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Architecture of CuO_2 Layer Based High Temperature Superconductors and Related Materials

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We propose a modified classification scheme for the crystal structures of the CuO_2 layer based high temperature superconductors (Cu-HTSs) and related materials. Six layers of different atomic arrangements are derived from the perovskite, rock-salt, and fluorite structures. Stacking sequences of these six building layers are used to describe the crystal structures of all Cu-HTSs and related materials. The copper–oxygen configuration, the approximate unit cell size, and general symmetry information are easily obtained from the layer stacking sequence. A preference for certain elements due to charge and size considerations in different building layers is found. This elemental preference provides additional information in phase identification and in the design of new Cu-HTSs. © 1993 Academic Press, Inc.

Introduction

Following the discovery of high temperature superconductivity (*1*, *2*), a tremendous effort devoted to the search of new high temperature superconductors (HTSs) led to the identification of many superconducting compounds with more than two dozen different crystal structures. Among all known HTSs, the copper oxide layer based HTSs (Cu-HTSs) are particularly interesting because of their high superconducting transition temperatures and large variety of crystal structures. However, as more and more Cu-HTSs were identified, it became very important to have a classification scheme that could provide a simple and adequate description of each structure so that common structural features could be found and used as the basis of theoretical studies of high temperature superconductivity as well as in the search for new Cu-HTSs (*3–9*).

It is well known that all the Cu-HTSs' crystal structures can be viewed as a layer stacking of perovskite (including oxygen-deficient perovskites), rock-salt, and fluorite structures (hereafter: the basic structures). Therefore, a simple way to describe the crystal structures of Cu-HTSs is by the number and stacking sequence of these basic structures (*3*). The drawback of this method is that it does not distinguish between superconducting CuO_2 layers and charge-supplying CuO_x layers. For example, the crystal structure of $YBa_2Cu_3O_7$ could be described as a triple oxygen-deficient perovskite layered structure. But the three perovskite layers are not all the same, as one CuO_x layer is in the Cu–O chain configuration acting as a charge reservoir for the other two CuO_2 layers. Furthermore, a description of the crystal structure by the number of layers of the basic structures is not quite correct as the crystal structure of Cu-HTSs is generally composed of only halves of the unit cells of the basic structures. Consequently, a classification scheme using half of the unit cells of the basic structures as building blocks was later proposed (*5*). Unfortunately, this method

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is not easily applied to the design of new structures because in each block the lattice points are not occupied by whole atoms but rather by halves of the atoms. Extra caution has to be taken in order to ensure that the combination of two half unit cells restores the unity of the atoms. To avoid dealing with halves of the atoms, Santoro *et al.* (*4*) used layers of atoms as the building blocks and identified all the different layer atomic arrangements in the crystal structures of Cu-HTSs. Their method gives a clear picture of the crystal structures, but the number of basic layers they proposed can be reduced by considering translation relationships between the layers.

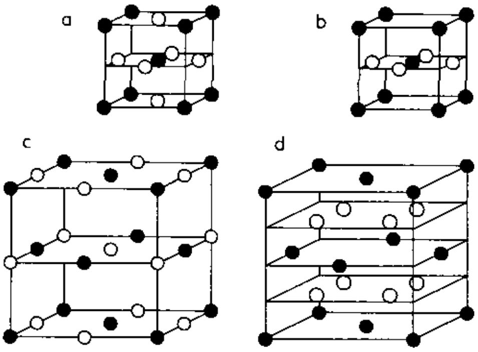

FIG. 1. Crystal structures of (a) the perovskite, (b) an oxygen-deficient perovskite, (c) the rock-salt and (d) the fluorite. The filled circles are cations and the open circles are anions.

