High–Temperature Oxide Superconductors :
Structural and Compositional Aspects
in the Manifestation of Superconductivity[*]

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ABSTRACT

A series of recently discovered high-temperature cuprate
superconductors are reviewed and compared mainly from the
standpoint of structural and chemical aspects.

All the compounds are based on the perovskite structure
and exhibit characteristic layered structures consisting of
stackings of two-dimensionally connected copper-oxygen poly-
hedra.   The shapes and the combinations of the connected poly-
hedra vary depending on the degree of stacking and on the nature
of ordering of other constituent cations and seem to determine
the approximate range of maximum T_c.   However, appropriate
concentrations of the charge carriers, either electrons or elec-
tron holes, being accomplished by chemical doping, is quite
important in the manifestation of superconductivity.

At this stage, the reason for the extraordinarily high-T_c
observed in cuprate compounds has not been clarified, and it is
still quite difficult to predict T_c values for new materials to
be discovered in near future.

INTRODUCTION

Almost three years have passed since high-T_c (critical temperature) superconductivity was discovered in a La-Ba-Cu-O system[1], and a considerable number of oxide superconductors with various chemical compositions as summarized in Table 1 have now been found. They are mostly based on rare earth or alkaline earth cuprates and possess crystal structures closely related to the perovskite-type. However, they commonly exhibit a distinct layered nature and show strongly two-dimensional characteristics of electronic structure as well as physical properties. In this respect, a single exception is the $(Ba,K)BiO_3$ system which has a three-dimensional ideal perovskite structure.

Quite interestingly, the first discovered high-T_c cuprate, $(La,Ba)_2CuO_4$ was initially found by Bednorz and Muller[1] by aiming at the perovskite composition, $(La,Ba)CuO_3$. This is because they selected the $Ba(Pb,Bi)O_3$ system[2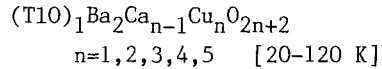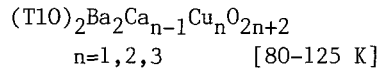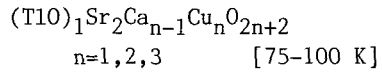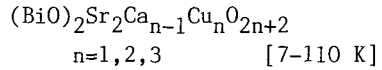] which had the highest T_c among the oxides at that time, as a prototype compound for the search for new materials. Whether this approach was the most effective way or not in search for new superconductors, all of the discovered cuprate superconductors do exhibit structures quite closely related to the perovskite. Moreover, a non-cuprate $(Ba,K)BiO_3$ with T_c=30 K[3], has been discovered through a close re-examination of the Ba-Bi-O system only after the birth of perovskite-related high T_c cuprates.

In this paper, I would like to review the crystal structures of various known cuprate superconductors and discuss correlations among composition, ionic nature of constituent elements and T_c. Although it would be desirable to extend the discussion also to non-cuprate superconductors, recent research efforts on those oxides based on other elements such as Ti, Nb, or W, have not been extensive enough to permit detailed comparison. Readers are referred to some review papers[4-6] in this direction.

Table 1. List of High-T_c Oxide Superconductors
(cationic and oxygen compositions are
ideal and vary in actual compounds.
T_c's are approximate maximum values)

"CuO$_x$ Single-Layered" Compounds

$(La_{1-x}M_x)_2CuO_4$ (x=0.08)
    M=Ba,Sr,Ca,Na,none   [20-40 K]

$(Nd_{0.8}Sr_{0.2}Ce_{0.2})_2CuO_4$ [30 K]

$(Ln_{1-x},M_x)_2CuO_4$ (x=0.08)
    Ln=Nd,Pr,Sm,Eu M=Ce,Th   [25 K]
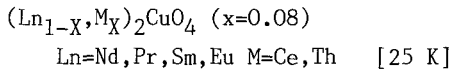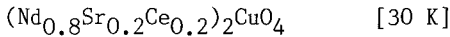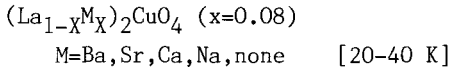
"CuO$_x$ Multiple-Layered" Compounds

