Covalency of Cu—O Bonds in R123, R124, and Y247 (R = Rare Earth)

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The covalency of Cu—O bonds in $La_{0.5}R_{0.5}Ba_2Cu_3O_7$ (R = Pr, Nd, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm, Yb, Lu), $Pr_{0.5}R_{0.5}Ba_2Cu_3O_7$ (R = La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm, Yb, Lu), $RBa_2Cu_3O_7$ (R = Pr, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm), and $Y_2Ba_4Cu_7O_{14.3}$ was calculated using the complex crystal chemical bond theory. The result indicated that the bond covalency in CuO_2 plane was smaller than that in CuO chain in 123 and 124 systems. Based on our previous study, our result indicated that $La_{0.5}R_{0.5}Ba_2Cu_3O_7$ and $Pr_{0.5}R_{0.5}Ba_2Cu_3O_7$ are all superconductors. However, the nonsuperconducting behaviour of some of the title compounds indicated that further study is needed.

In recent years, polycrystalline ceramics $La_{0.5}R_{0.5}Ba_2Cu_3O_7$ (R = Pr, Nd, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm, Yb, Lu) (La—R123), $Pr_{0.5}R_{0.5}Ba_2Cu_3O_7$ (R = La, Nd, Sm, Eu, Gd, Dy, Ho, Y, Er, Tm, Yb, Lu) (Pr—R123), $RBa_2Cu_3O_7$ (R = Pr, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm) (R123) [1, 2] were synthesized by solid reaction technique. The crystal structures were given and the relationship between crystal structure and superconducting temperature was discussed. The experimental results showed that with the decrease of ionic radius of lanthanide (average value between La/Pr and R in La/Pr—R123) cell constants decreased. However, for Pr-doped 123 structures, the cell constant in c direction behaved like structures with smaller rare earth ionic radius (e.g. Dy). The distance between CuO_2 planes (CuO_2—R—CuO_2) was also diminished with the decrease of ionic radius of lanthanide because the bond distance of Cu(2)—O(1) decreased, meanwhile the bond distance of Cu(1)—O(1) remained unchanging, namely, the oxygen in apex moved closer to CuO_2 plane. In comparison with R123, the doping of La caused that the average bond distance R—O(2,3) shortened in La—R123, while this phenomenon was not observed in Pr—R123 [2]. This could mean that strain existed in La—R123.

On the other hand, although a lot of work has been focused on the study of Y123 structure, the drawback of Y123 structure was that it was unstable with the increase of temperature because part of the oxygen would be lost, which made the structure changing from orthorhombic to tetragonal phase [3]. For Y124, however, it was quite stable with respect to

its oxygen content and structure [4]. Because of its later discovery and need to prepare it at high oxygen temperatures, it was only in recent years that attention was paid to it. As in the 123 system, most of lanthanide can be substituted for the yttrium in Y124. Recently polycrystalline $RBa_2Cu_3O_8$ (R = Nd, Sm, Eu, Gd, Dy, Y, Ho, Er, Tm) has been prepared and studied by several groups [5—7]. It was found experimentally that with the increase of ionic radius the superconducting temperature decreased. Different from Y123, the superconducting temperature in R124 can be enhanced by doping, for instance, the doping of Ca on Y site increased the superconducting temperature from 80 K to 90 K. Recently, single crystals $RBa_2Cu_4O_8$ (R = Yb, Tm, Er, Ho, Dy) and Ca-doped $YBa_2Cu_4O_8$ were synthesized at 1100 °C and 60 MPa [8]. However, for rare earth with larger radius, stable 124 structure was not yet found. For $Y_2Ba_4Cu_7O_{14.3}$ (Y247) [9], the structure consists of single $YBa_2Cu_3O_{6+x}$-type blocks containing single corner-sharing CuO_4 square-planar chains, alternating with single $YBa_2Cu_4O_8$-type blocks containing double edge-sharing CuO_4 square-planar chains. The space group is Ammm. The superconducting temperature is 40 K and it is related to the oxygen content or the intergrowth of the different sequences.

