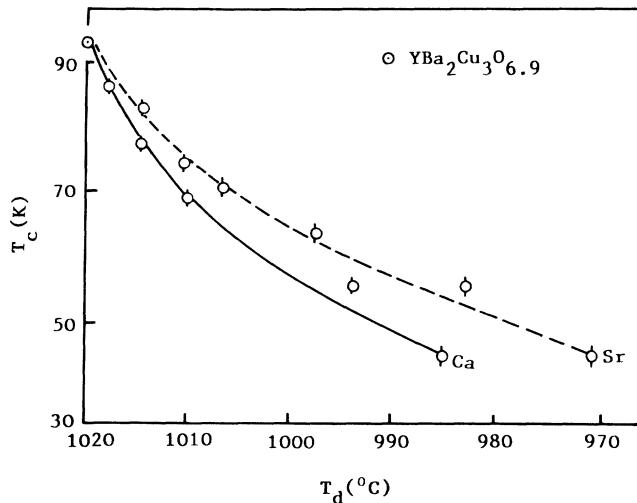


FIG. 4. The relationship between T_c (mid) and the thermal decomposition temperature (T_d) of the $\text{YBa}_{2-x}\text{M}_x\text{Cu}_3\text{O}_{7-y}$ ($M = \text{Sr}, \text{Ca}$) system.

replaced by Pr, although the structure of the sample is a good orthorhombic 1:2:3 phase, T_c and the thermal decomposition temperature are dropped dramatically; Table III lists these results. There is a strong correlation between T_c and the thermal decomposition temperature in the three systems. Because the ionic radii and the electronic structures of Gd, Dy, and Y are very similar, the change in coupling strength between the positive and the negative ions caused by the substitution of Gd and Dy for Y is very little, and so also in the lattice energy and T_c . In contrast, part of the Pr appears in the Pr^{4+} oxidation state, the electronic structure of it is quite different from that of Y, and the change of coupling strength caused by Pr substitution is more than that by Gd and Dy. Because of this, the T_c and the thermal decomposition temperature are suppressed remarkably.

Based on the preceding results and analysis, it is evident that there is a close relationship between T_c and the thermal decomposition temperature or lattice energy. This result provides a way to understand the origin of superconductivity from energy.

TABLE II. Some parameters of the $\text{YBa}_{2-x}\text{M}_x\text{Cu}_3\text{O}_{7-y}$ ($M = \text{Sr}, \text{Ca}$) system.

M	x	a (Å)	b (Å)	c (Å)	Oxygen content	T_c (mid) (K)
Ca	0.05	3.833	3.884	11.658	6.84	88.0
	0.075	3.836	3.880	11.648	6.80	86.0
	0.10	3.842	3.876	11.689	6.84	85.0
	0.15	3.843	3.873	11.656	6.92	83.5
	0.20	3.846	3.871	11.657	6.90	81.5
	0.25	3.840	3.871	11.668	6.91	79.0
Sr	0.10	3.826	3.887	11.673	6.89	89.0
	0.25	3.830	3.885	11.670	6.88	87.0
	0.50	3.835	3.879	11.672	6.89	85.0
	0.75	3.835	3.872	11.680	6.92	82.0
	0.10	3.840	3.871	11.668	6.91	79.0

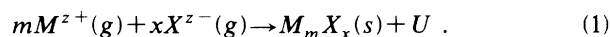
TABLE III. Some parameters of the $Y_{1-x}M_xBa_2Cu_3O_{7-y}$ ($M = Gd, Dy, Pr$) system.

M	X	a (Å)	b (Å)	c (Å)	Oxygen content	T_c (mid) (K)	T_c (°C) ^a
Gd	0.1	3.811	3.883	11.649	6.88	91.5	1016
	0.3	3.811	3.884	11.645	6.95	91.0	1019
	0.5	3.820	3.888	11.666	6.90	91.0	1012
	0.7	3.826	3.891	11.673	6.95	90.0	1011
	0.9	3.830	3.893	11.683	6.90	90.5	1016
	1.0	3.847	3.900	11.703	6.86	90.5	1012
Dy	0.1	3.809	3.882	11.652	6.89	92.0	1009
	0.3	3.813	3.885	11.659	6.96	92.0	1003
	0.5	3.817	3.887	11.674	6.90	91.0	1009
	0.7	3.807	3.892	11.682	6.85	90.5	1007
	0.9	3.811	3.883	11.642	6.92	91.0	1010
	1.0	3.825	3.888	11.659	6.82	91.0	1004
Pr	0.1	3.818	3.872	11.619	6.95	78.0	1010
	0.3	3.826	3.874	11.639	7.05	49.0	1003
	0.5	3.828	3.880	11.657	7.10	21.5	995
	0.7	3.828	3.876	11.668	7.13		989

^a T_d : thermal decomposition temperature.

To understand the origin of the superconductivity from energy

According to Pauling's²⁵ rule, the ionic character between the Cu—O bond is 47%, Ba—O 77%, Y—O 67%. It is reasonable to consider that Y-Ba-Cu-O is an ionic compound. For an ionic compound, the higher the lattice energy is, the higher the thermal decomposition temperature.²⁴ Because of this, the thermal decomposition temperature may be used as a sign of lattice energy. For a simple two-component compound, the reaction equation is



Here U is the lattice energy. The calculation formula for U is as follows:

$$U_i = A \frac{NZ_+Z_-e^2}{r_e} \left[1 - \frac{\rho}{r_e} \right] \quad (2)$$

Here A is the Madelung constant, which is determined by the coordination number around the ions, N is Avogadro's constant, and r_e is the distance between the positive and the negative ions. ρ is the other constant that is determined by the repelling between the positive

and negative ions. For a multicomponent compound, such as Y-Ba-Cu-O, the lattice energy of it can be considered as the sum of that of several two-component compounds. This dealing method is reasonable for discussing the question quantitatively. Therefore, for a multicomponent compound, the lattice energy can be written as follows:

$$U = \sum_i U_i \quad (3)$$

From the preceding equations, it can be seen clearly that the lattice energy includes the parameters of size, charge, attraction, repelling, and situation of the ions. We can say that lattice energy is a characteristic factor determined by the whole crystal. In this paper, the experimental results show that there is a close relationship between T_c and thermal decomposition temperature; we think the reason may be that said above. In conclusion, thermal decomposition temperature, we believe is the most probable predominant factor for superconductivity.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China.

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