$Ba_2LnCu_3O_7$ [90 K]

$Ba_2LnCu_4O_8$ [80 K]

$Ba_4Ln_2Cu_7O_{15}$ [85 K]
    Ln= Y,La,Nd,Sm,Eu,Gd
        Dy,Ho,Er,Tm,Yb,Lu

$(Ba,Ln)_2(Ce,Ln)_2Cu_3O_8$ [43 K]
    Ln=Nd,Sm,Eu
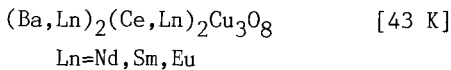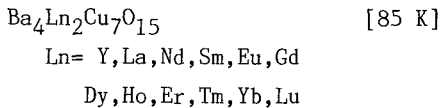
"AO$_x$-CuO$_x$ Complex-Layered" Compounds

$(BiO)_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$
    n=1,2,3   [7-110 K]

$(TlO)_1Sr_2Ca_{n-1}Cu_nO_{2n+2}$
    n=1,2,3   [75-100 K]

$(TlO)_2Ba_2Ca_{n-1}Cu_nO_{2n+2}$
    n=1,2,3   [80-125 K]

$(TlO)_1Ba_2Ca_{n-1}Cu_nO_{2n+2}$
    n=1,2,3,4,5   [20-120 K]

$Pb_2Sr_2(Y,Ca,Sr)Cu_3O_8$ [80 K]
    Ln= Y,La,Pr,Nd,Sm,Eu,
        Gd,Dy,Ho,Er,Tm

$Pb_2(Sr,Ln)_2Cu_2O_6$ [32 K]
    Ln=La

Non Cuprates

$Ba_{1-x}K_xBiO_3$ [30 K]
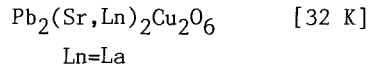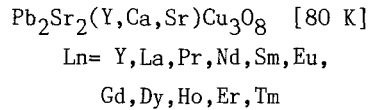
CuO_x SINGLE-LAYERED COMPOUNDS

All of the cuprate superconductors exhibit characteristic layered struc-
tures. They consist of alternate stackings of two-dimensionally connected
Cu-O polyhedra (CuO_x layers) and similarly connected AO_x layers where A is
typically Bi,Tl, or Pb. Rare earth and/or alkaline earth ions are sandwiched
between these layers.

Among these materials, those having chemical compositions expressed as
$(Ln,M)_2CuO_4$ exhibit the simplest crystal structures; there are three such
structures. Each structure contains only a single type of connected CuO_x
layer without any AO_x layers. Although their T_c's are in the range of only 25
to 40 K and chemical compositions are quite similar, there are two classes of
compounds that are totally different in terms of their electronic transport
properties. Since this point seems to be the most essential and critical
issue in the current understanding of cuprate superconductors, I would like to
emphasize this group of materials in particular.