In this paper, the covalency of Cu—O bonds in La—R123, Pr—R123, R123, $RBa_2Cu_3O_8$, and $Y_2Ba_4Cu_7O_{14.3}$ was calculated using the complex crystal chemical bond theory. The method can be found in Ref. [10] and the details will not be given here. Here we only briefly outline the definition for the

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bond covalency and ionicity. In analogy with the previous work [10], the average energy gap E_g^μ appearing for every type of μ bond can be separated into covalent or homopolar E_h^μ and ionic or heteropolar C^μ parts as the following

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \qquad (1)$$

The bond ionicity f_i^μ and bond covalency f_c^μ of any type of μ bond are defined as

$$f_i^\mu = (C^\mu)^2/(E_g^\mu)^2 \qquad (2)$$

$$f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 \qquad (3)$$

The physical interpretation of C^μ is that it is the difference between the screened Coulomb potentials produced by the two atoms composing the bond or, in other words, it is contributed by the interaction of point charge, while E_h^μ is contributed by the interaction of dipole moment and other multiple moments.

According to crystallographic data [1, 2] and theoretical method [10], $La_{0.5}R_{0.5}Ba_2Cu_3O_7$ can be decomposed as

$La_{0.5}R_{0.5}Ba_2Cu_3O_7 =$
$= La_{0.5}R_{0.5}Ba_2Cu(1)Cu(2)_2O(1)_2O(2)_2O(3)_2O(4)_1 =$
$= Ba_{4/5}O(1)_{4/3} + Ba_{2/5}O(2)_{2/3} + Ba_{2/5}O(3)_{2/3} +$
$+ Ba_{2/5}O(4)_{2/3} + La_{0.5/2}O(2)_{2\times0.5/3} +$
$+ La_{0.5/2}O(3)_{2\times0.5/3} + R_{0.5/2}O(2)_{2\times0.5/3} +$
$+ R_{0.5/2}O(3)_{2\times0.5/3} + Cu(1)_{1/2}O(4)_{1/3} +$
$+ Cu(1)_{1/2}O(1)_{1/3} + Cu(2)_{2/5}O(1)_{1/3} +$
$+ Cu(2)_{4/5}O(2)_{2/3} + Cu(2)_{4/5}O(3)_{2/3}$

Similar decomposition can be obtained for $Pr_{0.5}R_{0.5}Ba_2Cu_3O_7$ and $RBa_2Cu_3O_7$ and will not be given here. For the labels of elements, see Ref. [2]. In this paper bond valence was calculated by bond valence sums (BVS) scheme [11], in which bond valence is bond distance-dependent. According to BVS [11], valence of element i can be written as

$$V_i = \sum_\mu s_i^\mu \qquad (4)$$

where s_i^μ is the bond valence for μ-type bond and it is given as

$$s_i^\mu = \exp[(R_i^\mu - d_i^\mu)/b] \qquad (5)$$

where R_i^μ is the bond valence parameter. It is an empirical parameter dependent on the species of atoms and on the oxidation states. Their values have been tabulated for a wide variety of atomic pairs [11]. d_i^μ is the bond distance (in $\mathring{A}$), and b is a constant equal to 0.37. For detailed discussion, see Refs. [10, 11]. The calculated results are given in Fig. 1a—d.

The results indicated that for La—R123 (Fig. 1a) with the decrease of ionic radius of lanthanide, the trend of bond covalency of Cu(2)—O(2) and Cu(2)—O(3) was opposite (but symmetric), the former increased, while the latter decreased. The two lines intersected at $r = 1.09$ $\mathring{A}$ and the averaged covalency for Cu(2)—O(2) and Cu(2)—O(3) was less than that in CuO chain. In addition, the average value of Cu(2)—O(2) and Cu(2)—O(3) remained nearly unchanging with the changing of ionic radius. The bond covalency of Cu(2)—O(1) decreased with the decrease of ionic radius. The bond covalency of Cu(1)—O(1, 4) was not sensitive to the changing of ionic radius for $r > 1.09$ $\mathring{A}$, then oscillated for $r < 1.09$ $\mathring{A}$. For Pr—R123 (Fig. 1b) and R123 (Fig. 1c), similar regularity was observed as in La—R123 except that the oscillating magnitude was smaller. The bond covalency of Cu(2)—O(3) was less than that of Cu(2)—O(2) in Pr—R123 and R123, while this was true only when $r < 1.09$ $\mathring{A}$ for La—R123, when $r > 1.09$ $\mathring{A}$, opposite trend was observed. The bigger oscillation occurring in La—R123 was caused by the anomaly of the oxidation state of La. According to our calculation, the calculated oxidation state of La in some cases exceeded 4.0, which was much larger than its normal state 3.0, while this anomaly was not found in Pr—R123 and R123. This was because R—O bond distance in La—R123 was shorter (particularly for R—O(3) bond) than that in Pr—R123 (for instance, the bond distance of La/Pr—O(3) in $La_{0.5}Pr_{0.5}123$ [1] was much shorter than that in $Pr_{0.5}La_{0.5}123$ [2]), which made the oxidation state of rare earth in the former higher than that in the latter according to the BVS scheme [11], in particular for La. The increasing oxidation state of La made the oxidation states of copper in La—R123 less than those in Pr—R123 and R123. The combining effects made the covalency of Cu—O bonds in La—R123 oscillating dramatically.