So far, the latest and most comprehensive list of the crystal structures of the Cu-HTSs and related materials has been provided by Tokura and Arima (*8*), who classified these materials according to the crystal structures and the constituent elements simultaneously. As a result, from the structural point of view, there is some redundancy because of the isostructural analogues in different groups (e.g., Bi-2122 and Tl-2122). Their list could be improved by first grouping the Cu-HTSs and related materials according to their crystal structures, and then itemizing the constituent elements in each category. By doing so, the structural chemistry of the Cu-HTSs and related materials can be properly outlined. In the period between 1990 and 1992, several new superconducting and nonsuperconducting CuO_2 layer based compounds have been synthesized and identified (*10–16*). In the preparation of an up-to-date list of the crystal structures of Cu-HTSs and related materials, we have combined the concepts proposed by Santoro *et al.* (*4*) and Tokura and Arima (*8*) and present a modified classification method. Six building layers having the same translation relationship for the cations and approximately the same layer thickness are used in this modified scheme. Basic structural information of Cu-HTSs is easily obtained from the stacking sequence. A preference for certain elements in each different building layer is found. This elemental preference provides helpful guidance in phase identification and in the search for new Cu-HTSs and related materials.

The Basic Structures and the Six Building Layers

Figure 1 shows the perovskite, one oxygen-deficient perovskite, the rock-salt, and the fluorite crystal structures. Four different kinds of atomic layers are found (Fig. 2) in these structures: the MO_2 layer (M:

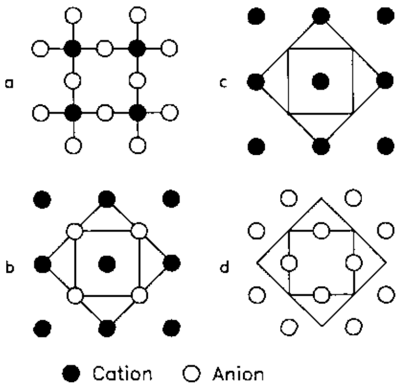

FIG. 2. Four different layer atomic arrangements identified in the perovskite, oxygen-deficient perovskite, rock-salt, and Fluorite structures: (a) MO_2 layer, (b) MO layer, (c) M layer, and (d) O_2 layer. The small square is the two-dimensional unit cell of the perovskite structure and the large square is the two-dimensional unit cell of the rock-salt and fluorite structures.

cation) in the perovskite and oxygen-deficient perovskite structures; the *M*O layer in perovskite and rock-salt structures; the *M* layer in oxygen-deficient perovskite and fluorite structures; and the O_2 layer in the fluorite structure. We will call the *M*O and *M* layer arrangements found in Cu-HTSs and related materials the **RS** and **V** layers respectively. The O_2 layer always appears sandwiched between two *M* layers in the Cu-HTSs' crystal structures. As seen below, it is convenient to term this M–O_2–M configuration the **F–F** layers (two **F** layers). As mentioned earlier, depending on the function performed, there are two different Cu–O layers. The superconducting CuO_2 layer, which has the MO_2 layer structure, will be identified as the **P** layer. The charge supply CuO_x layer will be called the **C** layer. Experimentally, the structure of the **C** layer can be MO_2 (as in the –223 crystal of Table I), *M* (as in –213 of Table I: $YBa_2Cu_3O_6$), or a chain configuration (as in –213 of Table I: $YBa_2Cu_3O_7$) depending on the oxygen content *x*. Experimentally, it is also found that the Cu in the **C** layer can be totally substituted by other elements like Co (*17*), Ta (*10, 18*), Nb (*11, 19*), or Ga (*12*). Therefore, the definition of the **C** layer is generalized to include metal oxide MO_x layers, where *M*: Co, Ta, Nb, and Ga. The substituted **C** layer can have the MO_2 structure as in the Nb- and Ta-substituted materials or a zigzag chain configuration as in the Ga-substituted materials.

