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New directions in synthetic and structural solid state chemistry: the legacy of high temperature superconductivity beyond cuprate chemistry

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The synthetic and structural chemistry of copper in complex oxides has developed extremely rapidly since the first reports of high temperature superconductivity in 1986. This progress in cuprate solid state chemistry has far outpaced that in many other areas of complex oxide chemistry. Significant new developments have included the formation of new complex oxides incorporating the volatile post transition oxides of Tl, Hg, Pb and Bi, the generation of complex structures based on stacked perovskites and/or other building blocks, the use of very high pressures during synthesis and the stabilisation of complex anions in oxides. Many of these advances are now being developed outside cuprate chemistry particularly with other late first row transition metals such as iron, nickel and cobalt. The aim of this article is *not* to review cuprate chemistry but to demonstrate where work on high T_c superconductors has resulted in significant recent progress for other transitional metal oxide systems. The syntheses and structures of these new complex oxides are described and areas where developments, derived from the discoveries in cuprate chemistry, can be expected in the next decade are also proposed.

Introduction

Since the discovery of high temperature superconductivity in complex cuprates in 1986[1] the solid state chemistry of copper in complex oxides has developed enormously. As well as synthesising more than 60 distinct structures that exhibit superconductivity, many hundreds of further oxide phases based on copper have been characterised and are now described in the literature. This desire to produce new cuprate structures, with the aim of producing enhanced superconducting characteristics, has led to the materials chemist undertaking reactions under conditions and between compounds that had hitherto not been investigated in detail. The compositions and structures of many of the new materials thus synthesised are genuinely novel, redrawing the frontiers of synthetic and structural solid state oxide chemistry. However, while the solid state chemistry of copper has been rapidly driven forward through this unprecedented level of worldwide effort, the same can not be said generally of the oxide chemistry of most other transition metals. One possible exception is manganese where recent interest in the magnetoresistive behaviour of complex manganese oxides has led to the development of several new materials containing trivalent and/or tetravalent manganese.[2]

The novel structural chemistry developed for complex cuprates has demonstrated several concepts that had previously been barely recognised and used by the solid state chemist. These include complex stacking sequences of perovskite and other simple oxide structure building units, the incorporation of volatile oxides such as those of thallium, mercury and bismuth and the stabilisation of small complex anions in association with oxides. This article briefly addresses the novel structural chemistry that has been developed with cuprates, but it is not the intention to review that subject as it has been carried out extensively elsewhere.[3] It concerns, more specifically, how the novel structural and synthetic chemistry developed for cuprates has since impacted generally in the area of solid state oxide chemistry and will continue to do so. It should, perhaps, be noted that the legacy of high temperature superconductivity in revolutionising materials chemistry also extends beyond the compositional and structural chemistry to advances in, for example, synthesis methods *e.g.* sol–gel processing and techniques routinely used for characterising complex oxides; however such developments lie outside the scope of this article.

Background

Much of the chemistry of complex cuprates can be described in terms of the stacking of simpler structure blocks such as perovskite, rock salt and fluorite, Fig. 1, and the extension of high temperature superconductor chemistry to non-cuprate systems can be described analogously. In addition non-purely oxide systems, such as oxide carbonates and oxide borates, can often be derived structurally from cuprates by locally replacing units such as CuO_4^{n-} by CO_3^{2-} and BO_3^{3-}. As these methods of describing the structures of complex cuprates have been so successful this review is categorised along similar lines. The shorthand nomenclature used for many such materials is also used here, where, appropriate. Thus $YBa_2Cu_3O_7$ is represented by the series of numbers 123 summarising the cation ratios in the compound and distinguishing, as far as possible, the different cation environments; hence $Tl_2Ba_2Ca_3Cu_4O_{12}$ is represented by the numeric acronym 2234 where the thallium, copper, calcium and barium occupy, mainly, distinct sites within the structure.

