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CHEMISTRY AND HIGH T_c SUPERCONDUCTIVITY IN THE La-Ba-Cu-O SYSTEM

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Abstract - A systematic investigation of the chemistry and superconductivity in the La-Ba-Cu-O system was carried out, using X-ray powder diffraction, resistivity and TGA measurements. A phase diagram for the La-Ba-Cu-O quasi-ternary system at 950°C has been determined and the relationship between the phases in this system is discussed. A series of A-cation (ABO_3-type perovskite) deficient compounds of the type of $(LaBa_2)_xCu_3O_{7-\delta}$ ($0.67 < x < 0.96$) were prepared. Cation deficiencies appear to stabilize the structure but depress T_c. Partial substitution of La and Ba in $LaBa_2Cu_3O_{7+\delta}$ by other rare earth and alkali earth cations, respectively, were also investigated. An enhancement in T_c, compared with $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$, was found in $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$ ($0 < x < 1.0$), providing further evidence for the importance of reduced lattice dimensions in stabilizing the superconducting phase of La-123.

INTRODUCTION

Since the discovery of the high T_c superconductor $YBa_2Cu_3O_{7-\delta}$ (often referred to as the 123 compound) which was shown to be an oxygen deficient perovskite-type compound[1], the substitution of yttrium by other elements has become a very active field in the chemistry of high T_c superconducting materials. Yttrium can be substituted for by all of the rare-earth elements except cerium and terbium,[2] to form the same type of perovskite-like structure with the stoichiometry of $ReBa_2Cu_3O_{7-\delta}$ (Re = Rare-earth). However, some of these rare-earth analogues show superconducting properties different from that of $YBa_2Cu_3O_{7-\delta}$. For example, $PrBa_2Cu_3O_{7-\delta}$ can be prepared with the identical structure of $YBa_2Cu_3O_{7-\delta}$ but it does not show superconductivity, possibly, because of the mixed-valence of praseodymium cations. 123 compounds containing the heavier rare-earths (Er-Lu) and yttrium can display bulk superconductivity at 90 K, while the lanthanum analogue, $LaBa_2Cu_3O_{7+\delta}$ becomes superconducting at about 55-75 K[3,4,5]. Moreover, it is very difficult to prepare the La analogue in pure phase form; $BaCuO_2$ is always present as an impurity phase together with nominal $LaBa_2Cu_3O_{7+\delta}$. Recently, the T_c for $LaBa_2Cu_3O_{7+\delta}$ was reported to be 90 K, but the Meissner effect measurement indicated only about 30% bulk superconductivity.[6,7]

It is known that lanthanum can form various cuprate phases with perovskite-related structures, e.g. La_2CuO_4, $La_2SrCu_2O_7$[8] and $LaCuO_3$[9]. Yttrium and other heavy rare earths do not form these phases. The structure of $LaBa_2Cu_3O_{7+\delta}$ was recently determined by neutron diffraction techniques[4]. Compared with $YBa_2Cu_3O_{7-\delta}$, some notable differences in the oxygen content, oxygen distribution, symmetry of the crystal lattice, and the disordering between the La^{3+} and Ba^{2+} cations in the lattice were found in the $LaBa_2Cu_3O_{7+\delta}$ system. In general, the La-Ba-Cu-O perovskite-type structure appears to be more stable than the Y-Ba-Cu-O system; therefore, variations in the $LaBa_2Cu_3O_{7+\delta}$ stoichiometry might be more feasable.

The copper chemistry in the La-Ba-Cu-O system is also very interesting. Several La-Ba-Cu-O compounds show very high formal oxidation states for copper. For example, $La_4BaCu_5O_{13+\delta}$ has a copper valence of 2.50. However, it is metallic and not superconducting. In $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ the copper valence does not change with x, however, T_c decreases with increasing x for $0.2 < x < 0.5$ (i.e. the range of superconductivity).[7,9] Although the existance of Cu^{3+} species in these high T_c superconducting materials is arguable,[10] the significance of some form of mixed valent copper (or oxygen) is apparent.

