# Homologous series of layered cuprates

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## Abstract

A variety of new homologous series of cuprate superconductors has been discovered during the last three years utilizing the high-pressure synthesis technique. The present paper discusses the structures, classification and design of the different cuprate families in general. Furthermore, to illustrate some interesting features in more detail, the so-called $02(n-1)n$, $Cu-12(n-1)n$ and $Pb-12(n-1)n$ series are used as representative examples.

## 1. Introduction

The structures of superconducting cuprates consist of three different types of building blocks: the perovskite blocks including the so-called infinite-layer block, the rock-salt block and the fluorite block. The rock-salt blocks possessing positive charge are considered to act as hole donators for the infinite-layer blocks, while the fluorite blocks with their negative charge are electron donators. Based on the above-defined structural blocks, the existing superconducting cuprate phases can be categorized into two groups [1]. The structures of the first compound group contain only infinite-layer and rock-salt blocks, while in the second group the structures may be built up from all the three possible block types. This type of structural categorization is useful for making "designs" for new superconducting phases.

To further simplify the notation, the various stoichiometries and structures of high-$T_c$ cuprates and related phases can be described by viewing the unit cells as collections of sheets rather than blocks. For this purpose, the four-integer naming scheme as described by Shaked et al. [2] has been widely accepted, although it fails to describe structures containing the fluorite blocks or anions other than oxygen [3]. The first entry in this number series tells the number of consecutively stacked layers in the so-called charge-reservoir block between the adjacent infinite-layer blocks. These layers are usually built up with various heavy metals or transition metals and oxygen. The second entry tells the number of spacing alkaline earth or rare earth oxide layers which are located between the charge-reservoir and infinite-layer blocks. The fourth and third entries, respectively, correspond to the number of conducting $CuO_2$ planes and the number of bare alkaline earth or rare earth layers separating these $CuO_2$ planes in one infinite-layer block. If the fourth figure is indicated by $n$, the third figure is $n-1$ in all existing superconducting cuprates except in the so-called infinite-layer compounds and in those structures containing a fluorite block. In the present paper all the

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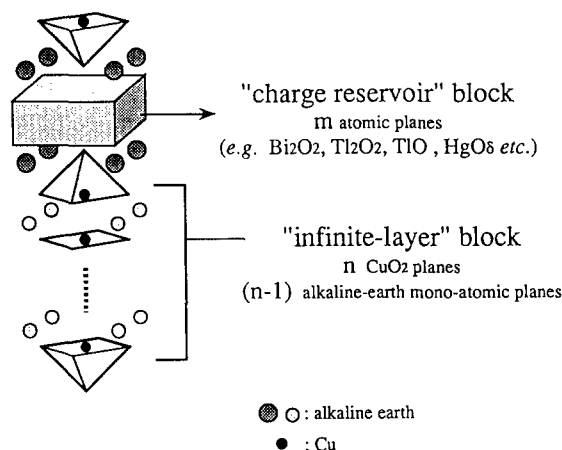e-mail: yamauch1@rlem.titech.ac.jp.

Fig. 1. Schematic crystal structure of a layered cuprate phase, "$m2(n-1)n$". The members with $n = 1, 2, 3, \ldots$ form a "homologous series".

crystal structures will be designated by M $- m2(n - 1)n$, where M is the chemical name of the cation in the charge reservoir block (Fig. 1).

## 2. Homologous series

The concept of a homologous series in the case of cuprate superconductors can be defined as "a family of layered copper oxides that differ from one another only by the number of pairs $(n - 1)$ of $CuO_2$ and bare cation planes in the infinite-layer block". Each member of one homologous series thus has the same charge-reservoir block (M $- m$ is fixed) but the number of $CuO_2$ planes $(n)$ is different. Furthermore, it is feasible to speak about a homologous series only if the members at least up to $n = 3$ have been experimentally found. In order to successfully synthesize higher members (n $\geq$ 3) of homologous series, the following semi-empirical rule based on a simple electrostatic consideration has proven to be useful: the average valence of cations in the bare cation layer (third entry) sandwiched by two adjacent $CuO_2$ planes must be equal to or less than $+2$ in an infinite-layer block containing more than two $CuO_2$ planes [1,4]. On the other hand, when building up new types of series the connection criteria between the adjacent blocks become important. That is, (1) sharing of a common cation sheet with/without

oxygen by the rock-salt/fluorite and infinite-layer blocks, (2) lattice constant ($a$ and/or $b$) matching between all the blocks, and (3) electrostatic matching between the adjacent perovskite blocks [1].

By the end of the year 1992, only three homologous series fulfilling the above definition, i.e. Bi-22$(n - 1)n$, Tl-22$(n - 1)n$ and Tl-12$(n - 1)n$, had been verified. In January 1993, the $n = 2$–5 members of the O2$(n - 1)n$ series were synthesized in the Sr–Ca–Cu–O system [5,6] and since then many other homologous series have been discovered (Table 1). All these new cuprate series, with the exception of Hg-12$(n - 1)n$, are stabilized only under very high oxygen pressures ($\sim$ 2–8 GPa) [7].