After examining the Cu-HTSs' crystal structures, it is found useful to distinguish two types of **RS** layers: **R1** and **R2**. The **R1** layer is the **RS** type layer that is adjacent to the **P** layer. The cation in the **R1** layer always has a coordination number equal to or greater than eight: four oxygens in the neighboring **P** layer and another four oxygens in its own **R1** layer, and thus prefers large cations like Ba, Sr, Ca, or large size rare earth elements. The **R2** layer is the **RS** type layer that is not adjacent to the **P** layers. The coordination number of the cation in the **R2** layer is typically 6, therefore, the cation in the **R2** layer prefers to be a small cation like Tl, Bi, and Pb.

The concept of layer building blocks is illustrated in Fig. 3 by using the *Ln*–214–*T** phase (–222 of Table I) as an example. The structure is separated into layers, which are labeled **P, R1,** and **F–F** according to their atomic arrangement.

Table I lists the stacking sequence and idealized formula of the crystal structures of all known Cu-HTSs and related materials based on the six building layers: **P, V, F–F, C, R1,** and **R2**. All the different stacking sequences between two **P** layers are identified and listed in column 1 and row 1 of Table I. Structures listed in column 2 and row 2 contain only one kind of stacking sequence and the others (a_{ij}, i and $j > 2$) contain two kinds of stacking sequences (a_{i1} and a_{1j}) that alternate in the crystal structure of these compounds. The idealized formula is based on the (**R2**) (**R1**)(**V** and **F–F**)(**P** and **C**) sequence and does not count oxygen. For instance, the idealized formula of the **P–V–P–R1–R1** sequence will be $(\mathbf{R2})_0(\mathbf{R1})_2(\mathbf{V})_1(\mathbf{P})_2$, which is abbreviated as –212. The layer sequences that have not been found in the Cu-HTSs and related materials are left blank without idealized formulae. Table I is subdivided into five tables: IA–IE. Each table groups crystal structures with common structural features and gives examples of different constituent elements.

The superconducting $Y_2Ba_4Cu_7O_{15}$ structure (*20*) is not included in Table I. This compound is a metastable phase under ambient pressure at high temperature and can be viewed as an alternating arrangement of $YBa_2Cu_3O_7$ (–213 of Table I) and $YBa_2Cu_4O_8$ (–214 of Table I) structures. In order to simplify Table I, the structure of $Y_2Ba_4Cu_7O_{15}$ has been intentionally left out. The synthesis of metastable Cu-HTSs, which have a crystal structure consisting of two existing Cu-HTSs structures like the $YBa_2Cu_3O_7$–$Y_2Ba_4Cu_7O_{15}$–$YBa_2Cu_4O_8$ example, would be very interesting from the stability of structure point of view.

TABLE I

A LIST OF CRYSTAL STRUCTURES OF Cu-HTSs AND RELATED MATERIALS

Layer sequence	Formula	**P–V–**	**(P–V–)$_n$[a]**	**P–F–F–**	**P(–F)$_n$[a]**
		—11		—21	
P–R1–R1–	–2–1	–212		–222	
P–R1–C–R1–		–213		–223	–233[b]
P–R1–C–C–R1–		–214			
P–R1–R2–R1–	12–1	1212	n = 2, 1223	1222[c]	1232[b]
P–R1–R2–R2–R1–	22–1	2212	n = 2, 2223	2222[c]	
P–R1–R2–C–R1–		1213		1223[c]	n = 3, 1233[b]
P–R1–R2–C–R2–R1–	22–2	2213		2223[c]	n = 3, 2233[b]

[a] n: number of repeat layer.

[b] Non S.C.

[c] Pb-1222 and Bi-2222 are S.C. but Tl-1222 and Tl-2222 are non-S.C.