In this work, we report on a systemetic study of the La-Ba-Cu-O system. We have investigated the phase diagram at 950°C and will discuss the relationship between the various phases present. The dependence of the T_c on the formal copper valence, oxygen content, impurity phases, cation vacancies, and the disordering of trivalent and divalent A-cations in the structure were examined.

EXPERIMENTAL

All the samples were prepared using conventional solid state reaction procedures. Stoichiometric mixtures of La_2O_3, $BaCO_3$ and CuO were calcined at 950°C for 24 hrs with repeated grindings, then quenched to room temperature and pressed into pellets at 80,000 psi. The pellets were then sintered at 950°C for 24 hrs, followed by oxygen annealing at 450°C-500°C for another 24 hrs. Samples were identified by powder x-ray diffraction on a SCINTAG PAD IV system with Si as an internal standard. The lattice parameters were calculated using a least-square refinement of the observed x-ray diffraction data. The oxygen stoichiometry of the samples was determined using a Du Pont 951 thermogravimetric analyzer. The standard four-probe technique was used to measure the resistivity of all samples. Indium leads were attached to rectangularly-shaped pellets using either ultrasonic soldering or silverprint.

RESULTS AND DISCUSSION

1. The phase diagram of $LaO_{1.5}$-BaO-CuO system and its basic properties.

An effort to find new compounds in the La-Ba-Cu-O system resulted in the phase diagram, as shown in Fig 1. The $LaO_{1.5}$-BaO-CuO system includes several previously known phases:

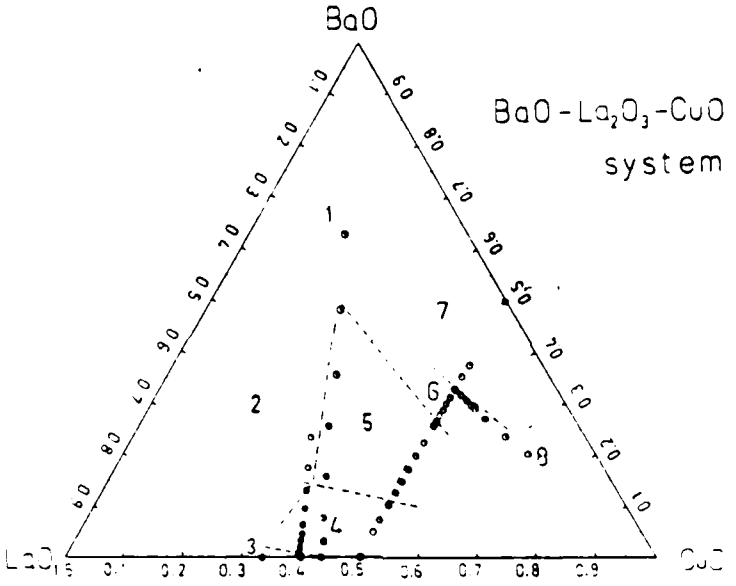

Fig. 1 Phase diagram of $LaO_{1.5}$-BaO-CuO system
1) $BaCuO_2$ + unknown; 2) $La_{2-x}Ba_xCuO_4$ + unknown;
3) $La_{2-x}Ba_xCuO_4$; 4) $La_4BaCu_5O_{13+\delta}$ + $La_{2-x}Ba_xCuO_4$;
5) $La_4BaCu_5O_{13+\delta}$ + $La_3Ba_3Cu_6O_{14+\delta}$ + $La_{2-x}Ba_xCuO_4$;
6) $LaBa_2Cu_3O_{7+\delta}$-type (La-123); 7) La-123 + $BaCuO_2$;
8) La-123 + CuO