Systems

(1) Layered perovskites

The major structural feature of a superconducting cuprate is the presence of a layer of stoichiometry CuO_2 formed from corner sharing square planar MO_4 units, square pyramidal MO_5 or, normally axially elongated, MO_6 octahedra, M = Cu. In each case this structural feature is derived from a layer taken

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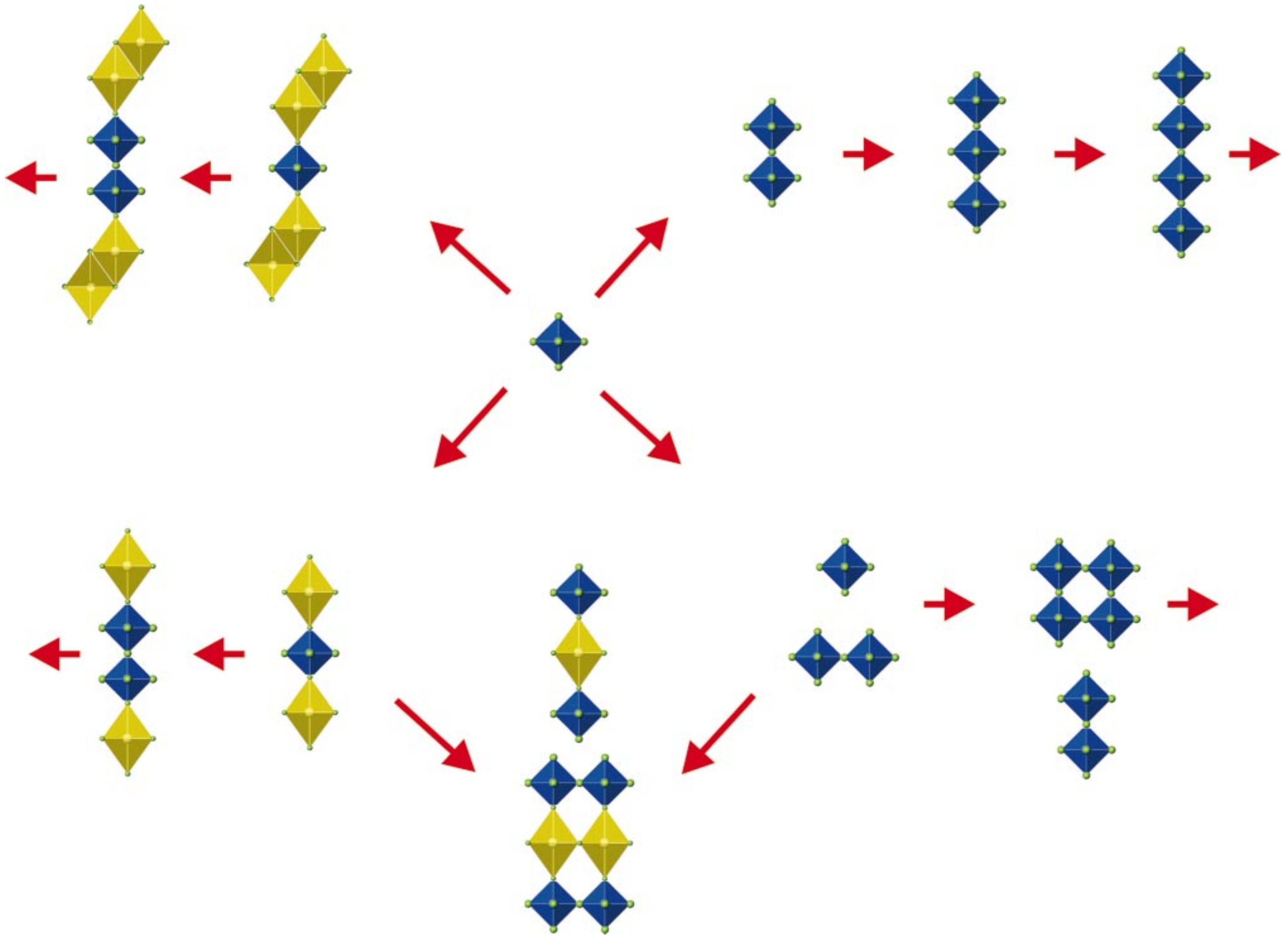

Fig. 1 Schematic of how many complex oxide structures can be derived from simple perovskite and rock salt-type layers. Clockwise, from the top right, multiple perovskite layer structures *e.g.* the tripled perovskite $YBa_2Cu_3O_7$; staggered perovskite blocks as a result of the introduction of rock salt (Ruddlesden–Popper) or fluorite type cation arrangements between the perovskite units; staggered combined perovskite/single aligned rock salt blocks *e.g.* $TlBa_{1.6}La_{2.4}Cu_2O_{9\pm\delta}$ and $(Hg,Pr)Sr_4Fe_2O_9$; combined perovskite/aligned single and double rock salt units as in $TlSr_2CuO_5$ (bottom left) and $Bi_2Sr_2MnO_{6+\delta}$ (top left).

from the perovskite structure with two, one or no apical oxygen atoms in the MO_6 octahedron removed, Fig. 2. This individual perovskite layer may be interleaved with a variety of other structural features which include more perovskite layers or other common structural building blocks in oxide chemistry, such as rock salt or fluorite; these structure types are discussed in the later sections of this article.