A. Cu in square–coplanar coordination

Sequence	Formula	Examples		Ref.
P–V–	—11	$(Sr_{1-x}Ln_x)CuO_2$, *Ln:* La, Pr, and Nd	$T_c \sim 40$ K	(1, 2)
		(Sr, Ba)CuO_2	$T_c \sim 80$–100 K	(3)
P–F–F–	—21	$Ln_{1.85}Ce_{0.15}CuO_2$, *Ln:* Pr, Nd, Sm, and Eu; *M:* Ce and Th,	$T_{c\,\max} = 28$ K	(4, 5)
		Ln: Gd	Non-S.C.	(5)

References:

A-1. M. G. Smith *et al.*, *Nature* **351,** 549 (1991).
A-2. G. Er *et al.*, *Physica C* **181,** 206 (1991).
A-3. Z. Hiroi *et al.*, *Physica C* **185–189,** 523 (1991).
A-4. Y. Tokura *et al.*, *Nature* **337,** 345 (1989).
A-5. J. T. Markert *et al.*, *Physica C* **158,** 178 (1989).

B. Cu in octahedral coordination

Sequence	Formula	Examples		Ref.
P–R1–R1–	–2–1	$La_{1.85}M_{0.15}CuO_4$, *M:* Ba, Sr, and Ca	$T_c \sim 40$ K	(1)
P–R1–R2–R1–	12–1	(T1, Tb)$(Ln, Sr)_2CuO_5$	$T_c \sim 16$ K	(2)
		$(Pb_{0.6}Cu_{0.5})(SrLa)CuO_5$	$T_c \sim 25$ K	(3)
P–R1–R2–R2–R1–	22–1	$Tl_2Ba_2CuO_6$	$T_c \sim 80$ K	(4)
		$Bi_2Sr_2CuO_6$	$T_c \sim 10$ K	(5, 6)
P–R1–R2–C–R2–R1–	22–2	$(Pb, Bi)_2(Sr_{0.4}La_{0.6})_2Cu_2O_6$, $x = 0.6$	$T_c \sim 30$ K	(7)

References:

B-1. J. G. Bednorz *et al.*, *Z. Phys. B* **64,** 189 (1986).
B-2. T. Itoh *et al.*, *Jpn. J. Appl. Phys.* **28,** L200 (1989).
B-3. S. Adachi *et al.*, *Jpn. J. Appl. Phys.* **29,** L890 (1990).
B-4. Z. Z. Sheng *et al.*, *Phys. Rev. Lett.* **60,** 937 (1988).
B-5. C. Michel *et al.*, *Z. Phys. B* **68,** 421 (1987).
B-6. J. Akimitsu *et al.*, *Jpn. J. Appl. Phys.* **26,** L2080 (1987).
B-7. H. W. Zanbergen *et al.*, *Physica C* **159,** 81 (1989).

C. Cu in pyramid coordination and structure containing a **V** layer

Sequence	Formula	Examples		Ref.
P–V–R–R1–R1–	–212	$(La_{1.6}Sr_{0.4})CaCu_2O_6$,	$T_c \sim 60$ K	(1)
P–V–P–R1–C–R1–	–213	$Ba_2YCu_3O_7$	$T_c \sim 90$ K	(2)
		$Ba_2YCoCu_2O_7$	Non-S.C.	(3)
		$Ba_2YTaCu_2O_8$	Non-S.C.	(4)
		$Ba_2YNbCu_2O_8$	Non-S.C.	(5)
		$Ba_2(Y_{1-x}Ca_x)GaCu_2O_7$	$T_{c\,\max} = 70$ K	(6)
P–V–R–R1–C–C–R1–	–214	$Ba_2YCu_4O_8$	$T_c \sim 80$ K	(7)
P–V–P–R1–R2–R1–	1212	$(Tl_{0.5}Pb_{0.5})Ba_2CaCu_2O_7$	$T_c \sim 85$ K	(8)
		$(Pb_{0.5}Sr_{0.5})Sr_2(Y_{1-x}Ca_x)Cu_2O_7$, $x = 0.5$–0.6	$T_c \sim 50$–70 K	(9)
P–V–P–R1–R2–R2–R1–	2212	$Tl_2Ba_2CaCu_2O_8$	$T_c \sim 110$ K	(10)
		$Bi_2Sr_2CaCu_2O_8$	$T_c \sim 80$ K	(11)
P–V–P–R1–R2–C–R1–	1213	$Pb(BaSr)(Y_{0.7}Ca_{0.3})Cu_3O_7$	$T_c \sim 37$ K	(12)
P–V–P–R1–R2–C–R2–R1–	2213	$Pb_2Sr_2(Y_{0.5}Ca_{0.5})Cu_3O_{8+y}$	$T_c \sim 68$ K	(13)