La_2CuO_4, $La_4BaCu_5O_{13+\delta}$,[11] $La_3Ba_3Cu_6O_{14+\delta}$,[12] $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$, $LaCuO_3$, and $BaCuO_2$. All of these phases, except $BaCuO_2$, may be considered to form oxygen deficient perovskite-related structures. However, the compounds differ in oxygen content and oxygen distribution with formation of different coordination around the copper, lanthanum and barium cations in the various structures as shown in Fig. 2. These differences are undoubtedly important in determining the electrical properties of these compounds. $LaCuO_3$ has a rhombohedrally distorted perovskite structure, and it only forms at high oxygen pressure; therefore, it will not appear in the phase diagram. $La_4BaCu_5O_{13+\delta}$ may be prepared as a homogeneous pure phase only in a very small region of the phase diagram. It forms in a tetragonal perovskite-like structure with space group P4/mmm, with a = 8.648A, c = 3.859A. However, $La_4BaCu_5O_{13+\delta}$ is found together with $La_{2-x}Ba_xCuO_4$ and $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ ($0 < x \leq 0.5$) in a large region in the middle of the phase diagram. It disappears as the ratio of Ba/La exceeds one in the nominal starting compositions. Raveau et al have reported detailed studies of the structural and basic conduction properties of this compound in the temperature range from 100 K to 300 K.[13] We measured the temperature dependence of the resistivity for $La_4BaCu_5O_{13+\delta}$ down to 4 K and the data are shown in Fig. 3.