For multiple perovskite structures of the general formula $(A,A',A''......)(B,B',B''......)O_3$, where a variety of cations can adopt either the A or B type cation sites in the structure, what defines whether these ions are randomly distributed or form various ordered arrays? In terms of high temperature superconducting cuprates this behaviour is obviously essential in that the copper ions must segregate into perfect CuO_2 layers in order to form the superconducting pathway. So, with respect to the remit of this article, it is of interest to discuss whether other, non-copper, B type cations form, or might be induced to form, layers.

Layered double perovskites. The structural chemistry of perovskites has been discussed in detail and more recently

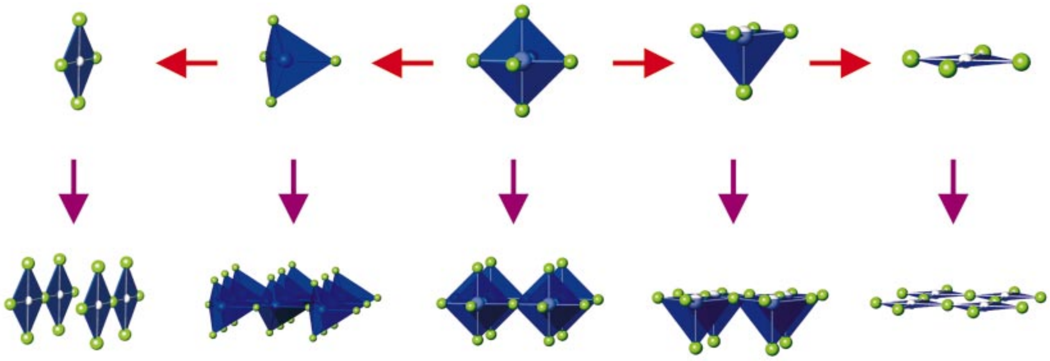

Fig. 2 Derivation of layer building blocks from the MO_6 unit and perovskite layer (centre). To the right square pyramidal (MO_5) and square planar (MO_4) units are formed from the octahedron by removal of apical oxygen atoms; these can also linked into infinite sheets, bottom row. To the left are tetrahedral units, which may be derived by elimination and displacement of oxygen atoms from the MO_6 octahedron, as in Brownmillerite, and vertical square planar MO_4 units formed by removing equatorial oxygens; both these units may be used to link other sheet-like structural units in multiple-layer perovskite-type structures.

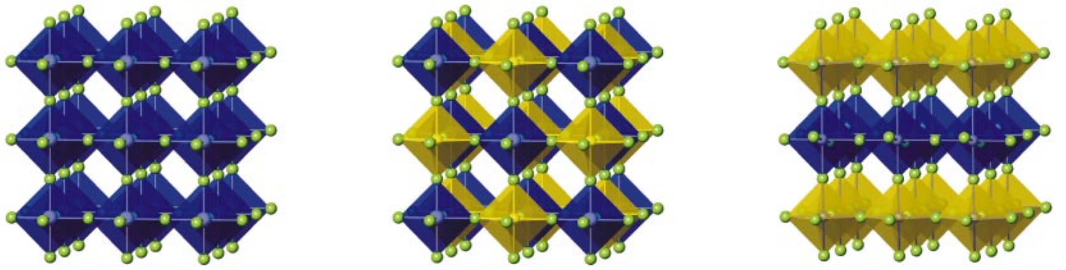

Fig. 3 Possible arrangements of B type cations in double perovskites (AA′)(B,B′)O_6. Left — simple perovskite structure or random arrangement of B and B′ where all the octahedra are equivalent, centre — the "rock salt" or face centred cubic arrangement of B and B′, right — layers of B and B′ based octahedra.

specific examples of this structure type, such as double perovskites (A,A′)(B,B′)O_3 where two cations occupy the B cation sites, have been analysed.[4] This latter work was prompted by the desire to find structures where copper segregates into a layered arrangement for high temperature superconductivity. Of the several hundred double perovskites, with two B cation types, very few form layered structures; the disordered and alternating ordered structures (face centred cubic), Fig. 3, are adopted far more commonly.

