

HIGH PRESSURE SYNTHESIS OF NOVEL HIGH T_c SUPERCONDUCTORS

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We discuss the advantages of high pressure in studying high T_c superconductors (HTSs). HTSs, in general, can be viewed as perovskite derivatives containing a $[\text{CuO}_2]$ plane. We will describe the crystal structure assembly of HTSs on the basis of the 'extended infinite layer model'. Then, we introduce some topics related to high pressure synthesized superconductors in A–Cu–O systems (A represents alkaline earth elements) like the $\text{Cu-}12(n-1)n$ superconducting homologous series. Also included in the article is the high pressure high temperature synthesized $\text{Cl-}02(n-1)n$ superconducting homologous series, highlighting the 'apical oxygen doping' mechanism to generate p-type superconductivity.

Keywords: High pressure synthesis; High T_c superconductors; Perovskite-like compounds; Multilayered $[\text{CuO}_2]$ planes; Oxyhalide cuprates; Infinite layer model

INTRODUCTION

Since the discovery of high T_c superconductors (HTSs) of cuprate oxide in 1986 by Bednorz and Müller [1], a lot of HTSs compounds have been synthesized [2]. HTSs are crystallographically a kind of perovskite derivative with the $[\text{CuO}_2]$ plane being the central configuration [3]. High pressure provides a unique thermodynamic environment to get such high density compounds like perovskites, as it is very well established that the lower mantle of the Earth, which is under high pressure and high temperature states, consists of minerals primarily with ABO_3 perovskite structures. Therefore, it is not surprising that high pressure is favorable to stabilize novel HTSs. One of the advantages of high pressure in studying HTSs is that high oxygen pressure could effectively modulate the copper valence, which is not only crucial to generate superconductivity, but also important in developing new structure. The empirical measure to justify the feasibility of the ABO_3 perovskite structure is the tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$, which in the ideal case is equal to 1, where r_A , r_B and r_O are the atomic radii of the relatively larger cation A, the smaller legend cation B and the oxygen, respectively. The t factor is conventionally modified by composition and temperature. As the A–O and B–O layers usually have different compressibility,

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pressure could be one more effective dimension to tune the t value. Therefore, the obvious merit of high pressure is to offer the opportunity to design and realize novel perovskite-like structures, which otherwise are hard to approach in ambient conditions. Moreover, high pressure is inclined to stabilize a structure with multilayered $[\text{CuO}_2]$ planes as demonstrated in most of homologous series of HTSs. Here, we will briefly introduce the crystal chemistry of HTSs on the basis of the ‘extended infinite layer assembly model’, followed by presenting the examples of high pressure synthesized multilayered $\text{Cu-}12(n-1)$, as well as the $\text{Cl-}02(n1)n$ superconducting homologous series.

GENERAL CRYSTAL CHEMISTRY OF HTSs: THE DERIVATIVES OF PEROVSKITE

As shown in Figure 1, structurally, HTSs consist of two blocks, *i.e.*, the conducting block containing the $[\text{CuO}_2]$ plane and the charge reservoir block [3–5]. The $[\text{CuO}_2]$ conducting block can be further divided into the alternating stack of a $[\text{CuO}_2]$ plane and a spacer sheet. The charge reservoir block consists of heavy metal layer(s) being connected by interface layer(s) to the outmost conducting $[\text{CuO}_2]$ plane. The interface layer is the part that directly connects with the $[\text{CuO}_2]$ plane, and is usually composed of an $[\text{AO}]$ rock salt or perovskite type sheet for p-type HTSs, or sometimes fluorite type sheets for n-type HTSs, where A represents alkaline earth or rare earth elements. The charge reservoir layer that is farther from the $[\text{AO}]$ interface sheet is called the ‘heavy metal’ layer, which usually consists of the oxide of transition or post transition metal like Bi, Cu, Hg, Tl, Pb, *etc.* The role of the charge reservoir block is to generate and inject charge carriers into the $[\text{CuO}_2]$ plane. The unit cell of an HTS could contain several consecutive $[\text{CuO}_2]$ planes being interlaced with the bare $[\text{Ca}]$ spacer sheet. The extreme case is that when the number of $[\text{CuO}_2]$ planes in a unit cell approaches infinity, the structure will simply become the periodic