Each homologous series found so far possesses at least one member whose critical temperature exceeds 100 K. In each series, $T_c$ increases until $n = 3$ or 4, and then slowly decreases with higher values of $n$. Whether, the highest $T_c$ is found for the $n = 3$ or 4 member in a given series might depend on the amount of excess charge provided by the charge-reservoir layer; with large amounts of "initial" charge ($n = 1$) an increasing number of consecutively stacked $CuO_2$ layers are needed to "dissolve" the excess charge. To test this hypothesis, the under/over-doping character of the $n = 3$ and 4 phases should be thoroughly studied.

Table 1
Recently discovered homologous series

| Year | Series | $T_{c\ max}$ [K] (Phase) | High Pressure Synthesis (x = yes) |
|------|--------|--------------------------|-----------------------------------|
| 1993: | O2$(n - 1)n$ | 109 (0223) | x |
| | Hg-12$(n - 1)n$ | 136 (1223) | |
| | Ag-12$(n - 1)n$ (?) | | x |
| | Cu-12$(n - 1)n$ | 117 (1234) | x |
| 1994: | (Cu,C)-12$(n - 1)n$ | 117 (1234) | x |
| | ((Cu,C/Ba)-32$(n - 1)n$ | 113 (3234) | x |
| | Al-12$(n - 1)n$ | 110 (1234) | x |
| | Ga-12$(n - 1)n$ | 109 (1234) | x |
| | B-12$(n - 1)n$ | 110 (1234) | x |
| | (C,B)-12$(n - 1)n$ | 118 (1223) | x |
| | Pb-12$(n - 1)n$ | 115 (1223) | x |
| 1995: | (Cu,S)-12$(n - 1)n$ | $\sim$ 100 (1223) | x |
| | (Cu,P)-12$(n - 1)n$ | $\sim$ 100 (1234) | x |
| | O2$(n - 1)n$-F | 111 (0223) | x |

## 3. The $02(n-1)n$ series

Historically, the $02(n-1)n$ series in the Sr–Ca–Cu–O system was the first homologous series discovered in the recent rush utilizing the high-pressure synthesis technique [5,6,8,9]. The unique feature of this series is that the $02(n-1)n$ structures are built up only by alternating double-layer $(Sr,Ca)_2-O_{2(1-y)}$ rock-salt blocks and infinite-layer blocks, without any charge-reservoir blocks. The $n = 1$ member of the series (0201 phase) has the same structure as the original $(La,Sr)_2CuO_4$ compound of Bednorz and Muller, traditionally called the "214" phase, while the second member of the series (0212 phase) is isomorphous with the $La_2SrCu_2O_6$ compound, which was initially described as the "326" phase.

The apical oxygen sites in the $(Sr,Ca)_2-O_2$ blocks are believed to be partially vacant [10]. However, neutron diffraction data on the $n = 1$ phase suggest that not the $Sr_2O_2$ block but the $CuO_2$ plane is oxygen deficient [11]. According to Kawashima et al. [12], the $n = 1$ phase is non-superconducting while the $n = 2$, 3 and 4 phases of the Sr–Ca–Cu–O system exhibit critical temperatures of 73–79 K, 109 K and 86 K, respectively. Controversially, superconductivity with a large Meissner signal and $T_c$ values between 70 and 80 K have been reported for single-phase $Sr_2CuO_x$ samples as well [8,9]. In order to clarify this controversy, more experimental data are needed. In the Sr–Cu–O system, superconducting 0212 phase is also known to exist [8]. Although the $T_c$ of the phase is close to the values reported for the 0201 phase, the single-phase character of the 0201 samples studied excludes the possibility that the superconductivity would have been derived from this intermixed phase.

## 4. The $Cu-12(n-1)n$ series

Replacing Sr by Ba in the Sr–Ca–Cu–O system did not result in the $02(n-1)n$ structures but in the discovery of a new homologous series of cuprates with single Cu–O planes as a charge-reservoir block. So far, the $n = 3 - 6$ members of this $Cu-12(n-1)n$ series have been synthesized in the Ba–Ca–Cu–O system under high oxygen pressures [13–16]. The $n = 2$ member of the series (Cu-1212 phase) is noth-

ing else but the $YBa_2Cu_3O_7$ compound or the so-called "123" phase in the Ba–Y–Cu–O system. The $n = 3$–6 structures can be derived from that of $YBa_2Cu_3O_7$ by simply adding 1–4 additional $CuO_2$/cation-plane pairs, respectively, into the infinite-layer block. The $Cu-12(n-1)n$ structures thus differ from the corresponding $Tl-12(n-1)n$ structures with respect to the oxygen position in the charge-reservoir block. The highest $T_c$ value (117 K) in the $Cu-12(n-1)n$ series belongs to the $n = 4$ member.

