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Thermopiezic Analysis of Rare-Earth Cuprate Superconductors and Related Oxides

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A comparative study of oxygen thermal desorption characteristics of nine (La/Y)–(Ba/Sr)–Cu oxides shows a characteristic instability in the region 400–700°C whenever copper is present in sites with square-planar oxygen coordination. This instability is not directly related to the existence of superconductivity. © 1988 Academic Press, Inc.

1. Introduction

Thermopiezic analysis (TPA) is a technique for thermal analysis of solids based on monitoring the gas pressure in a small closed volume containing a solid sample of 1–100 mg which is heated at a programmed rate. The apparatus, illustrated in Fig. 1, has been described elsewhere by Ryan and Coey (*1, 2*). TPA has proved to be particularly well suited for rapid characterization of oxide superconductors, and for preparation of samples with a known oxygen deficit (*3, 4*).

The quantity and distribution of oxygen vacancies in copper oxides with structures related to that of perovskite is critical for the determination of their physical properties (*5–7*). Superconductivity exists in orthorhombic $YBa_2Cu_3O_{7-\delta}$ when $0 \leq \delta < 0.4$ (Fig. 2b), but the compound becomes tetragonal (Fig. 2c) and antiferromagnetic when $1 \geq \delta > 0.6$ (*8*). The range of oxygen content over which the compound remains orthorhombic and superconducting may be extended to $0 < \delta < 0.7$ when oxygen is removed by gettering at low temperatures (*9*). The disappearance of superconductivity might be related to the oxygen loss and the consequent change in coordination of Cu1 sites. In the $La_{2-x}Sr_xCuO_{4-\delta}$ system, it is found that the oxygen-diffusion coefficient is greatest when $x = 0.15$ (*10*), which corresponds to the maximum T_c. There appears therefore to be some relation between the stability of the copper–oxygen coordination and the existence of superconductivity.

It was to investigate this point that we decided to make a comparative study of the oxygen stability and intercalation properties of high-T_c superconductors and several related nonsuperconducting compounds. The study reveals that oxygen stability is closely related to the crystal chemistry of the compounds, and in particular to the

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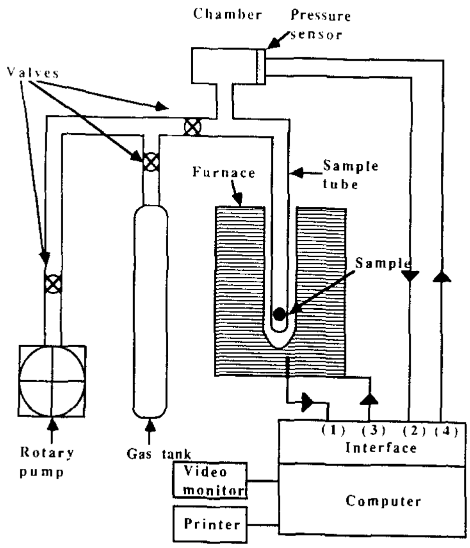

FIG. 1. Diagram of the thermopiezic analyzer. (1) Temperature sensor input, (2) pressure sensor input, (3) furnace power supply, (4) sensor power supply.

copper–oxygen coordination, but no relation is found between oxygen stability and superconductivity.

2. Sample Preparation

Samples of nine different lanthanum or yttrium copper oxides were prepared by the oxalate coprecipitation or direct solid state reaction methods.

Oxalate coprecipitation with the desired ratio of metal cations was carried out from 0.52 *M* aqueous solutions of $Y(NO_3)_3 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, and $Cu(C_2H_2O_2)$ $CuO \cdot 6H_2O$ and 0.26 *M* aqueous solutions of $Ba(NO_3)_2$ and $Sr(NO_3)_2$. Sky blue powders are obtained after drying in an oven at 80°C. They are then heated to 500°C for 2 hr where the oxalate transform into black oxides and carbonates. The black powders are compressed into pellets at 0.5 GPa, and then fired at high temperatures.