From our results we also noticed that the bond covalency for Pr—R123 structures did not reveal irregularity. We knew that from our previous study superconductivity should occur if the bond covalency in CuO_2 plane (averaged for Cu(2)—O(2) and Cu(2)—O(3)) was less than that in CuO chain [12] in $Y_{1-x}Pr_xBa_2Cu_3O_7$. If this were true for 123 systems, we can deduce that Pr—R123, La—R123, and R123 in this study should all have superconductivity. However, the experimental results showed that superconductivity was not found in $La_{0.5}Pr_{0.5}Ba_2Cu_3O_7$, $R_{0.5}Pr_{0.5}Ba_2Cu_3O_7$ (R = La, Nd, Sm, Eu, Gd), this means further study is needed to solve the discrepancy.

$RBa_2Cu_4O_8$

According to crystallographic data [8], we have

$RBa_2Cu_4O_8 =$
$= RBa_2Cu_2(1)Cu_2(2)O_2(1)O_2(2)O_2(3)O_2(4) =$
$= Ba_{4/5}O_{4/3}(1) + Ba_{2/5}O_{2/3}(2) + Ba_{2/5}O_{2/3}(3) +$
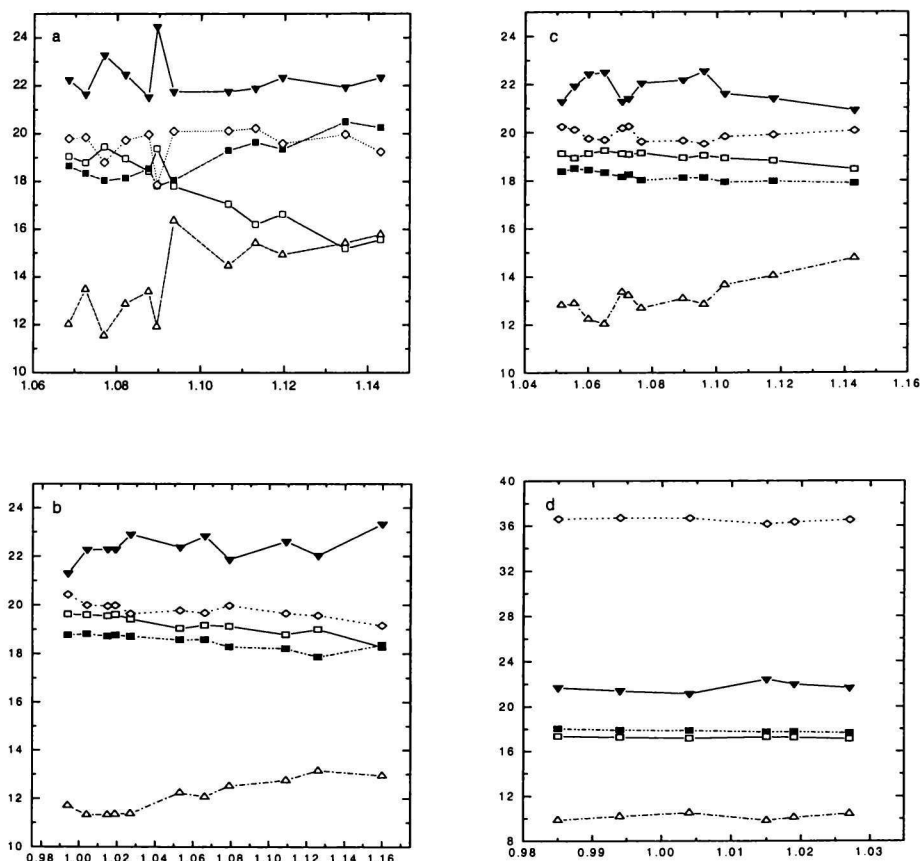
**Fig. 1.** Covalency of Cu—O bonds (%) *vs.* ionic radius ($\mathring{A}$) of lanthanide. *a)* La—R123, *b)* Pr—R123, *c)* R123, *d)* R124. In the case of La/Pr—R123, the average ionic radius of La/Pr and R was used. In Fig. 1*a*, an intersection for Cu(2)—O(2) and Cu(2)—O(3) can be seen at $r = 1.09$ $\mathring{A}$. Cu(1)—O(1) was represented by solid down-triangles, Cu(1)—O(4) by open diamonds, Cu(2)—O(2) by open squares, Cu(2)—O(3) by solid squares, Cu(2)—O(1) by open triangles. Cu(2)—O(2, 3) are in CuO plane, Cu(1)—O(1, 4) are treated in CuO chain (although O(1) is in apex), Cu(2)—O(1) in apex.