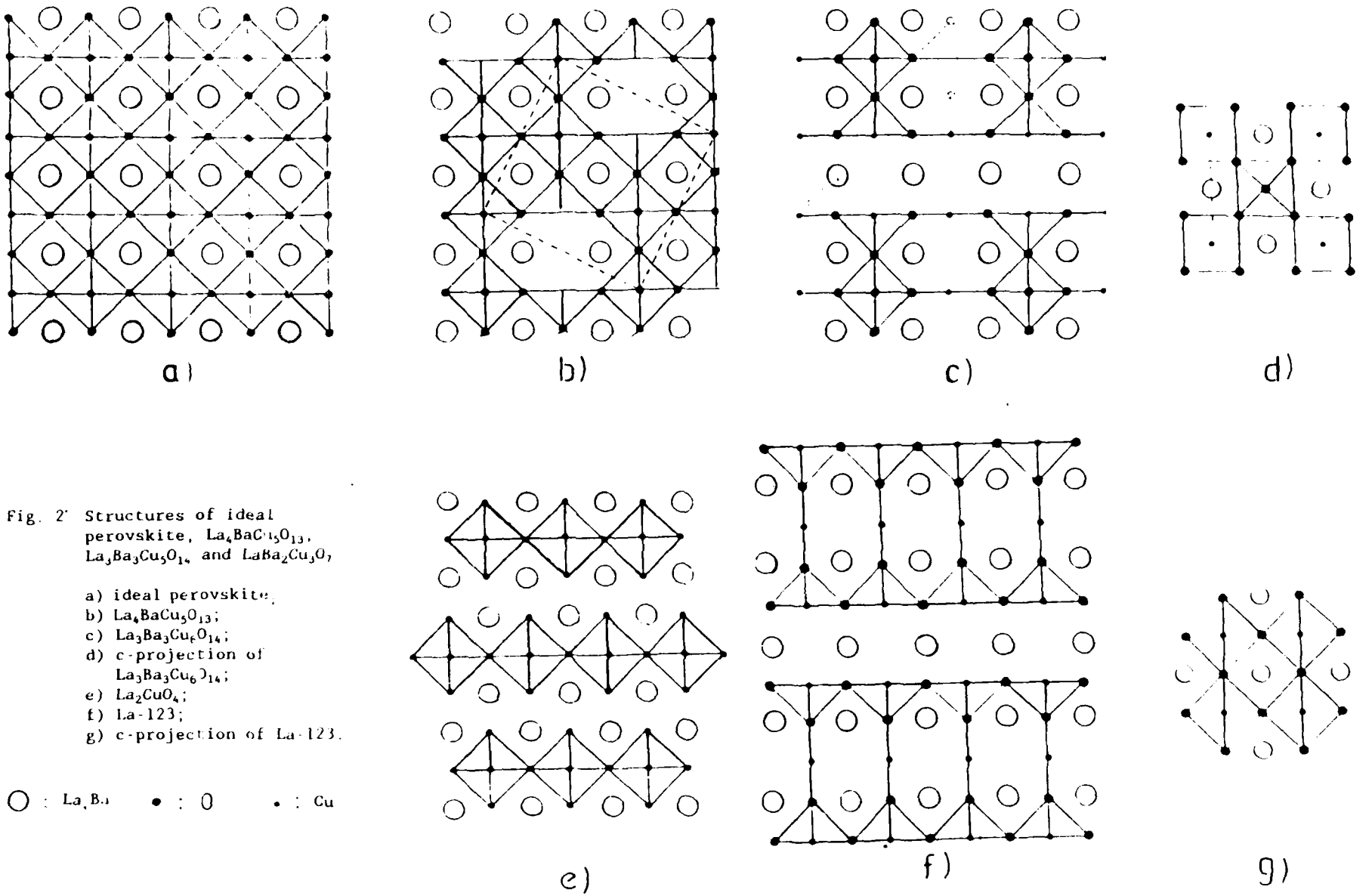

Fig. 2 Structures of ideal perovskite, $La_4BaCu_5O_{13}$, $La_3Ba_3Cu_5O_{14}$ and $LaBa_2Cu_3O_7$

a) ideal perovskite;
b) $La_4BaCu_5O_{13}$;
c) $La_3Ba_3Cu_6O_{14}$;
d) c-projection of $La_3Ba_3Cu_6O_{14}$;
e) La_2CuO_4;
f) La-123;
g) c-projection of La-123.

○ : La, Ba • : O • : Cu

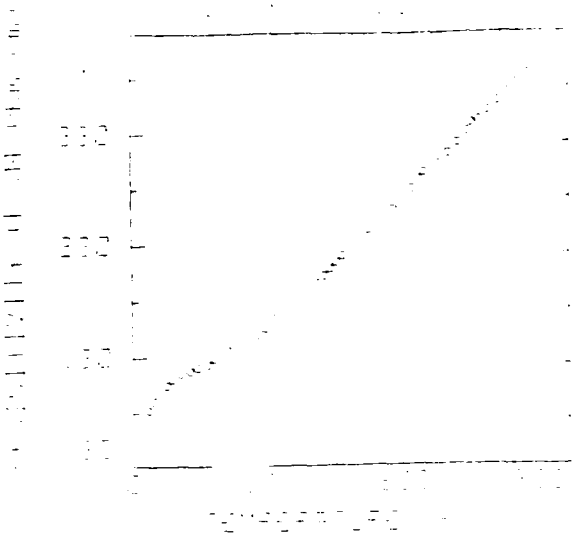

Fig. 3 Resistivity vs. temperature of $La_4BaCu_5O_{13+\delta}$

At temperatures above 60 K, typical metallic behavior is observed. At lower temperatures, the ρ vs. T relationship deviates from linearity. Recently, Rao et al reported an anomaly at about 100 K for a sample of $La_4BaCu_5O_{13+\delta}$,[14] but this anomaly is not seen in our data (Fig. 3). Partial substitution by other rare-earth ions including Pr, Nd and Sm for La ($La_{4-x}Re_xBaCu_5O_{13+\delta}$, $0 < x < 1.6$), as well as strontium or calcium for barium, ($La_4Ba_{1-x}M_xCu_5O_{13+\delta}$, (M = Ca or Sr, $0 < x < 0.3$) were also investigated. Although single phase solid solutions were formed, these substitutions have little or no effect on the temperature dependence of the resistivity.

As the Ba/La ratio is increased from 0.25 (Fig. 1), $La_3Ba_3Cu_6O_{14+\delta}$ appears as a competing phase. The higher the Ba/La ratio, the more $La_3Ba_3Cu_6O_{14+\delta}$ is in the mixture. Interestingly, this mixture of $La_4BaCu_5O_{13+\delta}$ and $La_3Ba_3Cu_6O_{14+\delta}$ exhibits an X-ray diffraction pattern very similar to that of $YBa_2Cu_3O_{7-\delta}$ (Fig. 4).