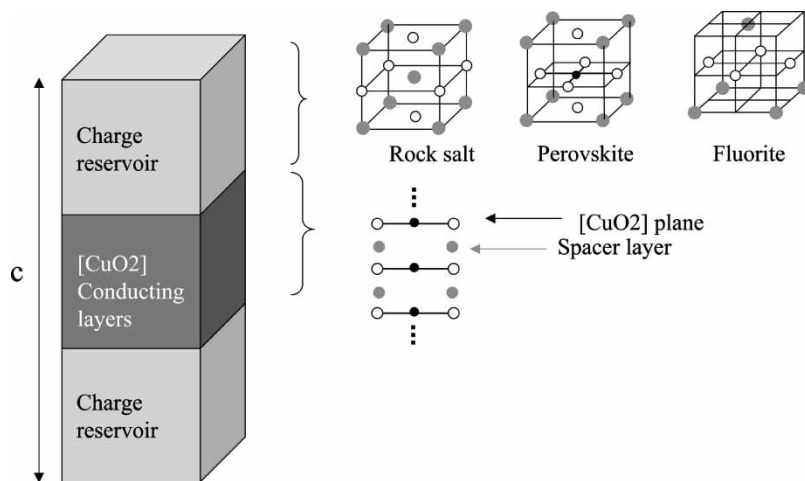


FIGURE 1 A schematic view of the crystal structure of HTSs, which in principle are composed of the charge reservoir sub-block and the $[\text{CuO}_2]$ conducting sub-block. There are three types of charge reservoir substructures: rock salt, perovskite and fluorite. The $[\text{CuO}_2]$ conducting block contains the periodical stacking of the $[\text{CuO}_2]$ plane and a spacer sheet.

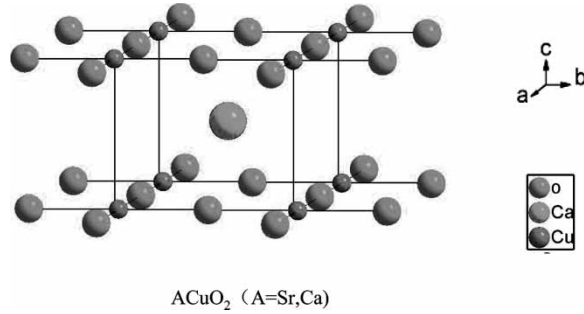


FIGURE 2 The $CaCuO_2$ infinite layer is the simplest compound containing the $[CuO_2]$ plane.

stacking of $[CuO_2]$ planes and $[Ca]$ spacer sheets. This structural form is consequently named the infinite layer [7] as shown in Figure 2. The infinite layer structure is the simplest cuprate containing a $[CuO_2]$ plane. Actually, the infinite layer is a deficit $ACuO_3$ perovskite wherein two oxygen atoms at the $[AO]$ plane are missing. Figure 3 shows three types of Cu–O coordinations in HTSs, *i.e.*, (a) the six-coordinated octahedron, (b) the five-coordinated pyramid and (c) the four-coordinated square. They result simply from an $ACuO_3$ perovskite with full oxygen stoichiometry, missing one oxygen atom at the $[AO]$ sheet and missing two oxygen atoms at both $[AO]$ sheets. But all in all they keep the $[CuO_2]$ plane complete and intact. Therefore, the four-coordinated $[CuO_2]$ square plane is the most basic configuration of an HTS. This oxygen deficient $[ACuO_2]$ perovskite cell is nothing but the infinite layer