The origin of such B cation ordering seems to originate in the sizes and preferred coordination geometries of these species. Hence a large charge difference promotes the face centred cubic (rock salt-like) arrangement.[4] The Cu^{2+} ion with its associated Jahn–Teller distortion also promotes ordered arrays and in this case the formation of layers. As a result materials such as La_2SnCuO_6 synthesised under atmospheric pressure,[5] and the phases Ln_2SnCuO_6 (Ln = Pr and Nd), and La_2ZrCuO_6, when synthesised under high pressure,[6] adopt ordered layers. In oxygen deficient perovskites further layered compositions become possible and compounds such as $Ba_2InCuO_{4+\delta}$ and $Ba_2ScCuO_{4+\delta}$ form.[7] These materials possess layered structures with alternating planes of linked MO_6 octahedra and $CuO_{4+\delta}$ square planes/pyramids.

If formally large-scale reductions in the oxygen stoichiometry are introduced into the perovskite arrangement, then structures such as Brownmillerite with layers of octahedra and tetrahedra, which can be considered as derived from octahedra by elimination of oxygen, are adopted by many materials including Ca_2FeAlO_5.[8]

Outside cuprate chemistry layered doubled perovskite structures are not known. Anderson *et al.*[4] have suggested a layered structure might form for (A,A′)(B,B′)O_6, where the difference in charge on B and B′ is 2+, the difference in B cation size is less than 0.15 Å and B′ is a Jahn–Teller ion. Non-copper possibilities for B are thus Ti^{3+}, Mn^{3+}, Fe^{4+} and Ni^{3+}. The former, in purely trivalent form, is difficult to stabilise in oxides but the latter three are potentially of considerable interest as these ions form perovskite based layers in other structures, as discussed later in this article.

Triple perovskites. Without doubt the best known superconducting cuprate is $YBa_2Cu_3O_{7-\delta}$,[9] commonly referred to as YBCO or Y-123, which possesses a structure derived from three oxygen deficient perovskite blocks stacked upon each other,[10] Fig. 4. The material consists of corner sharing CuO_5 square pyramids separated by a yttrium ion and connected through CuO_4 square planar chains. Many hundreds of papers exist in which the partial replacement of copper by other metal ions has been undertaken.[11–13] These materials generally show a decrease in T_c for doping levels up to 5% and the complete loss of superconductivity at higher concentrations.

There are a more limited number of triple perovskite phases of the formula $Ln(Ba,Sr)_2MCu_2O_y$, in which the central copper chain site has been completely replaced by a different metal ion. Examples include the pentavalent ions M = Nb and Ta,[14] in which oxygen stoichiometric MO_6 octahedra connect the CuO_2 planes, as well as the trivalent M = Co, Ga and Al materials that contain MO_4 tetrahedra.[15–17] Recently the unusual coexistence of ferromagnetism and superconductivity has been observed in the ruthenate $GdSr_2RuCu_2O_8$,[18] which is isostructural with the non-superconducting $LnBa_2Nb^{5+}Cu_2O_8$ materials. It is believed that magnetic order is confined to the ruthenium spins of the central RuO_6 octahedra while superconductivity occurs in the CuO_2 planes.

To date, however, there are only a few examples in the literature of ordered layer triple perovskites that do not contain copper. These are the iron based materials $R(Ba,Sr)_2Fe_3O_8$, R = Y, Dy, Ho, Er,[19,20] and the cobalt containing phase $Y(Ba,K)_2Co_3O_{7.9}$.[21] $YBa_2Fe_3O_8$ was first reported in 1991 and, like YBCO, it exists in both tetragonal[19] and orthorhombic[22] forms depending on the synthesis conditions. Subsequent studies revealed that, unlike the cuprate materials, the lanthanide size has a large impact upon the structure, with triple perovskites only forming for Y and the lanthanides Dy, Ho and Er. For the larger rare earths cation disordered, oxygen defective, perovskites form.[20] The higher, trivalent oxidation state, favoured by iron results in full occupancy of all the oxygen sites within the $RBa_2Fe_3O_8$, R = Y, Dy, Ho and Er phases. Consequently the iron ions corresponding to the Cu-chain site are arranged in layers of apex sharing octahedra

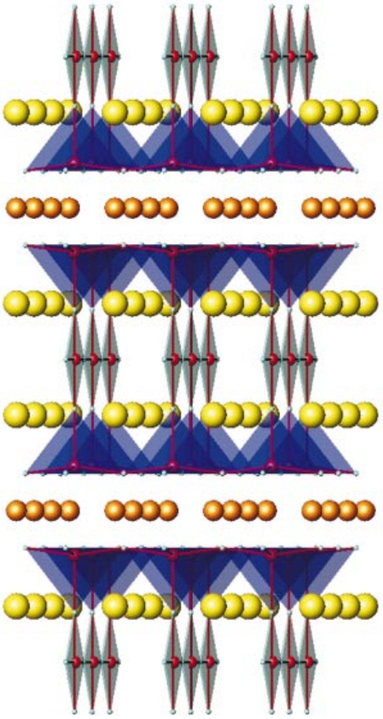

Fig. 4 The triple perovskite structure of $YBa_2Cu_3O_7$. CuO_5 square based pyramids — blue, CuO_4 square planes — cyan, yttrium — orange and barium — yellow.