TABLE I—*Continued*

References:
C-1. R. J. Cava *et al.*, *Nature* **345,** 602 (1990).
C-2. M. K. Wu, *et al.*, *Phys. Rev. Lett.* **58,** 908 (1987).
C-3. Y. K. Tao *et al.*, *J. Mater. Res.* **3,** 248 (1988).
C-4. N. Murayama *et al.*, *Jpn. J. Appl. Phys.* **27,** L1623 (1988).
C-5. C. Greaves *et al.*, *Physica C* **161,** 245 (1989).
C-6. B. Dabrowski *et al.*, *Physica C* **193,** 63 (1992).
C-7. P. Marsh *et al.*, *Nature* **334,** 141 (1988).
C-8. M. A. Subramanian *et al.*, *Science* **242,** 249 (1988).
C-9. T. Rouillon *et al.*, *J. Solid State Chem.* **84,** 375 (1990).
C-10. H. Maeda *et al.*, *Jpn. J. Appl. Phys.* **27,** L209 (1988).
C-11. Z. Z. Sheng *et al.*, *Nature* **332,** 138 (1988).
C-12. A. Tokiwa *et al.*, *Physica C* **168,** 285 (1990).
C-13. R. J. Cava *et al.*, *Nature* **336,** 211 (1988).

D. Cu is in pyramid coordination and structure contains **F–F** layers

Sequence	Formula	Examples		Ref.
P–F–F–P–R1–R1–	–222	$(Nd_{0.59}Sr_{0.41})(Nd_{0.73}Ce_{0.27})CuO_4$	$T_c \sim 20$ K,	*(1)*
P–F–F–P–R1–C–R1–	–223	$(Ba_{0.667}Eu_{0.333})_2(Eu_{0.667}Ce_{0.334})_2Cu_3O_x$	$T_c \sim 40$ K	*(2)*
		$Y_2(Ba_{1.5}Ca_{0.5})Cu_3O_x$,	$T_c \sim 82$ K	*(3)*
		$Sr_2(Nd, Ce)_2TaCu_2O_y$	Non-S.C.	*(4)*
		$Sr_2(Nd_{1.5}Ce_{0.5})NbCu_2O_{10}$	$T_c \sim 28$ K	*(5)*
P–F–F–P–R1–R2–R1–	1222	$Tl_{1.3}Sr_{1.6}Pr_2Cu_2O_9$, $Tl_{1.3}Ba_{1.7}Pr_2Cu_2O_9$		
		$Tl_{1+x}Ba_{2-y}(NdCe)Cu_2O_9$	Non-S.C.	*(6)*
		$(Pb_{0.5}Cu_{0.5})(Eu_{0.75}Ce_{0.25})_2(Sr_{0.875}Eu_{0.125})_2Cu_2O_9$	$T_c \sim 25$ K	*(7)*
P–F–F–P–R1–R2–R2–R1–	2222	$Tl_2Ba_2(Eu_{1-x}Ce_x)_2Cu_2O_{10}$, $x = 0.1$,	Non-S.C.	*(8)*
		$Bi_2Sr_2(Ln_{1-x}Ce_x)_2Cu_2O_{10}$, $x = 0.18$,		
		Ln: Y, Nd, Sm, Eu, Gd, Dy, Ho	$T_c \sim 34$ K	
		Ln: Pr, Tb, Er, Tm,	Non-S.C.	(9)
P–F–F–P–R1–R2–C–R1–	1223	$Pb(Ba_{0.8}Sr_{1.2})(PrCe)Cu_3O_9$,	Non-S.C.	*(10)*
P–R–F–P–R1–R2–C–R2–R1–	2223	$Pb_2Sr_2(LnCe)Cu_3O_{10}$, *Ln:* Pr, Nd, Sm, La,	Non-S.C.	*(11)*