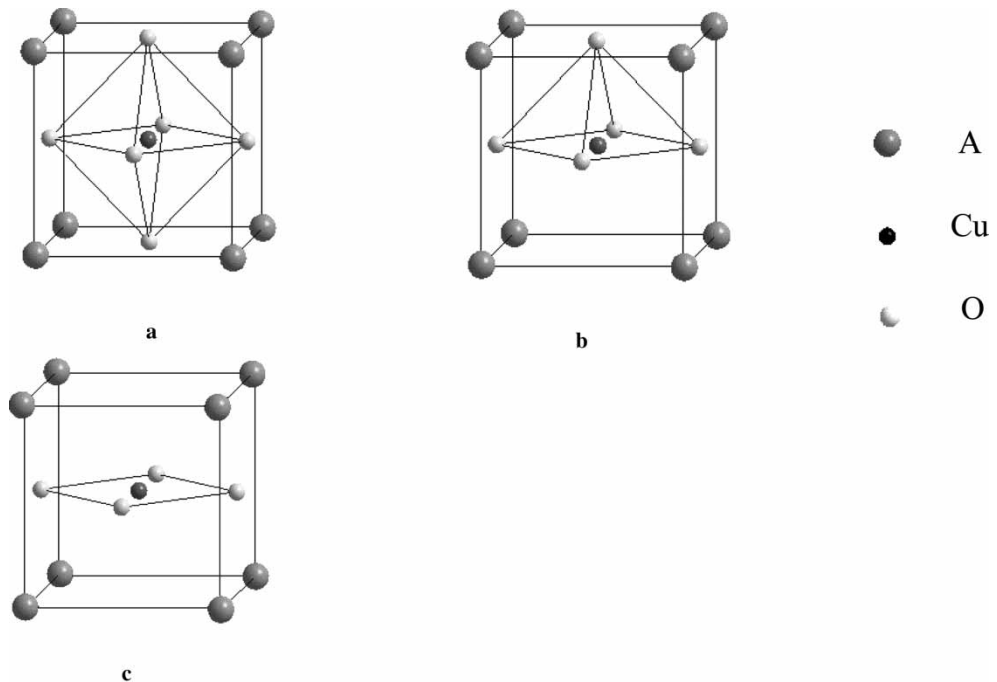


FIGURE 3 Three types of Cu–O coordinations in HTSs: (a) the six-coordinated octahedron, (b) five-coordinated pyramid and (c) four-coordinated square.

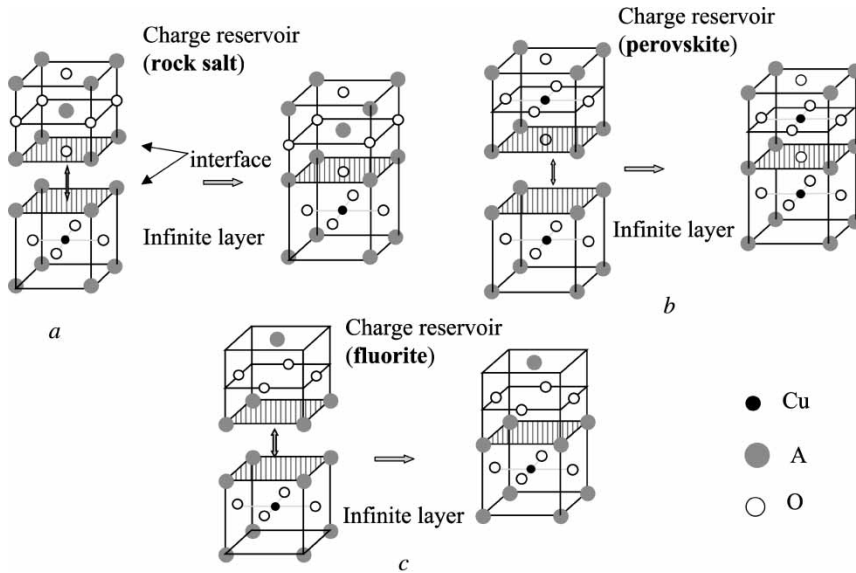


FIGURE 4 The combination of the infinite layer block with three types of charge reservoir blocks: (a) rock salt, (b) fluorite and (c) perovskite.

structure. Figure 4 shows the three main types of stacking of infinite layer cells with different types of interface layers of charge reservoir blocks, *i.e.*, the connection to (a) the rock salt type, (b) the perovskite type and (c) the fluorite type. The different combinations of these three types of connections thus could give rise to various possible structural forms of HTSs with different charge reservoir block configurations. Of course, the infinite layer can stack itself, leading to multi $[\text{CuO}_2]$ layer characteristics of HTSs in one unit cell. We called this structural building-up form the 'extended infinite layer structure assembly model' as it is formally constructed on the basis of the infinite layer cell. Here, the outmost $[\text{ACuO}_2]$ configuration, where A is usually an alkaline or rare earth element, is termed the 'primary infinite layer cell', from which the $[\text{CuO}_2]$ conducting block is extended to the charge reservoir. The $[\text{A}'\text{CuO}_2]$ configuration inside the $[\text{CuO}_2]$ conducting block is named the 'central infinite layer cell', where the A' is usually the bare $[\text{Ca}]$ sheet in between two neighboring $[\text{CuO}_2]$ planes, but sometimes the rare earth element sheet for the double layered $[\text{CuO}_2]$ planes' case such as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Table I provides the detail of the sub-block structure of some HTSs. In the four digit nomenclature, crystal structure of an HTS is usually termed $\text{M} - m_1m_2(n-1)n$ [3–6]. Here, M is the heavy metal element (Bi, Cu, Hg, Tl, Pb, etc.), and m_1 is its layer number which could be 0, 1, 2 or up to 3 thus far being reachable; m_2 is the number of the interfacial layer; $(n-1)$ is the number of the spacer layer, whereas n is the number of consecutive $[\text{CuO}_2]$ planes in the unit cell. Figure 5 shows the schematic view of the Hg-1223 expressed in the terminology. The research on HTSs greatly enhanced the understanding of crystal chemistry – the novel compound synthesis and the property *vs.* structure correlation of the perovskite-like compounds with the application of high pressure. Here, we will briefly introduce the superconducting homologous series synthesized under high pressure. They are the $\text{Cu-}12(n-1)n$ compounds with the perovskite-like charge reservoir and the $\text{Cl-}02(n-1)n$ compounds with the rock salt type oxyhalide charge reservoir.