$+ \mathrm{Ba}_{2/5}\mathrm{O}_{4/5}(4) + \mathrm{R}_{1/2}\mathrm{O}_{2/3}(2) + \mathrm{R}_{1/2}\mathrm{O}_{2/3}(3) +$
$+ \mathrm{Cu}_{1/2}(1)\mathrm{O}_{1/3}(1) + \mathrm{Cu}_{3/2}(1)\mathrm{O}_{6/5}(4) +$
$+ \mathrm{Cu}_{2/5}(2)\mathrm{O}_{1/3}(1) + \mathrm{Cu}_{4/5}(2)\mathrm{O}_{2/3}(2) +$
$+ \mathrm{Cu}_{4/5}(2)\mathrm{O}_{2/3}(3)$

$\mathrm{Y}_{0.98}\mathrm{Ca}_{0.02}\mathrm{Ba}_2\mathrm{Cu}_4\mathrm{O}_8 =$
$= \mathrm{RBa}_2\mathrm{Cu}_2(1)\mathrm{Cu}_2(2)\mathrm{O}_2(1)\mathrm{O}_2(2)\mathrm{O}_2(3)\mathrm{O}_2(4) =$
$= \mathrm{Ba}_{4/5}\mathrm{O}_{4/3}(1) + \mathrm{Ba}_{2/5}\mathrm{O}_{2/3}(2) + \mathrm{Ba}_{2/5}\mathrm{O}_{2/3}(3) +$
$+ \mathrm{Ba}_{2/5}\mathrm{O}_{4/5}(4) + \mathrm{Y}_{0.98/2}\mathrm{O}_{2\times0.98/3}(2) +$
$+ \mathrm{Y}_{0.98/2}\mathrm{O}_{2\times0.98/3}(3) + \mathrm{Ca}_{0.02/2}\mathrm{O}_{2\times0.02/3}(2) +$
$+ \mathrm{Ca}_{0.02/2}\mathrm{O}_{2\times0.02/3}(3) + \mathrm{Cu}_{1/2}(1)\mathrm{O}_{1/3}(1) +$
$+ \mathrm{Cu}_{3/2}(1)\mathrm{O}_{6/5}(4) + \mathrm{Cu}_{2/5}(2)\mathrm{O}_{1/3}(1) +$
$+ \mathrm{Cu}_{4/5}(2)\mathrm{O}_{2/3}(2) + \mathrm{Cu}_{4/5}(2)\mathrm{O}_{2/3}(3)$
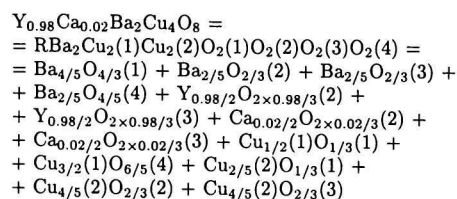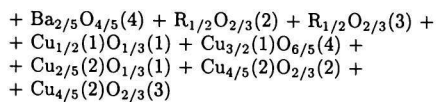
It is seen that (Fig. 1*d*) with the decrease of ionic radius from Dy to Yb, Cu—O bond covalency is not sensitive to the change of ionic radius. On the other hand, it is also evident that the bond covalency of Cu(1)—O(4) (O(4) is five-coordinated) is much larger than that of the other Cu—O bonds. The bond covalency in CuO$_2$ plane is smaller than that in CuO chain, and the studied compounds are all superconductors. This regularity is the same as observed in our present and previous calculation on R123 system [12].

$\mathrm{Y}_2\mathrm{Ba}_4\mathrm{Cu}_7\mathrm{O}_{14.3}$ (Y247)

The decomposition was given as

Table 1. Bond Covalency (%) in $Y_2Ba_4Cu_7O_{14.30}$

Cu(1)—O(1)	Cu(1)—O(8)	Cu(1)—O(9)	Cu(2)—O(1)	Cu(2)—O(2)	Cu(2)—O(3)
17.83	11.04	11.56	14.89	20.45	20.43
Cu(3)—O(4)	Cu(3)—O(5)	Cu(3)—O(6)	Cu(4)—O(6)	Cu(4)—O(7)	
17.52	17.50	12.35	16.55	35.09	