References:
D-1. E. Takayama-Muromachi *et al.*, *Jpn. J. Appl. Phys.* **27,** L2283 (1988).
D-2. Sawa *et al.*, *J. Phys. Soc. Jpn.* **58,** 2252 (1989).
D-3. R. G. Kulkarni *et al.*, *Solid State Commun.* **73,** 511 (1990).
D-4. L. Rukang *et al.*, *Physica C* **176,** 19 (1991).
D-5. R. J. Cava *et al.*, *Physica C* **191,** 237 (1992).
D-6. C. Martin *et al.*, *Mod. Phys. Lett.* **3,** 993 (1989).
D-7. T. Maeda *et al.*, *Physica C* **169,** 133 (1990).
D-8. Y. Tokura *et al.*, *Nature* **342,** 890 (1989).
D-9. T. Arima *et al.*, *Physica C* **168,** 79 (1990).
D-10. T. Rouillon *et al.*, *J. Solid State Chem.* **97,** 19 (1992).
D-11. T. Rouillon *et al.*, *Physica C* **167,** 107 (1990).

E. Others

Sequence	Formula	Examples		Ref.
((*n*)P–V)–P–R1–R2–R1–	$n = 2$, 1223	$(Tl_{0.5}Pb_{0.5})Ba_2Ca_2Cu_3O_9$	$T_c \sim 120$ K	*(1)*
((*n*)P–V)–P–R1–R2–R2–R1–	$n = 2$, 2223	$Tl_2Ba_2Ca_2Cu_3O_{10}$	$T_c \sim 125$ K	*(2)*
		$Bi_2Sr_2Ca_2Cu_3O_{10}$	$T_c \sim 110$ K	*(3)*
P–F–F–F–P–R1–C–R1–	–233	$Sr_2(Ho, Ce)_3Cu_3O_x$	Non-S.C.	*(4)*
P–F–F–F–P–R1–R2–R1–	1232	$(Pb, Cu)Sr_2(Ho, Ce)_3Cu_2O_{11}$	Non-S.C.	*(4)*
		$(Tl, Cu)Sr_2(Ho, Ce)_3Cu_2O_{11}$	Non-S.C.	*(5)*
P–(*n*)F–P–R1–R2–C–R1–	$n = 3$, 1233	$PbSr_2(Ln, Ce)_3Cu_3O_y$	Non-S.C.	*(6)*
P–(*n*)F–P–R1–R2–C–R2–R1–	$n = 3$, 2233	$Pb_2Sr_2(Ln, Ce)_3Cu_3O_y$	Non-S.C.	*(6)*

References:
E-1. M. A. Subramanian *et al.*, *Science* **242,** 249 (1988).
E-2. Z. Z. Sheng *et al.*, *Nature* **332,** 138 (1988).
E-3. H. Maeda *et al.*, *Jpn. J. Appl. Phys.* **27,** L209 (1988).
E-4. T. Wada *et al.*, *Physica C* **171,** 344 (1990).
E-5. T. Wada *et al.*, *Physica C* **175,** 529 (1991).
E-6. A. Tokiwa *et al.*, *Physica C* **181,** 311 (1991).

Note. Formula based on the (R2)(R1)(V and F–F)(P and C) sequence.

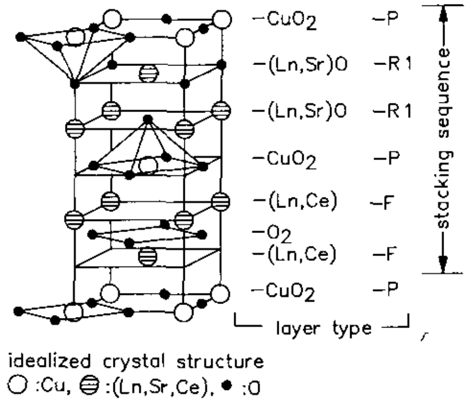

FIG. 3. An example showing the layer stacking sequence of the idealized *Ln*214–*T** structure based on the six basic building layers.