TABLE I The construction of the charge reservoir and the conducting layer block of the HTSS on the basis of the 'extended infinite layer structure assembly model'.

Assembly	$02(n-1)n$			$12(n-1)n$			$22(n-1)n$		
	0201	0212	0223	1201	1212	1223	2201	2212	2223
Superconductors	La ₂ CuO ₄ (Sr,Ca) ₂ CuO _{3+δ} (Sr,Ca) ₂ CuO _{2+δ} Cl ₂	(La,Ca) ₃ Cu ₂ O ₆ (Sr,Ca) ₃ Cu ₂ O _{5+δ} (Sr,Ca) ₃ Cu ₂ O _{4+δ} Cl ₂	(Sr,Ca) ₄ Cu ₃ O _{7+δ} (Sr,Ca) ₄ Cu ₃ O _{6+δ} Cl ₂	HgBa ₂ CuO _{4+δ} TlBa ₂ CuO _{4+δ}	YBa ₂ Cu ₃ O ₇ HgBa ₂ CaCu ₂ O _{6+δ} TlBa ₂ CaCu ₂ O _{6+δ}	CuBa ₂ Ca ₂ Cu ₃ O _{8+δ} HgBa ₂ Ca ₂ Cu ₃ O _{8+δ} PbSr ₂ Ca ₂ Cu ₃ O _{8+δ} TlBa ₂ Ca ₂ Cu ₃ O _{8+δ}	Bi ₂ Sr ₂ CuO _{4+δ} Tl ₂ Sr ₂ CuO _{4+δ}	Bi ₂ Sr ₂ CaCu ₂ O _{6+δ} Tl ₂ Sr ₂ CaCu ₂ O _{6+δ}	Bi ₂ Sr ₂ Ca ₂ Cu ₃ O _{8+δ} Tl ₂ Sr ₂ Ca ₂ Cu ₃ O _{8+δ}
Charge reservoir block Heavy metal layer/ structure type	-	-	-	[HgO]/R [TlO]/R	[CuO ₂]/P [HgO]/R [TlO]/R	[CuO ₂]/P [HgO]/R [PbO]/R [TlO]/R	[BiO][BiO]/R [TlO][TlO]/R	[BiO][BiO]/R [TlO][TlO]/R	[BiO][BiO]/R [TlO][TlO]/R
Interface layer/ structure type	[LaO][LaO]/R [SrO][SrO]/R [SrCl][SrCl]/R	[LaO][LaO]/R [SrO][SrO]/R [SrCl][SrCl]/R	[LaO][LaO]/R [SrO][SrO]/R [SrCl][SrCl]/R	[BaO]/R [BaO]/R	[BaO]/P [BaO]/R [BaO]/R	[BaO]/P [BaO]/R [SrO]/R [BaO]/R	[SrO][SrO]/R [SrO][SrO]/R	[SrO][SrO]/R [SrO][SrO]/R	[SrO][SrO]/R [SrO][SrO]/R
[CuO ₂] Conducting block The primary infinite layer	[LaCuO ₂] [(Sr,Ca)CuO ₂] [(Sr,Ca)CuO ₂]	[LaCuO ₂] [(Sr,Ca)CuO ₂] [(Sr,Ca)CuO ₂]	[LaCuO ₂] [(Sr,Ca)CuO ₂] [(Sr,Ca)CuO ₂]	[BaCuO ₂] [BaCuO ₂]	[BaCuO ₂] [BaCuO ₂] [BaCuO ₂]	[BaCuO ₂] [BaCuO ₂] [SrCuO ₂] [BaCuO ₂]	[SrCuO ₂] [SrCuO ₂]	[SrCuO ₂] [SrCuO ₂]	[SrCuO ₂] [SrCuO ₂]
The central infinite layer	-	[CaCuO ₂] [CaCuO ₂]	[CaCuO ₂] [CaCuO ₂]	-	[YCuO ₂] [CaCuO ₂] [CaCuO ₂]	[CaCuO ₂] [CaCuO ₂] [CaCuO ₂] [CaCuO ₂]	-	[CaCuO ₂] [CaCuO ₂]	[CaCuO ₂] [CaCuO ₂]