The pellets, with a 1:2:3 Y:Ba:Cu ratio, were sintered at 920°C for 20 hr and then annealed in O_2 at 600°C followed by slow cooling. They show the well-known superconducting transition near 90 K (*11*). Y_2BaCuO_5 was fired at 1000°C for 42 hr, yielding a pure green phase. Lattice parameters deduced from X-ray powder diffraction agree with other reports (*12*). They are shown in Table I. $YBa_3Cu_2O_y$, $YBa_4Cu_3O_9$, and $Y_3Ba_8Cu_5O_{18}$ (*13, 14*) were sintered at 950°C for 48 hr. La_2CuO_4, $La_{1.85}Sr_{0.15}CuO_4$, and $La_{1.85}Ba_{0.15}CuO_4$ were sintered at 1100°C for 24 hr. All of these compounds, except $YBa_4Cu_3O_9$, which contained $BaCuO_2$ impurity, gave X-ray diffraction patterns characteristic of a pure phase, and the lattice parameters are listed in Table I. All

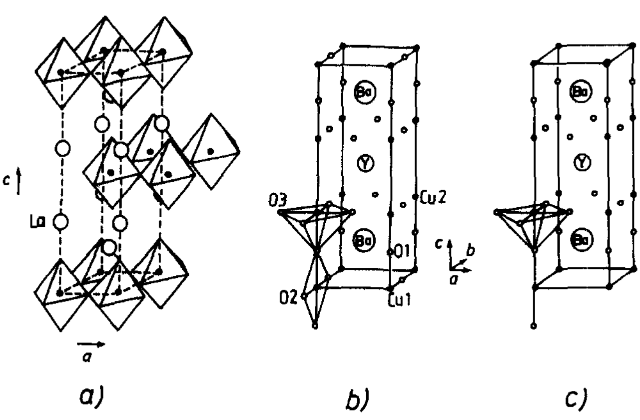

FIG. 2. Schematic representation of the structures of some of the oxides. La_2CuO_4: La atoms (large circles), Cu atoms (small filled circles). Oxygen atoms at vertices of the polyhedra (CuO_6 octahedra). (b) $YBa_2Cu_3O_7$. (c) $YBa_2Cu_3O_{7-\delta}$. When O2 is completely missing, $\delta = 1$.

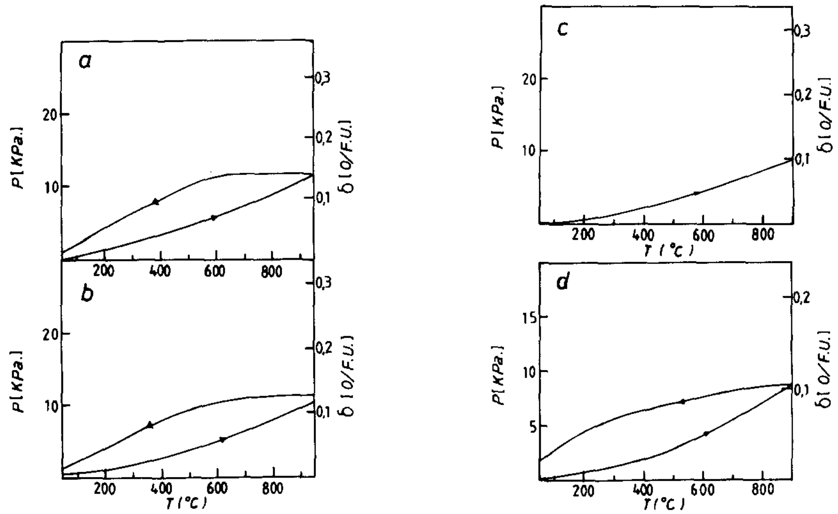

FIG. 3. Thermopiezic analysis. Oxygen loss as function of temperature is represented by both pressure change and oxygen loss per formula unit δ. (a) La_2CuO_4. $La_{1.85}Ba_{0.15}CuO_4$. (c) $La_{1.85}Sr_{0.15}$ CuO_4. (d) Y_2BaCuO_5.

samples were annealed in oxygen before analysis.

X-ray diffraction was carried out on a Phillips powder diffractometer using Cu*Kα* radiation, with a Si standard being used for the lattice parameter determinations.

3. Results and Discussion

The $La_{2-x}(Sr/Ba)_xCuO_{4-y}$ system has been thoroughly studied, and structural changes and oxygen deficiencies related to substitutions of La by Ba or Sr (*5, 15*). The compounds have the perovskite layer structure shown in Fig. 2a; copper is in sixfold octahedral coordination, and neighboring Cu–O octahedral layers are shifted by ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). As only 1% oxygen deficiency (*10*) was detected for this system, we take y to be zero for oxygen annealed samples and the oxygen loss δ at the start of thermopiezic analysis to be zero also. On heating at 10°C/min to 900°C from vacuum in the analyzer there is a small progressive oxygen loss, corresponding to δ (oxygen loss per formula unit) $\simeq$ 0.1 as shown in Fig. 3a–c. There is no evident difference in the TPA curves of La_2CuO_4, $La_{1.85}Sr_{0.15}CuO_4$, and $La_{1.85}Ba_{0.15}CuO_4$. No change is seen in the X-ray pattern when the sample is heated to 700°C and then vacuum cooled to room temperature.