$Y_2Ba_4Cu_7O_{14.3} =$
$= Y_2Ba_2(1)Ba_2(2)Cu(1)Cu_2(2)Cu_2(3)Cu_2(4)O_2(1)-$
$O_2(2)O_2(3)O_2(4) O_2(5)O_2(6)O_2(7)O_{0.1}(8)O_{0.2}(9) =$
$= Ba_{8/8.6}(1)O_{4/3}(1) + Ba_{4/8.6}(1)O_{2/3}(2) +$
$+ Ba_{4/8.6}(1)O_{2/3}(3) + Ba_{0.2/8.6}(1)O_{0.2/3}(8) +$
$+ Ba_{0.4/8.6}(1)O_{0.4/3}(9) + Ba_{2/5}(2)O_{2/3}(4) +$
$+ Ba_{2/5}(2)O_{2/3}(5) + Ba_{4/5}(2)O_{4/3}(6) +$
$+ Ba_{2/5}(2)O_{4/5}(7) + Y_{1/2}(2)O_{2/3}(2) +$
$+ Y_{1/2}(2)O_{2/3}(3) + Y_{1/2}(2)O_{2/3}(4) +$
$+ Y_{1/2}(2)O_{2/3}(5) + Cu_{2/2.6}(1)O_{1/3}(1) +$
$+ Cu_{0.2/2.6}(1)O_{0.1/3}(8) + Cu_{0.4/2.6}(1)O_{0.2/3}(9) +$
$+ Cu_{2/5}(2)O_{1/3}(1) + Cu_{4/5}(2)O_{2/3}(2) +$
$+ Cu_{4/5}(2)O_{2/3}(3) + Cu_{4/5}(3)O_{2/3}(4) +$
$+ Cu_{4/5}(3)O_{2/3}(5) + Cu_{2/5}(3)O_{1/3}(6) +$
$+ Cu_{1/2}(4)O_{1/3}(6) + Cu_{3/2}(4)O_{5/6}(7)$
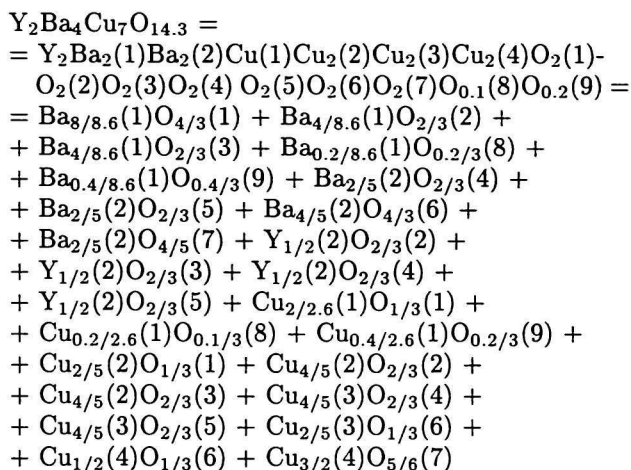
Because the valence of Cu is very complicated in Y247, the BVS scheme was not adopted (because no corresponding bond valence parameters were available). Therefore, the valence of Cu was calculated by electro-neutral principle. The calculated valence of Cu was: Cu(1) 1.40; Cu(2) 2.10; Cu(3) 2.30; Cu(4) 2.20, the average valence was 2.09, in good agreement with the reported results [9]: Cu(1) 1.0; Cu(2) 2.24; Cu(3) 2.24; Cu(4) 2.51, average valence: 2.09. The calculated bond covalency is listed in Table 1. The bond covalency related to O(8), O(9) was very small because our data were averaged results. Similar with the 124 structure, bond covalency related to five-coordinated O(7) was much larger than that in the other Cu—O bonds.

CONCLUSION

The results showed that the averaged bond covalency in CuO_2 plane was smaller than that in CuO chain in R123 and R124 systems. For 123 systems, our previous study indicated that if the averaged bond covalency in CuO_2 plane was less than that in CuO chain, superconductivity should occur. If this were true for 123 systems, our research indicates that the studied 123 systems in this paper should all have superconductivity. However, superconductivity in $La_{0.5}Pr_{0.5}Ba_2Cu_3O_7$, $R_{0.5}Pr_{0.5}Ba_2Cu_3O_7$, R = La, Nd, Sm, Eu, Gd was not found in experiment. This indicates that further study is needed to solve the discrepancy. For 124 systems, it seems that the regularity between the bond covalency in Cu—O plane and Cu—O chain and superconductivity also holds, at least for the studied compounds in this paper.

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