Note: The four digit nomenclature is expressed in the formula $M - m_1 m_2 (n - 1)n$: M is the heavy metal in the charge reservoir, m_1 is the [MO] layer number, m_2 is the number of the {AO} interface layer, $(n - 1)$ is the number of the spacer layer and n is the number of the [CuO₂] plane. To a specified homologous series, its constituted member is related to the number of center infinite layers. 'R' means the sub-block is of rock salt type structure; 'P' means the sub-block is of perovskite type structure.

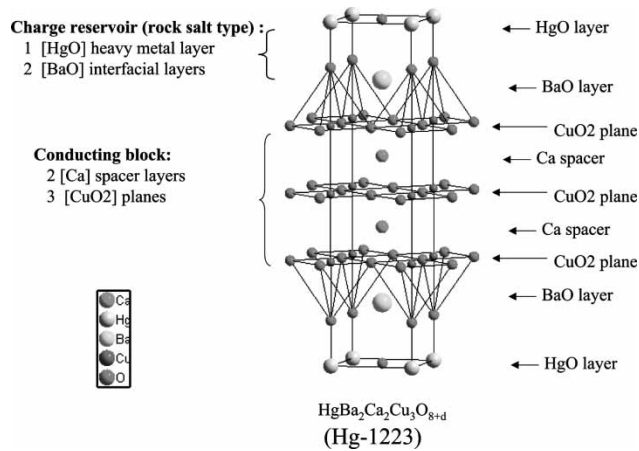
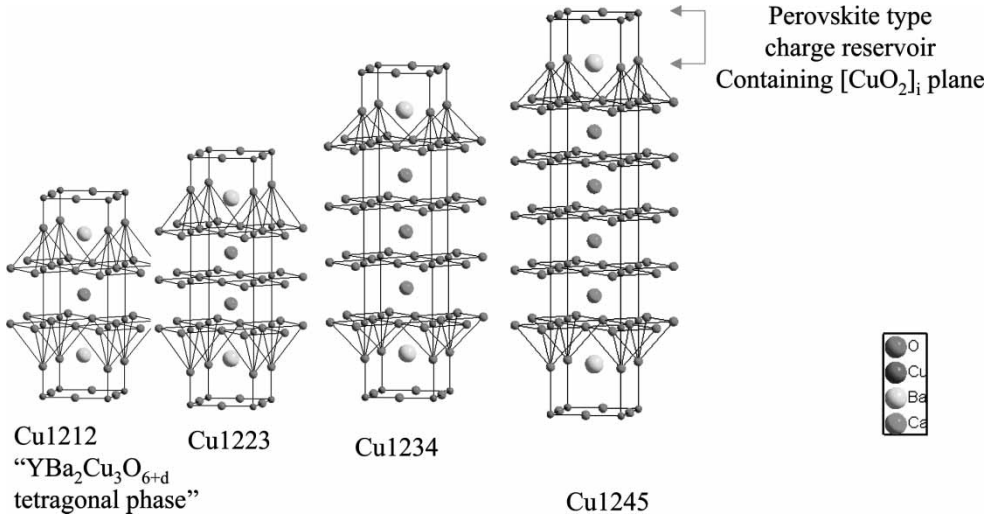


FIGURE 5 The crystal structure of Hg-1223.