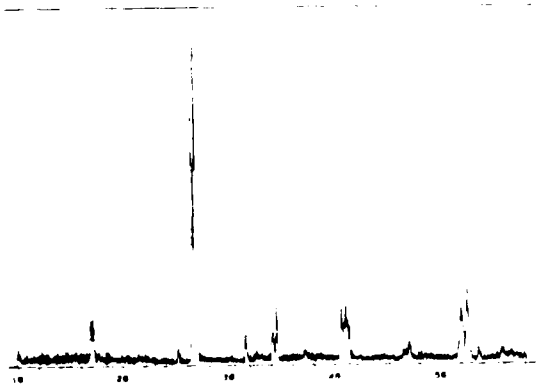

Fig. 4 The X-ray powder diffraction pattern of a mixture of $La_4BaCu_5O_{13+\delta}$ and $La_3Ba_3Cu_6O_{14+\delta}$, quite similar to that $YBa_2Cu_3O_{7-\delta}$

When the Ba/La ratio equals one, pure $La_3Ba_3Cu_6O_{14+\delta}$ is formed. The electrical and structural properties of this compound have been investigated by Raveau.[12,15] A recent neutron diffraction study of $La_3Ba_3Cu_6O_{14+\delta}$ indicates a tetragonal lattice with a = 3.9[illegible]Å and c = 11.69Å,[4] compared to the lattice parameters of a = 5.52Å and c = 11.72Å reported by Raveau [12]

$La_3Ba_3Cu_6O_{14+\delta}$ is semiconducting and the copper valence and the oxygen distribution can be varied by intercalation of oxygen into the structure. Fig. 5 shows the temperature dependence of the resistivity for $La_3Ba_3Cu_6O_{14+\delta}$ and our data are consistent with those previously reported.[15] When $1 < Ba/La < 2$, the high T_c superconducting phase $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$, La-123 is formed. It has either tetragonal symmetry with a = 3.923Å and c = 11.78Å or a slight orthorhombic distortion from tetragonal symmetry.[4,6] However, it is very difficult to prepare $LaBa_2Cu_3O_{7+\delta}$ as a pure phase. Even when $BaCuO_2$ is not detectable by X-ray diffraction, it has been shown to be present by other techniques, such as Raman spectroscopy.[7] We propose that at the preparative temperatures necessary for its formation, pure $LaBa_2Cu_3O_{7+\delta}$ tends to decompose by the following reaction.

$LaBa_2Cu_3O_{7+\delta}$ --------> $((3 - x)/3)La_{1+y}Ba_{2-y}Cu_3O_{7+\delta} + xBaCuO_2$

(where $y = x/(3 - x)$)

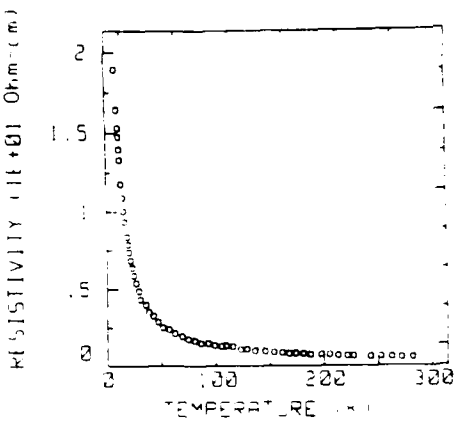

Fig. 5 Temperature dependence of the resistivity for $La_3Ba_3Cu_6O_{14+\delta}$

Therefore, the compound responsible for the high T_c superconductivity is $La_{1+y}Ba_{2-y}Cu_3O_{7+\delta}$ and not the compound with exact 1-2-3 stoichiometry. Thus, $La_{1.15}Ba_{1.85}Cu_3O_{7+\delta}$ was prepared without any $BaCuO_2$ impurity and this compound is superconducting at about 60 K, as shown in Fig. 6. Others have found similar results in the $La_{1+x}Ba_{2-x}Cu_3O_7$ system.[4]