Structural Features

Fig. 1(a) shows the structure of $(La,M)_2CuO_4$, the first discovered high-
T_c cuprate. The structure itself had been known as a K_2NiF_4-type (or the T-
type). The CuO_x layers basically consist of interconnected corner-sharing
octahedra as in the cubic perovskite structure. However, the connections are
made only in two-dimensions, giving rise to a layered structure. Between the
two CuO_x layers, La and M are situated with octahedral coordination of
oxygens, a situation quite similar to that found in the rock-salt structure.
When the total composition is designated as A_2BO_4, it may be interpreted as
$A_2BO_4=ABO_3+AO$. Because of this, the structure is sometimes described as
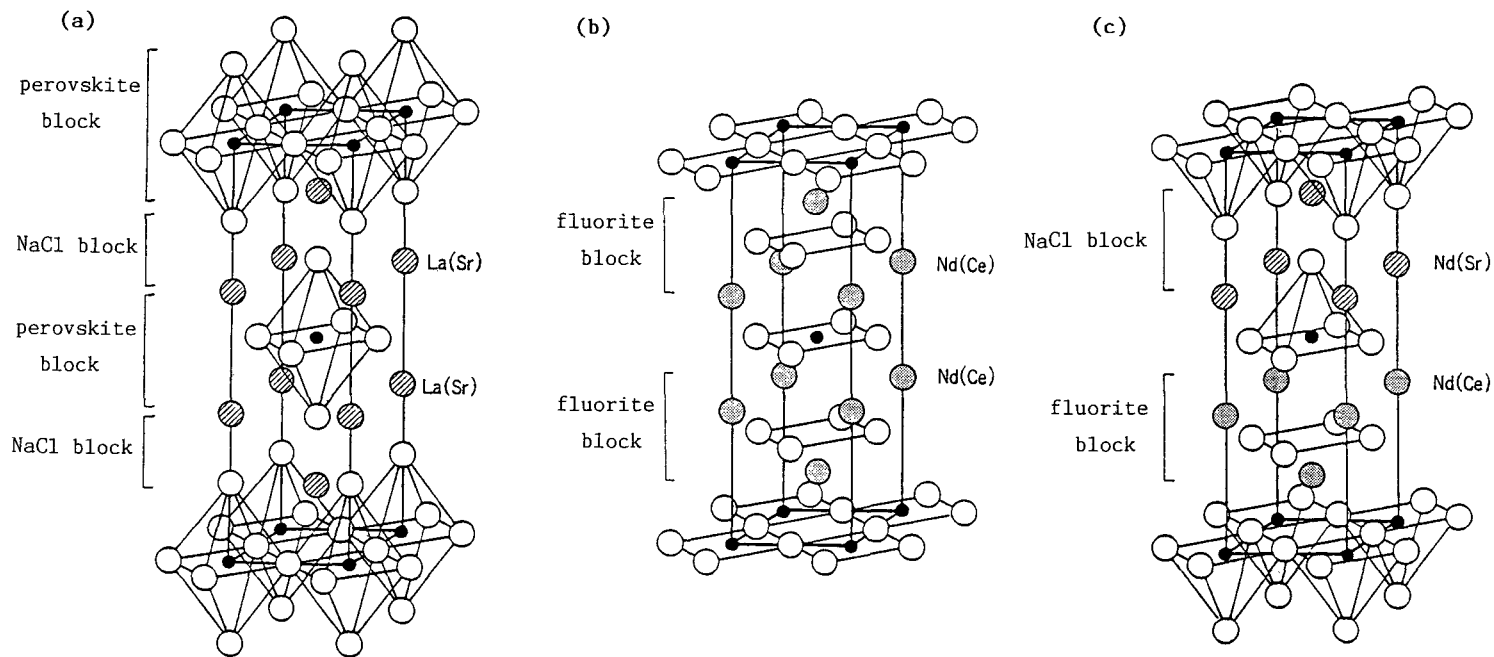
Fig. 1: Crystal structures of CuO_x single-layered $(Ln,M)_2CuO_4$.

(a) K_2NiF_4-type (T-type); $(La,Sr)_2CuO_4$

(b) Nd_2CuO_4-type (T'-type); $(Nd,Ce)_2CuO_4$

(c) Intermediate structures of (a) and (b); T^*-type; $(Nd,Ce,Sr)_2CuO_4$

In Figs. 1-5, black and white atoms reperesent copper and oxygen,

respectively.

alternate stacking of a perovskite block, ABO_3, and a rock salt block, AO, although it is not possible to distinguish these A's since they are crystallo-graphically equivalent.

If the Cu-O bond lengths of the coordinated oxygen octahedra are careful-ly examined, it is found[7] that they are 1.89 Å within the horizontal plane and 2.43 Å for the vertical direction. Compared to 2.13 Å which is a simple sum of ionic radii of Cu^{2+} and O^{2-}, it is found that the former is shorter whereas the latter is appreciably longer. This suggests that the chemical bonding of vertical oxygens is much weaker than the bonding within the plane; the layered structure must be viewed as the strongly-interconnected square coordination of CuO_2.