Cu-12($n - 1$): THE HIGH PRESSURE SYNTHESIZED SUPERCONDUCTING HOMOLOGOUS SERIES IN THE Ca–Ba–Cu–O SYSTEM

Intense interest has been growing in searching for new HTSs among the A–Cu–O systems [8–12] (A represents the alkaline-earth elements: Ca, Sr and/or Ba). The possible superconductivity in such a simple system as A–Cu–O poses an exciting challenge either for mechanism studies or for the application implementation of an HTS. Although details of the mechanism of HTSs are still open, the consensus is that the perovskite-like [CuO₂] plane is indispensable to ensure superconductivity. In addition to the paramount full [CuO₂] plane, the oxygen deficient [CuO_{2– δ}] plane, *e.g.*, in YBa₂Cu₃O_{7– δ} can serve as charge reservoir. Previously, we have reported 117 K bulk superconductivity in the Ba–Ca–Cu–O compound [13, 14], and identified that the superconducting phase belongs to a novel homologous series of Cu-12($n - 1$) n that has been synthesized under high pressure. The Cu-12($n - 1$) n are of tetragonal structures with space group P4/mmm. The structures are built up by the alternative periodic stacking of [CuO₂] planes versus ‘AO’ sheets. The stacking sequence along *c*-axis follows {[CuO₂]_{*i*}/[BaO]}/[CuO₂]–[CaCuO₂]_{*n–1*}}/[BaO]/[CuO₂]_{*i*}}, where {[CuO₂]_{*i*}/[BaO]} is the perovskite type charge reservoir block containing the imperfect [CuO₂]_{*i*} plane. Here, [CuO₂]–[CaCuO₂]_{*n–1*} represents the conducting block wherein [CaCuO₂] is the infinite layer structure. Figure 6 shows the schematic view of the crystal structure of Cu-1223, Cu-1234 and Cu-1245. Table II provides data of superconducting transition temperature as well as the lattice parameters of the Cu-12($n - 1$) n superconductor. Crystallographically, Cu-12($n - 1$) n have the same features as Hg(Tl)-12($n - 1$) n . Simply replacing the [Hg(Tl)O] rock salt layer with a deficient [CuO₂]_{*i*} plane will lead to Cu-12($n - 1$) n . It is noted that Cu-12($n - 1$) n are totally built up with perovskite type blocks from the charge reservoir to the [CuO₂] block, and particularly, ‘Cu-1212’ is isostructural to YBCO-123 tetragonal phase as shown in Figure 6. Hence, the structural affinity gives Cu-12($n - 1$) n unique characteristics in a higher T_c owing to multilayered [CuO₂] planes and YBCO-like superconducting properties. For example, Cu-1234 has improved high temperature high magnetic field properties [15] similar to those of YBa₂Cu₃O_{7– δ} showing a moderate critical current density J_c dependence on temperature, rather than the quick J_c drop with increasing temperature. The interlayer coupling of the neighboring [CuO₂] planes plays a key role to shape the intrinsic flux

FIGURE 6 The crystal structures of Cu-12($n - 1$) homologous series.TABLE II The superconducting transition temperature T_c and lattice parameters of Cu-12($n - 1$).

Parameters	$CuBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$		
	$CuBa_2Ca_2Cu_3O_{8+\delta}$ Cu-1223	$CuBa_2Ca_3Cu_4O_{10+\delta}$ Cu-1234	$CuBa_2Ca_4Cu_5O_{12+\delta}$ Cu-1245
T_c (K)	80	118	100
a (Å)	3.86	3.86	3.86
c (Å)	~15	~18.0	~21.0

Note: T_c value corresponds to the as-prepared samples.

dynamics. The coupling is closely related to the detail of the charge reservoir block, *e.g.*, the dimension, construction, composition, etc. It is suggested that the metallic [CuO_{2-δ}] chain layer could dramatically enhance the interlayer conductance. As a consequence, YBa₂Cu₃O_{7-δ} has the extremely short effective coupling distance along the *c*-axis and hence a much improved coupling force. This will generate a strong pinning effect on the pancake-like flux vortex and contribute much to the excellent high temperature high field properties as shown in Figure 7. For comparison, the absolute $J_c(T)$ were reduced to $J_c(T)/J_c(0)$ according to an empirical exponential relationship $J_c(T) = J_c(0) * \exp(-T/T_0)$, where T_0 and $J_c(0)$ are fitting parameters. According to the evolution rate, the $J_c(T)$ behavior presented can be roughly classified into three groups. The compounds of YBa₂Cu₃O_{7-δ} and Cu-1234 rank as the most steady ones characterized by an average $T_0 \sim 14$ K, followed by Hg-12($n - 1$) n and Cl-0212 with an average $T_0 \sim 7$ K, and then the bi-charge-reservoir-layered Bi-system with $T_0 \sim 4$ K. Both Cu-12($n - 1$) n and YBa₂Cu₃O_{7-δ} comprise the perovskite type $\{-[BaO]-[CuO_2]_x-[BaO]-\}$ charge reservoir block, containing the conducting deficient [CuO₂]_x layer. Referring to such structure affinity, the similarity in the physical properties between Cu-1234 and YBa₂Cu₃O_{7-δ} would be appreciable.