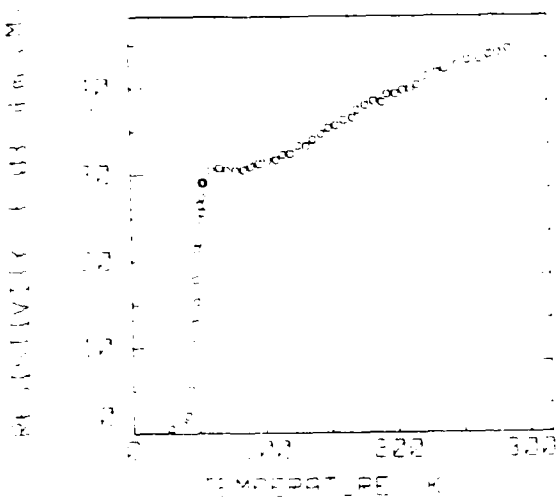

Fig. 6 Resistivity vs. temperature behavior of $La_{1.15}Ba_{1.85}Cu_3O_{7.3}$

with superconductivity for $0.2 < x < 0.5$ and decreasing values of T_c with increasing x.

The reason for the instability of $LaBa_2Cu_3O_{7+\delta}$ is not quite clear. It may be related to the A-cation size effect in the perovskite-type structure. It is well known that the stability of perovskite-type structure is affected by the A-cation size. In the case of pure $LaBa_2Cu_3O_{7+\delta}$, perhaps, the A-cations (33% La^{3+} + 67% Ba^{2+}) are too large, and the lattice is stabilized by reducing the Ba/La ratio, and hence the unit cell volume. Actually, the La-123 structure can form in a relatively large region of the phase diagram if the volume of the latice is reduced. We have prepared a series of A-cation deficient single phase compounds, $(LaBa_2)_xCu_3O_{7+\delta}$ $(0.67 < x < 0.96)$, which have smaller unit cells than near stoichiometric La-123. Table 1 summarizes the lattice parameters of $(LaBa)_xCu_3O_{7+\delta}$ phases. Substitution of La^{3+} by other rare-earth elements or the substitution of Ba^{2+} by Sr^{2+} and/or Ca^{2+} also facilitates the formation of pure compounds of the La-123 structure, as indicated by X-ray powder diffraction. This will be discussed in the following section.

The compounds, $La_{2-x}Ba_xCuO_4$ with the K_2NiF_4-type structure, also exist in a large area of the phase diagram as pure phases or as a competing phases. In addition to $BaCuO_2$, there is evidence of other binary Ba-Cu-O compounds, however, these could not be identified unambiguously, although Wang et al recently reported the existence of Ba_2CuO_3 and Ba_3CuO_4.[16]

A comparison of the phase diagram of the Y-Ba-Cu-O[16] and the La-Ba-Cu-O systems shows

Table 1. Lattice parameters of $(LaBa_2)_xCu_3O_{7.0}$ compounds

Sample	Stoichiometry(x)	a(Å)	c(Å)	T_c(K)
La-123	1.00	3.923	11.782	--
301	0.96	3.914(1)	11.771(2)	55.3
302	0.91	3.917(1)	11.752(2)	53.2
303	0.83	3.917(1)	11.748(2)	47.5
304	0.75	3.916(1)	11.745(2)	34.8(not sc)
305	0.67	3.907(2)	11.723(4)	no

some interesting differences. Generally, lanthanum and yttrium have quite different oxide chemistry, probably, partly due to the great differences in their effective ionic radii. Phases such as $Y_2Cu_2O_5$, Y_2BaCuO_5 and $YBa_3Cu_3O_7$ do not form in the La-Ba-Cu-O system. In the La-Ba-Cu-O system, only compounds with perovskite-related structures are found. Therefore, if the perovskite-type structure is essential for high T_c, the La-Ba-Cu-O system may be a worthwhile target, and should be further explored.

2. Superconductivity and copper chemistry in La-Ba-Cu-O system

The oxidation state of copper in $La_4BaCu_5O_{13.4}$ is 2.50, in $La_3Ba_3Cu_5O_{14.5}$ it is 2.35 and in $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ it is a constant 2.35. In the $(LaBa_2)_xCu_3O_{7.0}$ ($0.67 < x < 0.96$) phases studied here, the the formal valence of copper changes from 2.4 to 3.1. However, $La_4BaCu_5O_{13.4}$ is a typical p-type metal; $La_3Ba_3Cu_6O_{14.5}$ is semiconducting and only $La_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ ($0.2 < x < 0.5$) shows T_c to be compositional dependent, but not copper valence dependent. This suggests that the copper valence is not the only factor in determining the high T_c superconductivity.