When the Ln in $(Ln,M)_2CuO_4$ is replaced by the elements from Pr through Gd (the first half of the 4f elements), the structure transforms to the Nd_2CuO_4 (T'-type) shown in Fig. 1(b). The weakly coordinated apical oxygens in the vertical direction in the T-type structure are removed and the CuO_x layers become purely square-coordinated. The unbonded oxygens then move to the tetrahedral positions between two Nd layers, resulting in the local structure identical to that in the fluorite-type. If A_2BO_4 is interpreted as ABO_2+AO_2, then the present structure can be regarded as the alternate stacking of a defective perovskite block, ABO_2 and a fluorite block, AO_2.

Without the dopants M's, both of the above mentioned cuprates are merely semiconductors. They have clear energy gaps of basically a Mott-Hubbard type originating from strong correlations of electrons[8] in these systems. Super-conductivity appears only after partial substitution on the Ln^{3+} site by alio-valent dopant M's.

In this context it is interesting to see what kind of ions can be easily dissolved as dopants into the Ln sites and whether this is associated with the characteristics of each crystal structure. Experimental facts are that

alkaline earth ions such as Ba, Sr or Ca are easily soluble in the T-type structure while tetra-valent Ce and Th are easily soluble in the T'-type. The reverse combinations of these are difficult. This may be understood as follows. The most stable form of pure Ce and Th oxides, as binary systems, is the fluorite-type structure; thus, these ions prefer the tetrahedral site in the oxygen sublattice of the T' structure. Alkaline earth ions, on the other hand, favor the octahedral sites of the rock salt-type structure as in their native binary oxides.

(Nd,Sr,Ce)$_2$CuO$_4$ shown in Fig. 1(c) is very interesting in that it exhibits a structure intermediate between 1(a) and (b). The unit cell consists of an upper half being the T-type while the lower half is identical to the T'-type. The resulting total structure is frequently referred to as the T*-type. The dopants, Sr and Ce, are confirmed by a neutron diffraction[9] to be partially substituting the Ln sites on the T- and T'-type sides, respectively. This distribution exactly follows the tendency of the dopant ions described above in Figs. 1(a) and (b). It should also be noted that, in this structure, the two-dimensionally connected copper-oxygen polyhedra are composed of pyramids because the apical oxygen on the T'-type side is missing. Quite recently, (La,Sr)LnCuO$_4$ where Ln=Sm, Eu and Gd, were confirmed[10] to exhibit the T* structure.

Manifestation of Superconductivity by Doping

Considering the Ln$_2$CuO$_4$ with Ln=La, the formal valence of Cu is increased by doping alkaline earth ions onto La sites, provided the oxygen composition is fixed at four. This corresponds to the doping of electron holes into the semiconductors in an electronic picture. However, these holes are not spatially distributed as in the free electron model, but enter a narrow energy band having a rather strong O-2p character[8]. In addition to this , the

apical oxygens in the CuO_x polyhedra, octahedra or pyramids, were believed by many theorists to be particularly important in the manifestation of high-T_c superconductivity. However, these pictures were only valid until the end of 1988 when the T'-type superconductor was discovered.

Superconductivity in the T' structure was discovered by Tokura et al[11]. in $(Ln_{1-x}Ce_x)_2CuO_4$ with Ln=Nd, Pr, or Sm. The optimum Ce content, x, was found to be about 0.08, and T_c=25 K was obtained by quenching from high temperatures under reducing conditions. The valence of the Ce ion was confirmed to be +4 by XPS measurements. Doping of Th and F were also found[12-13] to be effective in making Nd_2CuO_4 superconductive. The Hall coefficient and thermoelectric power showed negative signs[14]. From all of these observations, it is clear that the doped carrier in this system is not electron holes, as has been observed in all other cuprate superconductors. The most significant aspects in the discovery of "electron-doped superconductors" are that neither holes in the O-2p band character nor the vertical apical oxygens around the Cu sites are indispensable to superconductivity.

While the T^*-type $(Nd,Ce,Sr)_2CuO_4$ (T_c=28 K)[15] had been a predecessor to T-type superconductors, it was a hole-doped conductor. It is now well recognized that the T-type $(La,Sr)_2CuO_4$ (T_c=40 K) is a typical hole-conductor.