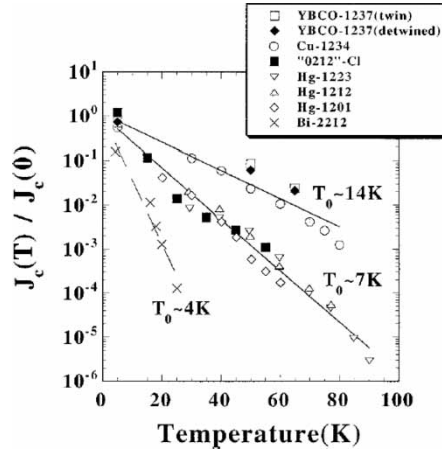


FIGURE 7 The critical current density as a function of temperature for a group of HTSs.

CI-02($n - 1$): THE SUPERCONDUCTING HOMOLOGOUS SERIES CONTAINING OXYHALIDE AT THE CHARGE RESERVOIR

The parent state of high temperature superconductivity is an antiferromagnetic Mott insulator with the nominal Cu^{2+} valence. Modifying the Cu valence to be $2 \pm \delta$ through doping will change the electronic ground state gradually from the Mott insulator to a complicated mediated state, to a superconducting state, then to a normal metal state. There are two types of carriers for HTSs, *i.e.*, hole and electron, resulting in p- or n-type high T_c superconductivity, respectively. So far, almost all HTSs are p-type, whereas only two material systems are n-type, *i.e.*, the $(\text{Nd}, \text{Ce})_2\text{CuO}_4$ system with T' 214 structure [16] and the $(\text{Sr}, \text{Nd})\text{CuO}_2$ system with infinite layer structure [17]. The superconducting transition temperature roughly follows a parabolic relation to the charge carrier density. T_c reaches maximum at an optimum doping level of 0.15–0.20 hole/Cu site, while T_c is lower in the underdoped as well as the overdoped regime. Usually, the carrier doping is conducted through chemical substitution of hetero valence elements or non-stoichiometry of oxygen in the charge reservoir block. Cation substitution, like the divalent alkaline earth element A^{2+} over the trivalent rare earth element R^{3+} , is very well established in HTSs, leading to the hole carrier in the compound such as $(\text{La}, \text{Sr}/\text{Ba}/\text{Ca})_2\text{CuO}_4$. The lattice or interstitial oxygen content change can also directly modulate the carrier concentration such as in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ or $\text{La}_2\text{CuO}_{4+\delta}$. In a sense, an eligible carrier doping method suitable to the specified charge reservoir construction becomes crucial to generate superconductivity in copper oxides containing a $[\text{CuO}_2]$ plane. The oxyhalide cuprates $\text{M}_2\text{CuO}_2\text{X}_2$ (M being alkaline earth, X being halogen) [18, 19] comprise an interesting cuprate family which is isostructural to La_2CuO_4 , with M residing at the La site and X at the apical anion position relative to the $[\text{CuO}_2]$ plane. The stoichiometric $\text{Sr}_2\text{CuO}_2\text{Cl}_2$ is an antiferromagnetic insulator showing a similar Cu^{2+} spin order to that of La_2CuO_4 . This affinity makes $\text{M}_2\text{CuO}_2\text{X}_2$ a favorable prototype material for developing new HTSs. Several superconducting oxyhalide cuprates have been synthesized [20–23]. Hole-like carriers were induced by incorporating interstitial fluorine [20], or by heterovalent cation substitution of alkaline metal for alkaline earth [21]. Taking into account the structural characteristics, we established a hole doping method to induce superconductivity in oxyhalide cuprates [22]. The doping is supposed to