General Structural Information

One advantage of our method is that several basic structural aspects of the compounds are quickly drawn from the layer sequence:

(*1*) *Local configuration for copper.* From Table I, only five different stacking sequences sandwiching the **P** layer are found. When sandwiched between identical layers as in **R1–P–R1, V–P–V,** or **F–F–P–F–F** the Cu in the **P** layer will have a symmetrical configuration: either octahedral or square–coplanar configuration. Since **V** and **F–F** layers provide no oxygen bonding to the Cu in the **P** layer, a square–coplanar coordination is found in the **V–P–V** and **F–F–P–F–F** layer sequences (Table IA). On the other hand, since the **R1** layer provides an apical oxygen to the Cu in the **P** layer, an octahedral coordination is found in the **R1–P–R1** stacking sequence (Table IB). Finally, if the **P** layer is sandwiched between different layers as in **R1–P–F–F** or **R1–P–V,** then the Cu is in a pyramid configuration (Tables IC, ID, and IE).

Geometrically, stacking sequences such as **F–F–P–V, C–P–V, P–P–V,** . . . are all possible. In the **F–F–P–V** sequence, the symmetrically square–coplanar coordinated CuO_2 layer is sandwiched in an asymmetric environment between the **F–F** layer on one side and **V** layer on the other side. Therefore, the **F–F–P–V** stacking sequence is not favored energetically and is not found in the crystal structures of Cu-HTSs and related materials. The absence of the **P–P–**type sequence is probably due to the coulomb repulsion between the negatively charged **P** layers. The same can be said about the missing **C–P–** type sequence. The **R2** layer is, by definition, the **RS** type layer that is not adjacent to the **P** layer and thus is not considered.

(*2*) *The symmetry information in general.* Even though the number and arrangement of the oxygen atoms are different in the six building layers, the geometric relationship among cations is the same. It is found that there is always a translation relationship $(\frac{1}{2}, \frac{1}{2})$ in the crystallographic *ab* plane of the cations in neighboring layers with the only exception of the **C–C** layer sequence as in the –214 structure, which is $(0, \frac{1}{2})$. As a result, the translation relationship between any two layers can be easily found by counting the layer sequence between the two layers. For example, the $YBa_2Cu_3O_7$ structure is described as a **–P–V–P–R1–C–R1–** stacking sequence. The Cu atoms in the two **P** layers are facing each other because of the two layer sequence (**P–V–P**). This stacking sequence also represents a complete $YBa_2Cu_3O_7$ unit cell because the even number of stacking layers (six layers) results in a primitive cell (in case of an orthorhombic distortion in the CuO_2 plane, then it is a *C*-centered cell). In the case of having an odd number of layers in one stacking sequence, the $(\frac{1}{2}, \frac{1}{2})$ translation results in a body-centered unit cell (in case of an orthorhombic distortion in the CuO_2 plane, then it is a *F*-centered cell).

Generally speaking, mirror symmetry perpendicular to the *c* axis is found to locate on the **P** layer when Cu is in the four- or sixfold coordination (row 2 and column 2 of Table I), and locate in the middle of two **P** layers when Cu is in the fivefold coordination.

(*3*) *The approximate unit cell size.* Another feature of our method is that the thickness of each layer, ~2 Å per layer, and the number of cations per unit cell of the layer, one cation per layer, are approximately the same for different building layers. (In the M–O_2–M stacking sequence, since there are two cation layers involved, they are identified as the **F–F** layers.) The advantage of doing so is that the approximate size of the unit cell can be calculated easily by counting the number of layers or number of the cations in one unit cell.