It is interesting to see that all of these CuO_2 single-layered compounds, T, T^* and T' types, exhibit quite similar and rather low T_c compared to other multi-layered compounds, regardless of the local CuO_x structure. The most essential feature is that the two-dimensional planes consisting of interconnected layers of CuO_x are necessary in superconductivity, provided the doping of either electrons or holes is made in this plane. However, it should be noted that there is an optimum carrier concentration for maximum T_c as excessive doping makes the system more metallic but not superconductive[16].

In the previous section, the doping of ions in the three types of com-

pounds was discussed from the viewpoint of local structures. The situation can also be considered from the perspective of carrier doping into the CuO_2 plane. Since negatively charged apical oxygen ions exist in the T-type structure, it is easier to dope, in the CuO_2 planes, electronically positive holes than electrons. Conversely, electrons are more easily doped than holes in the T'-type structure. More quantitative discussions along this line, using the calculation of Madelung energy on the various sites of these structures, can be found in the literature[17].

CuO_x MULTI-LAYERED COMPOUNDS

Structures with multi-layered CuO_x

A structure unknown before the birth of liquid nitrogen temperature superconductors but which immediately became one of the most famous ones in crystal chemistry, is $Ba_2YCu_3O_7$ (so-called 123 structure, shown in Fig. 2). The unit cell is based on triple unit cells of a perovskite, $(Ba,Y)_3Cu_3O_9$, from which oxygens are partially removed. Since two Ba ions and one Y ion line up in a regular manner, -Ba-Y-Ba-Ba-Y-Ba-, and oxygen becomes defective also in an ordered manner, two nonequivalent sites of Cu are formed.

Fig. 3 shows a closely related compound, $Ba_2YCu_4O_8$ (so-called 124 or 248). This 124 structure is quasi-quadruple in CuO_x layers, consisting of two interconnected pyramid CuO_x layers which face each other and two one-dimensional CuO chains. It should be noted that only a single chain was contained in the 123 structure. Another compound of this family is 247 (=123+124), $Ba_4Y_2Cu_7O_{15}$ which is made up by alternative stackings of the 123 and 124 structures. At first, these 123 related compounds were observed only in thin or thick film specimens, but recently they have been found to be a thermodynamically stable phase and can be synthesized[18] as bulk phases under high oxygen
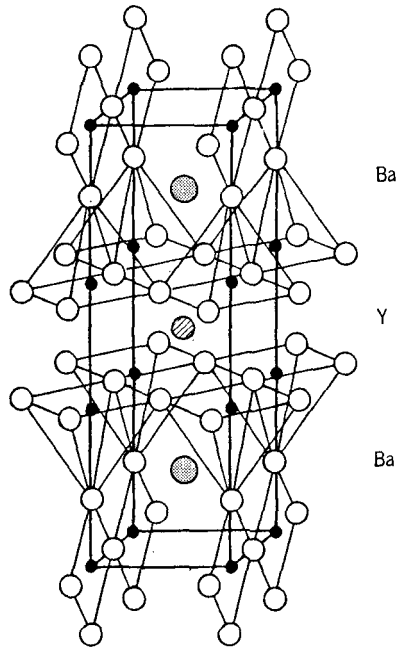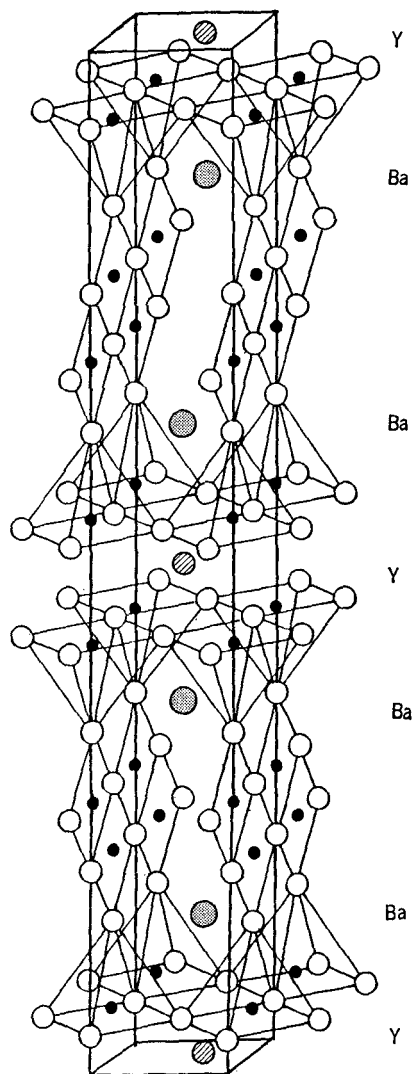
Fig. 2: Crystal structure of "123-type" $Ba_2YCu_3O_7$.