In $(LaBa_2)_xCu_3O_{7.0}$, the formal copper valence can be varied because of the Ba/La deficiency in the lattice. The T_c of the samples is a function of the nominal copper valence (Table 1, Fig. 7 and Fig. 8). Interestingly, $(LaBa_2)_{0.67}Cu_3O_{7.0}$ indicates an extraordinarily high copper valence; it may contain only Cu^{3+} species, but it is only

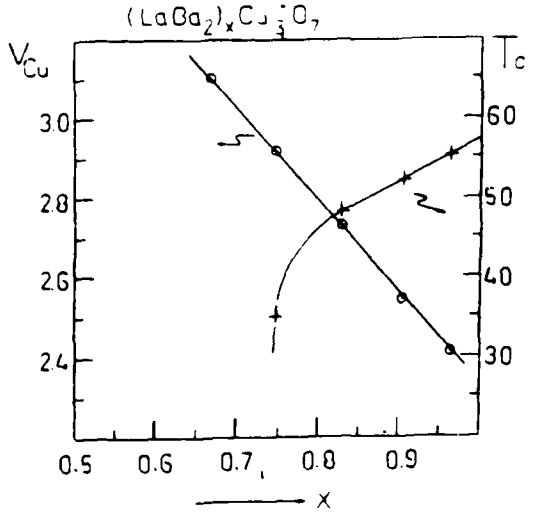

Fig. 7 Relationship between the formal copper valence and T_c for $(LaBa_2)_xCu_3O_{7.0}$ compounds

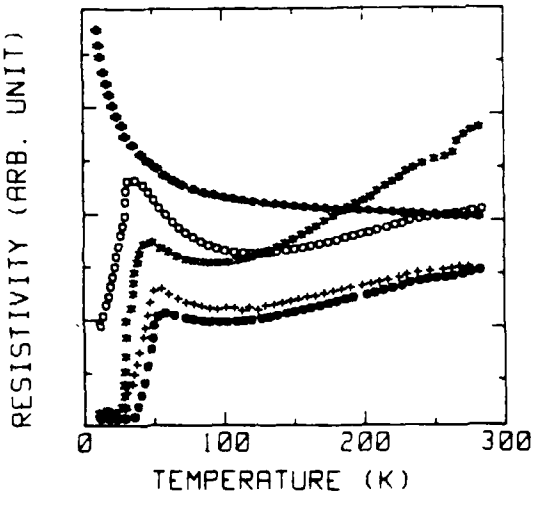

Fig. 8 Temperature dependence of the resistivity for $(LaBa_2)_xCu_3O_{7.0}$ •: x = 0.96; +: x = 0.91; *: x = 0.83; o: x = 0.75; #: x= 0.67

semiconducting. $(LaBa_2)_{0.75}Cu_3O_{7.0}$, displays a formal copper valence of 2.9 and a transition in the ρ vs. T at about 35 K (Fig. 8) but the resistivity does not go to zero down to 4 K. The phases with larger x values and correspondingly lower copper valences show superconductivity at higher T_c (Fig. 8).

All these compounds have the same seven oxygen content as determined by TGA. This oxygen stoichiometry is relatively high, compared with other high T_c compounds of the same class. The copper valence varies with the amount of deficiencies of the Ba/La cations in $(LaBa_2)_xCu_3O_{7.0}$. In $YBa_2Cu_3O_{7-\delta}$ the formal oxidation state of copper can vary only with the change in oxygen content. The conduction band of high T_c superconductors results from the

overlap of Cu $d_{x^2-y^2}$ and oxygen 2p-π orbitals. If both the copper formal valence (or possibly the oxygen valence) and oxygen content change, it is not clear which factor has a major effect on T_c in these materials. In $(LaBa_2)_xCu_3O_{7.0}$, there appears to be a relationship between the formal oxidation state of copper and T_c, since the oxygen content is constant at 7.0. But, both oxygen content and oxygen ordering are important factors for superconductivity as shown in the $YBa_2Cu_3O_{7-\delta}$ system.[17,18] Moreover, lattice distortions due to A-cation deficiencies may also affect the electrical properties significantly by oxygen and possibly Cu^{3+} ordering.