TABLE I

LATTICE PARAMETERS OF COPPER OXIDES (IN Å)

Samples	*a*	*b*	*c*
La_2CuO_4	5.365	5.409	13.149
$La_{1.85}Ba_{0.15}CuO_4$	5.342		13.260
$La_{1.85}Sr_{0.15}CuO_4$	3.774		13.220
Y_2BaCuO_5	7.122	12.164	5.612
$YBa_3Cu_2O_x$	5.798		7.937
$Y_3Ba_8Cu_5O_{18}$	5.786		8.041
$YBa_2Cu_3O_7$	3.821	3.892	11.679
$LaBa_2Cu_3O_{7-y}$	3.914		11.729
$YBa_4Cu_3O_9$	8.085		4.048

The oxygen desorption curve of Y_2Ba CuO_5, where the copper is all in fivefold square-pyramidal coordination (*12*), is similar to that of the La_2CuO_4-type oxides (Fig. 3d). There is very little oxygen release (δ $\simeq$ 0.1 at 900°C).

A different behavior is found in YBa_3 Cu_2O_x and $Y_3Ba_8Cu_5O_{18}$ (Figs. 4a and b).

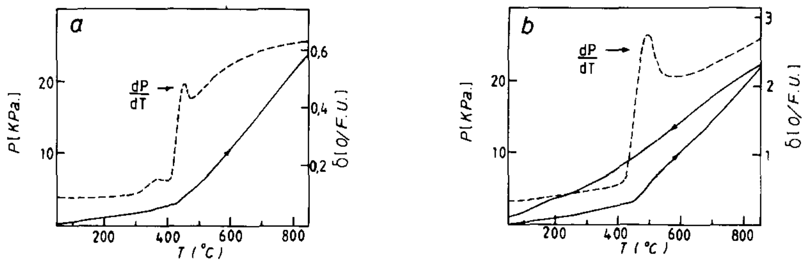

FIG. 4. Thermopiezic analysis. (a) $YBa_3Cu_2O_{7-x}$. (b) $Y_3Ba_8Cu_5O_{18}$.

These two compounds show similar X-ray diffraction patterns, with quite similar lattice parameters (Table I). Their TPA traces are also similar. After evacuation at 800°C ($\delta \simeq 2$ in $Y_3Ba_8Cu_5O_{18-\delta}$) there is a distinct change in lattice parameters; *a* increases while *c* decreases. According to de Leeuw *et al.* (*14*), the copper is present in square-planar and octahedral coordination in the $Y_3Ba_8Cu_5O_{18}$. Oxygen loss at 850°C measured by TPA is $\delta \simeq 0.6$ and $\delta \simeq 2.3$ for $YBa_3Cu_2O_x$ and $Y_3Ba_8Cu_5O_{18}$, respectively. Here $x = 7$ for $YBa_3Cu_2O_x$ has been supposed at room temperature to calculate oxygen loss δ.

The primary desorption characteristic for orthorhombic $YBa_2Cu_3O_7$ shows rapid oxygen loss at around 520°C (Fig. 5a) which can be clearly located by the peak in *dP*/*dT*. The well-known structure of $RBa_2Cu_3O_7$ includes copper in square-planar (Cu1) and square-pyramidal (Cu2) sites. Pseudo-cubic $YBa_4Cu_3O_9$ shows a similar feature at 700°C. The proposed structure there (*14*) has copper in square-planar and octahedral coordination. The oxygen loss found for both 1:2:3 and 1:4:3 compounds at 950 and 900°C, respectively, is $\delta \simeq 1.5$ and 1.15. The TPA curves of $YBu_2Cu_3O_7$ and YBa_4 Cu_3O_9 are similar although one is superconducting and the other is not.