Fig. 3: Crystal structure of "124-type" $Ba_2YCu_4O_8$.

pressure treatments around 1000°C.

All of these three compounds exhibit T_c in the range of 80 to 90 K, irrespective of the number of Cu-O linear chains. This clearly suggests that the superconducting path is the interconnected CuO_2 plane of corner-sharing pyramids. The linear chains are thought to act as a "charge reservoir"[19] for electron holes. Because the oxygens in this chain are not strongly bonded, the oxygen nonstoichiometry of the 123 phase is appreciable and its T_c varies easily from 90 K, 60 K and to 0 K (non-superconductor) depending the oxygen composition. It is interesting from a materials processing view-point to note that the 124 compound is less susceptible to oxygen loss due to the stronger bonding of oxygen in the chain sites. Thus, the low temperature annealing of the specimens is not necessary as in the 123 phase.

Quite recently, Sawa et al.[20] discovered $(Ln,Ce)_2(Ba,Ln)_2Cu_3O_{10}$; (Ln=Nd, Sm or Eu) having T_c=43 K. The structure is shown in Fig. 4. Although the combination of the constituent elements in this system is analogous to T^*-type $(Nd,Sr)_2CuO_4$, the local structure resembles that of the 123 compound. The mutual arrangement of Cu ions is identical to that in the 123 compound, it has been reported that the oxygen sites around the middle Cu sites are about 50% defective similarly as in the 123 structure. However, the structure is tetragonal and no evidence of oxygen ordering has been observed by electron diffraction. The relatively low T_c compared to the 123 compound may perhaps be attributed to the fact that the local configuration around the pyramids is different from the 123 structure but equivalent to that in the T^* phase.

Compounds with complex multi-layered structures

The complex multi-layered family compounds[21] can be denoted as $(AO)_mM_2Ca_{n-1}Cu_nO_{2n+2}$ where A=Bi, Tl or Pb and M=Ba, or Sr. Each combination of elements contains a series of homologous phases with various m and n values
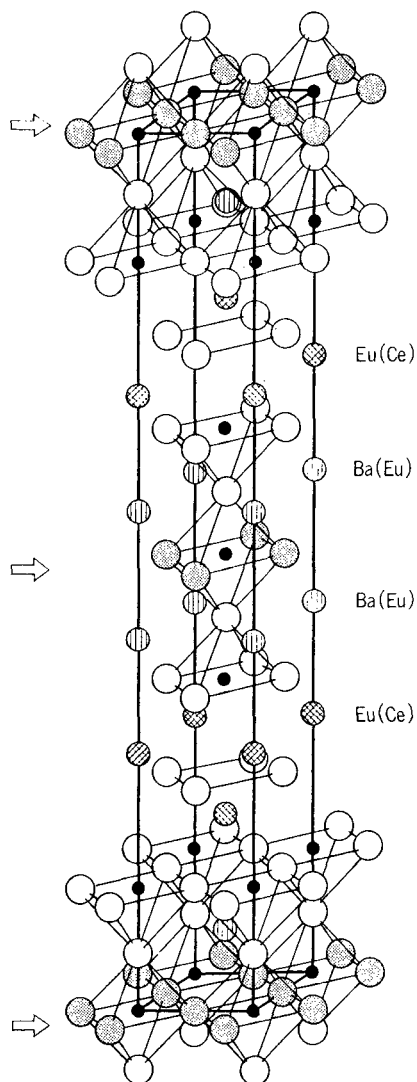
Fig. 4: Crystal structure[20] of $(Eu,Ce)_2(Ba,Eu)_2Cu_3O_z$.