3. Substitution for Ba^{2+} in the La-123 compound

Since we noted that a smaller lattice facilitates the stability of the La-123 structure, Ca-substituted La-123 compounds were prepared as $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$ ($0 < x < 1$). The lattice parameters of these compounds are summarized in Table 2.

Table 2. Lattice parameters and T_c of $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$.

Sample	x	a(Å)	C(Å)	T_c(K)
La-123	0	3.923	11.782	--
336	0.2	3.914	11.73(1)	60.0
337	0.4	3.893(0)	11.70(0)	75.5
338	0.6	3.883(2)	11.66(1)	77.0
339	0.8	3.877(1)	11.62(0)	78.4
340	1.0	3.868(1)	11.62(1)	80.5

The lattice parameters decrease uniformly with increasing x in $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$, relative to "pure" La-123 (Table 2). Calcium substitution eliminates the $BaCuO_2$ impurity from the product as indicated by X-ray powder diffraction. T_c increases from 60 K up to 80 K as the calcium content increases. Fig. 9 illustrates the temperature dependence of the resistivity of the $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$ samples. In $La_{1+x}Ba_{2-x}Cu_3O_7$, the La^{3+}, Ba^{2+}

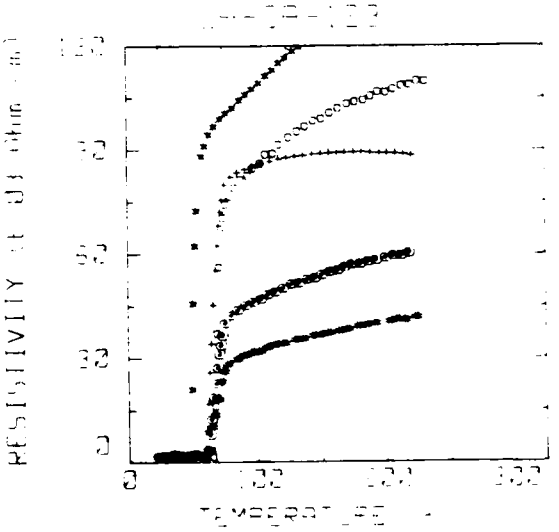

Fig. 9 Superconducting properties of $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$ compounds. *: x = 1.0; @: x = 0.8; +: x = 0.6; o: x = 0.4; *: x = 0.2

disordering is believed to affect the T_c. In the Ca^{2+} substituted phases, cation ordering similar to that found in $YBa_2Cu_3O_7$, may be occurring. It is noteworthy that the calculated lattice parameters of $LaBa_2CaCu_3O_{7+\delta}$ are very close to those of of $YBa_2Cu_3O_{7-\delta}$, further confirming that critical lattice dimensions are important for high superconducting transition temperatures in oxocuprates.

CONCLUSION

We have established the phase diagram of the La-Ba-Cu-O system in which compounds only with perovskite-type structures were found. The phase diagram is very different from that of Y-Ba-Cu-O. $(LaBa_2)_xCu_3O_7$ ($0.67 < x < 0.96$) phases were prepared with a large range of cation deficiencies. With careful oxygen annealing of these samples, the oxygen content in each was found to be constant at 7. Thus, the oxidation state of copper varied with x.

A clear relationship between the formal copper valence and T_c has been demonstrated. There is evidence that $LaBa_2Cu_3O_{7+\delta}$ is not stable. Cation deficiencies appear to reduce the lattice volume and stabilize the structure as demonstrated above. This is also confirmed by the formation of Ca substituted $LaBa_{2-x}Ca_xCu_3O_{7+\delta}$, where the T_c is enhanced with increasing x and the lattice parameters are comparable to those of Y-123 at $x = 1$.

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