## 5. The $Pb-12(n-1)n$ series

Although the elements around lead in the Periodic Table, i.e. Hg, Tl and Bi, were known to form homologous series of superconducting cuprates, the Pb-based superconductors found by the end of 1994 could not be considered as members of any homologous series since the $n \geq 3$ members had not been discovered. In all the known Pb-superconductors the bare cation planes between the $CuO_2$ planes in the infinite-layer blocks consisted of rare earth ions. However, according to simple electrostatic considerations, these cation planes should exhibit average valence of $+2$ or less in structures with $n \geq 3$ [1]. Based on the above semi-empirical rule, trivalent rare earth ions were replaced by divalent calcium in the Pb–Sr–RE–Cu–O system, and finally, new Pb-based superconducting compounds with 1212 and 1223 structures could be synthesized under high pressures; a new homologous series of $Pb-12(n-1)n$ had been found in the Pb–Sr–Ca–Cu–O system [4]. The $Pb-12(n-1)n$ phases $(n = 1–3)$ are isomorphous with the corresponding $Tl-12(n-1)n$ phases. The critical temperature of the Pb-1223 phase is 115 K, but since the members with $n$ higher than 3 have not been synthesized yet, it is not sure whether that value can be evaluated as the maximum $T_c$ in the $Pb-12(n-1)n$ series.

## 6. Conclusions

Recent discoveries of new superconducting cuprate families have already raised the number of the homologous series to close to 20. During this

Table 2
Cuprate structures consisting of perovskite and rock-salt blocks. For each structure type, representative superconducting compounds are given as well. The underlined compounds have not been superconducterized so far

| $01(n-1)n$ | $02(n-1)n$ | $12(n-1)n$ [a] | $22(n-1)n$ |
|---|---|---|---|
| 0101 | 0201 | 1201 | 2201 |
| LaCuO$_3$ | (La,Sr)$_2$CuO$_4$ | Tl(Ba,Y)$_2$CuO$_5$ | Tl$_2$Ba$_2$CuO$_6$ |
|  | Sr$_2$CuO$_3$ | HgBa$_2$CuO$_4$ | Bi$_2$Sr$_2$CuO$_6$ |
|  |  | (Pb,Cu)(Sr,La)$_2$CuO$_5$ |  |
| 0112 | 0212 | 1212 | 2212 |
| YBa(Cu,Fe)$_2$O$_5$ | La$_2$SrCu$_2$O$_6$ | TlBa$_2$CaCu$_2$O$_7$ | Tl$_2$Ba$_2$CaCu$_2$O$_8$ |
|  | Sr$_2$CaCu$_2$O$_5$ | HgBa$_2$CaCu$_2$O$_6$ | Bi$_2$Sr$_2$CaCu$_2$O$_8$ |
|  |  | CuBa$_2$YCu$_2$O$_7$ |  |
|  |  | (Pb,Cu)Sr$_2$(Y,Ca)Cu$_2$O$_7$ |  |
|  |  | (Pb,Sr,Ca)Sr$_2$(Ca,Sr)Cu$_2$O$_6$ |  |
| 0123 | 0223 | 1223 | 2223 |
|  | Sr$_2$Ca$_2$Cu$_3$O$_7$ | TlBa$_2$Ca$_2$Cu$_3$O$_9$ | Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ |
|  |  | HgBa$_2$Ca$_2$Cu$_3$O$_8$ | Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ |
|  |  | CuBa$_2$Ca$_2$Cu$_3$O$_8$ |  |
|  |  | (Pb,Sr,Cu)Sr$_2$(Ca,Sr)$_2$Cu$_3$O$_8$ |  |
| 0134 | 0234 | 1234 | 2234 |
|  | Sr$_2$Ca$_3$Cu$_4$O$_9$ | TlBa$_2$Ca$_3$Cu$_4$O$_{11}$ | Tl$_2$Ba$_2$Ca$_3$Cu$_4$O$_{12}$ |
|  |  | HgBa$_2$Ca$_3$Cu$_4$O$_{10}$ |  |
|  |  | CuBa$_2$Ca$_3$Cu$_4$O$_{10}$ |  |

[a] Cu-$12(n-1)n$ is *not* isomorphous with the other $12(n-1)n$ phases.

progress, application of high oxygen pressures to stabilize various layer structures has been essential. Since the number of new phases is increasing so rapidly, it has become more and more important to develop an unambiguous classification system. For this purpose a four-integer representation of the structures consisting of simple oxide and bare metal layers has been successfully applied. The description of layers carrying different anion groups, e.g. $CO_3^{2-}$, or halogenide ions still remains somewhat undefined.

Classification of the existing superconducting structures also promotes the design and synthesis steps of new materials and even of new structure types. In Table 2, cuprate structures consisting of perovskite and rock-salt blocks are summarized. The parent $01(n-1)n$ series of structures has not been superconducterized yet. The oxygen-defect LaCuO$_3$ perovskite is the first member of this series. The second member in the $01(n-1)n$ family, i.e. the 0112 structure of the BaY(Cu,Fe)$_2$O$_5$ compound [17], has been discovered as well. Finally, the oxygen-deficient Ba$_3$Cu$_3$O$_x$ triperovskite, stabilized so far only in thin film form [18], can be thought of as the third member of this homologous series. On the other hand, the discovery of the (Cu,C/Ba)-$32(n-1)n$

series (Table 1) demonstrates that it is possible to increase the number of superconducting structures, besides by increasing the $n$ value, also by making thicker (increasing $m$) charge-reservoir blocks.

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