The Elemental Preference

In phase identification of Cu-HTSs, it is found that the lattice constants of several different structures are very close. Additional information or detailed structural analysis is needed in order to unambiguously identify the phases from X-ray diffraction experiments. Furthermore, in designing new Cu-HTSs and related materials, we have also found that it is unrealistic to consider only the geometric stacking of different layers. Charge neutrality and size of constituent elements are also important considerations. This leads us to investigate the preference for certain elements in different layers.

Although many constituent elements in Cu-HTSs and related materials can exist in multivalence, the most commonly found oxidation states of different elements are used to simplify the charge balance consideration. Assuming a 2+ valence state for Cu and a 2− valence state for O in the **P** layer, the nominal valence of the **P** layer will be 2−. In order to maintain the charge balance of the whole structure, the charge supply building layers have to carry a positive charge by doping or by selecting proper elements. For example, La_2CuO_4–T phase (the -2–1 in Table I), the layer sequence of a complete unit cell is **P–R1–R1–P–R1–R1–**. Every set of two **R1** layers has to supply 2+ in order to balance one 2− **P** layer. Therefore, each **R1** layer has to be in a 1+ state. The nominal composition of the **R1** layer is MO. Since oxygen is normally considered as 2−, there will be a preference for the 3+ ion in the M position in this example.

TABLE II

THE PREFERENCE FOR CERTAIN ELEMENTS IN DIFFERENT BUILDING LAYERS

Layer	Elemental preference
P	Cu
C	Cu, Co, Nb, Ta, Ga, (Cu, Fe)
R1	Ba, Sr, Ca, and large size rare earth elements
R2	Tl, Bi, Pb, (Pb, Cu), (Pb, Sr)
V	Rare earth elements, Ca, and occasionally Sr
F–F	Medium size rare earth elements and Ce doping

Besides the charge consideration, the local atomic configuration (coordination number) could also induce a preference for certain elements as has already been discussed for **R1** and **R2** layers. The same reason might also explain the preference for the medium size elements such as rare earth elements, Ca, and occasionally Sr in the **V** layer (eightfold coordination).

The preference for Ce doping in the **F–F** layer is a very interesting observation. It seems that the Ce doping tends to stabilize the crystal structure containing the **F–F** layers. The phenomenon might be related to the fact that CeO_2 crystallizes in the fluorite structure. Actually, the crystal structures of the recently identified multifluorite-layered nonsuperconducting cuprate can be viewed as an intergrowth of neutral CeO_2 layers between the original **F–F** layers (*13–16*). The distance between two Ce in CeO_2 fluorite structure is 3.82 Å, which fits the Cu–Cu distance of ~3.8–3.9 Å in the **P** layer quite well (<2% mismatch). The medium size rare earth elements (e.g., Nd, Gd, Eu) are also found to preferentially form the **F–F** and multi-**F**-layer (e.g., **F–F–F**) structures experimentally. This can be understood from size considerations as discussed by Xue *et al.* (*21*).

The preference for certain elements in different layer is summarized in Table II. This elemental preference could be used to establish the stacking sequence and check the result of the crystal structure determination. For example, the crystal structure of the $PbSr_2CaCu_3O_{10}$ compound could be the **P–V–P–V–P–R1–R1–** stacking sequence, which has triple superconducting CuO_2 layers as original proposed (*22*), or the **–P–V–P–R1–R2–C–R1–** stacking sequence as later observed (*23*). Since, up to now, there are no Cu-HTSs that have a **V** or **R1** layer composed of Pb, the $PbSr_2CaCu_3O_{10}$ compound is more likely to be a double superconducting layered structure.

Summary

We have used the building block concept and six building layers to construct the crystal structures of all Cu-HTSs and related materials. The copper configuration, the approximate unit cell size, and general symmetry information are easily derived from the layer stacking sequence. A preference for certain elements due to charge and size consideration in different building layers is found. This elemental preference provides helpful guidance in phase identifications.

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