It is reported that oxygens in the CuO_2 plane indicated by arrows are 50% deficient.

and exhibits a wide range of T_c's. Among these, $(TlO)_2Ba_2Ca_2Cu_3O_8$ has been confirmed to have the highest T_c. Historically, the n=1 phases for A=Bi and Tl were discovered first and as the homologous phases having n≈2 and 3 were found, the T_c gradually increased. Therefore, the synthesis of phases with n=4 and 5 were eagerly anticipated. However, these multiple layered phases, recently synthesized in Bi and Pb systems, showed decreasing T_c over n=3[22].

Since it is not possible to compare various compounds of this family within the space available here, only the structure of $Bi_2Sr_2CaCu_2O_8$ is shown in Fig. 5. The corresponding Tl-compounds exhibit essentially the same structure. The stacking sequence of the structure in Fig. 5 is expressed as -(BiO-BiO)-SrO-CuO_2-Ca-CuO_2-SrO-(BiO-BiO)-, where BiO double layers are arranged like in rock salt structures. The local structural configuration in which the bottom faces of pyramids face each other is similar to that in the 123 phase, and it is interesting to observe that the T_c (about 80 K) is in a similar range.

When compared to the corresponding Tl-compounds, the spacing within BiO double layers is much longer and Bi-compounds show characteristic cleavage. Another point to be noted is that the Bi-compounds exhibit a distinctive modulation structure which is not shown in Fig. 5 in which only an averaged structure is given. While this modulation has been interpreted as the combination of compositional and displacive modulations, it exhibits quite complex behavior[23] depending on the value of n and the preparation conditions of the specimens. The origin of the modulation could be related to the electronic structure of Bi^{3+} ions whose $6s^2$ electrons have a tendency to behave in a lone-pair-like manner[24].

There have been more than twenty compounds including non-superconductors discovered in this complex multi-layered compound family. Recently, Pb-systems such as $Pb_2Sr_2(Sr,Ca,Ln)Cu_3O_8$ $(T_c=85K)$[25] and $Pb_2(Sr,Ln)_2Cu_2O_6$
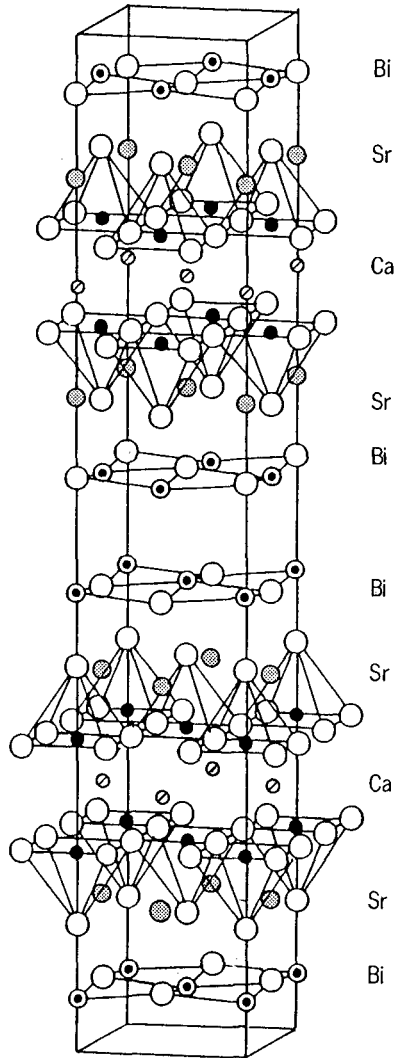
Bi

Sr

Ca

Sr

Bi

Bi

Sr

Ca

Sr

Bi

Fig. 5: Average crystal structure of $Bi_2Sr_2CaCu_2O_8$.

(T_c=32 K)[26] have been found, and the number of oxide superconductors in this family is expected to increase still very rapidly. However, as yet there is theoretically no rational basis for predicting the T_c of compounds exhibiting both new composition and structure. Unfortunately, we still have to take a relatively empirical path in our search for new high-T_c materials.

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