In contrast to other rare-earth 1-2-3 superconductors, $LaBa_2Cu_3O_{7-y}$ possesses a tetragonal structure for both oxygen and

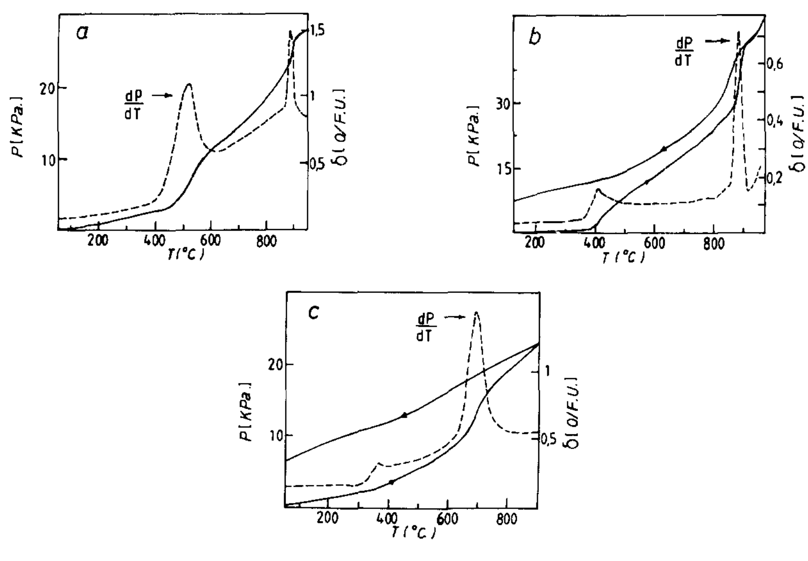

FIG. 5. Thermopiezic analysis. (a) $YBa_2CU_3O_7$. (b) $LaBa_2Cu_3O_{7-y}$. (c) $YBa_4CU_3O_9$.

vacuum annealed samples. According to Nakai *et al.* (*16*), O2 (2*f*) site occupancy in $LaBa_2Cu_3O_{7-y}$ after oxygen annealing is only 0.4 ± 0.1; the solid solution $Y_{1-z}La_z Ba_2Cu_3O_{7-y}$ studied by Chevalier *et al.* (*17*) indicated a phase transformation from orthorhombic to tetragonal at $z = 0.75$. Combining those results, $y = 0.4$ seems a reasonable value for the oxygen annealed sample of $LaBa_2Cu_3O_{7-y}$. In this way, our TPA results shown in Figs. 5a and b can be well understood. The primary desorption from O2 sites for $LaBa_2Cu_3O_{7-y}$ is quite a bit smaller than it is for $YBa_2Cu_3O_7$, suggesting there are fewer fourfold, but some five- or sixfold Cu1 sites in the tetragonal structure. Both compounds show the sharp upturn near 900°C which has been identified with the onset of melting and vitrification in other members of the $RBa_2Cu_3O_7$ series (*3*).

The reabsorption of oxygen, on cooling from high temperature in the thermopiezic analyzer is much slower for the La_2CuO_4 family or for Y_2BaCuO_5, where the oxygen loss was minimal, than for the oxides with some copper in square-planar coordination which lost a substantial fraction of their oxygen from 400 to 700°C. Oxygen diffusion is much more rapid in the latter, as illustrated by the cooling curves.

4. Conclusions

(1) There is very little oxygen loss up to 900°C in compounds where copper is only in octahedral and/or square pyramidal coordination (e.g., La_2CuO_4, Y_2BaCuO_5).

(2) Substantial oxygen desorption, starting somewhere in the range 400–700°C, on heating from vacuum, is found whenever some of the copper is present in square-planar coordination. The loss may be gradual ($Y_3Ba_8Cu_5O_{18}$) or abrupt, with the character of a collective phase transition (e.g., $YBa_2Cu_3O_7$, $YBa_4Cu_3O_9$).

(3) No direct link can be made between the oxygen desorption characteristic and the existence of superconductivity in these oxides. Both categories mentioned in (1) and (2) above include superconducting and nonsuperconducting members. The idea that the disappearance of superconductivity associated with oxygen loss in $RBa_2Cu_3O_7$ at the orthorhombic → tetragonal transition might be intrinsically related to the change in coordination of the Cu1 sites is not borne out by our study. Indeed it is becoming clear from the newer bismuth and thallium copper oxide superconductors that the indispensable structural element is $(CuO_2)_n$ planes, where the copper is in octahedral or square-pyramidal coordination.

Acknowledgments

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