go through a heterovalent anion substitution, *i.e.*, a partial substitution of divalent oxygen for monovalent halide. As all the Cl ions reside at the apex anion position, it is called ‘apical oxygen doping’ [22]. This term is to address that the doping not only creates p-type carriers, but also induces apical oxygen which is otherwise absent in the parent structure. Using high pressure synthesis, we have found the new homologous series $(\text{Sr}, \text{Ca})_{n+1}\text{Cu}_n\text{O}_{2n+\delta}\text{Cl}_{2-x}$ [22, 23]. In the ‘four digit nomenclature’, the compounds are named Cl-02($n-1$) n referring to the ‘02($n-1$) n ’ type structure. This means there are only two interfacial layers in the charge reservoir without heavy metal layers, while $(n-1)$ spacer layers and n $[\text{CuO}_2]$ planes in the conducting block, with charge reservoir being oxychloride instead of pure oxides. Cl-02($n-1$) n crystallize into a tetragonal phase with space group $I4/mmm$. The stacking sequence along the c -axis follows $\{[\text{SrCl}]/[\text{SrCl}]\}/\{[\text{CuO}_2]-[\text{CaCuO}_2]_{n-1}\}/\{[\text{SrCl}]/[\text{SrCl}]\}$; where $\{[\text{SrCl}]/[\text{SrCl}]\}$ is the rock salt type charge reservoir block. Figure 8 shows the schematic view of the crystal structure of Cl-0201, Cl-0212 and Cl-0223. Using apical oxygen doping, bulk superconductivity was realized in the high pressure synthesized samples whose T_c is 30 K in Cl-0201, 80 K in Cl-0212, whereas 80 K in Cl-0223. Table III provides the T_c and the lattice parameters of the Cl-02($n-1$) homologous

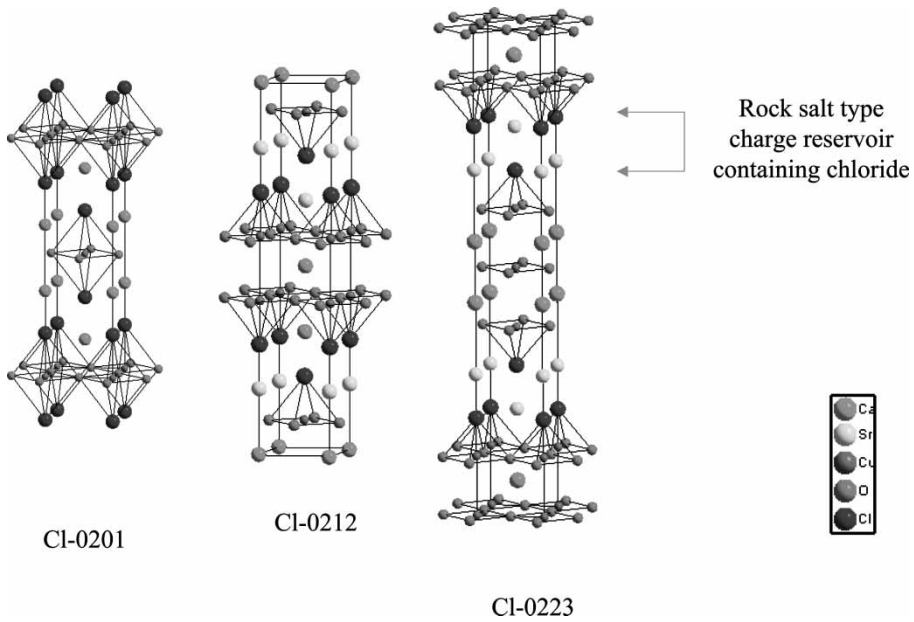


FIGURE 8 The schematic view of the crystal structure of (a) Cl-0201, (b) Cl-0212 and (c) Cl-0223.

TABLE III The superconducting transition temperature T_c and lattice parameters of Cl-02($n-1$) n .

Parameters	$(\text{Sr}, \text{Ca})_{n+1}\text{Cu}_n\text{O}_{2n+\delta}\text{Cl}_{2-x}$		
	$(\text{Sr}, \text{Ca})_2\text{CuO}_{2+\delta}\text{Cl}_{2-x\delta}$ Cl-0201	$(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_{4+\delta}\text{Cl}_{2-x}$ Cl-0212	$(\text{Sr}, \text{Ca})_4\text{Cu}_3\text{O}_{6+\delta}\text{Cl}_{2-x}$ Cl-0223
T_c (K)	30	80	80
a (Å)	3.9	3.86	3.83
c (Å)	~16	~22	~28

Note: T_c value corresponds to the as-prepared samples.

series. The unique structure aspects of the oxyhalide cuprates offer more to manipulate the structure modification, *e.g.*, it becomes possible to tune the crystal and electronic structures in the way of either by cation or by anion substitution, separately or simultaneously.

In summary, HTSs are crystallographically the structural assembly of extended infinite layer type perovskite derivatives with various charge reservoirs. High pressure can play significant role in synthesizing novel HTSs. Knowledge of the HTSs could be conducive to search new transition metal compounds using high pressure method.

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