rather than square planar chains. The higher oxygen content of the iron phases also increases the coordination of the barium ion from 10-fold in the cuprates up to 12-fold cubooctahedral. The greater oxygen content is reflected in the larger cell parameters of the iron phases, *i.e.* $a = 3.91$ Å, $c = 11.8$ Å for $YBa_2Fe_3O_8$,[19] compared with typical values of 3.86 and 11.68 Å for tetragonal $YBa_2Cu_3O_{7-\delta}$.[10] The metal–oxygen coordination reveals a significant Jahn–Teller induced elongation of the Cu–O apical distance for the square pyramidal site in comparison to the more regular iron coordination. However, the central square planar copper occupies far less space than the oxygen complete FeO_6 octahedra producing the smaller cell dimensions of the cuprate. The individual iron magnetic moments within the tetragonal $RBa_2Fe_3O_8$ materials order antiferromagnetically along all three crystallographic axes, with $T_{Néel} \approx 650$ K.[20]

The stabilisation of a cobalt analogue to YBCO was reported by Geremia *et al.*[21] and requires the replacement of around $\frac{1}{3}$ of the Ba ions by K^+ to give a phase of composition $Y(Ba_{1.44}K_{0.56})Co_3O_{7.9}$. The compound is tetragonal, $a = 3.84$ Å, $c = 11.176$ Å, with the central cobalt ion located in an octahedral coordination with apical bonds of 1.90 Å and basal bonds of 1.92 Å. This near perfect environment accounts for the significantly shorter *c*-parameter when compared with the vertically elongated octahedra found in $YBa_2Fe_3O_8$. The second cobalt ion is square pyramidal with apical and basal distances of 1.95 and 1.94 Å respectively. Once more the phase has significantly higher oxygen content than YBCO and the reported stoichiometry implies a cobalt oxidation state just above three.

A likely reason for there being relatively few non-cuprate triple perovskites is that the structure demands the adoption of two distinct coordination geometries from the transition metal. So far only iron and cobalt have shown the flexibility to match copper in this regard. Whilst the synthesis of further analogues containing a single transition element may prove to be difficult the isolation of a manganocuprate, $Eu_3Ba_2Mn_2Cu_2O_{12}$,[23] which adopts an intergrowth structure of the YBCO-like $EuBa_2Cu_2MnO_8$ and Eu_2MnO_4 blocks, indicates the possibilities. Further studies into mixed A site and B site triple perovskites drawing on the vast amount of work that already exists on YBCO are clearly merited.

Quadruple perovskites and multiple layer perovskites. The segregation of B type cations into triple perovskite structures was well characterised in the early stages of work on high T_c as a result of investigations into substituted $YBa_2Cu_3O_7$ derivatives. More complex stacking sequences or repeating units of perovskites are easily envisaged but the thermodynamics of phase formation leads to increasing difficulty in forming such phases. In order for a four layer material such as $(A,A',A''\ldots)_4(B_2B'_2)O(_{3-x})_4$, with a *c* axis B cation repeat BBB′B′ to form rather than a random arrangement of B cations or a double layer perovskite $(A,A',A''\ldots)_2(BB')O(_{3-x})_2$ the coordination preferences of the two B cations must be very different while also being of the correct ionic radii to fit together in the same perovskite derived structure. This behaviour has only been found for two pairs of B type cations copper(2+) with tin(4+) and copper(2+) with titanium(4+) in the series of compounds $Ln_2Ba_2Cu_2M_2O_{11}$, M = Sn, Ti, Fig. 5. For the tin based family the parent compound $La_2Ba_2Cu_2Sn_2O_{11}$ is readily synthesised.[24] However, for the series of materials containing titanium, the composition of the material first synthesised, $Gd_2Ba_2Ti_2Cu_2O_{11}$,[25] demonstrates the need for the correct choice of A type cation in relation to the two B type cations. While other larger (La and Nd–Eu) and smaller lanthanide cations permit the formation of this structure type their presence can lead to increasing disorder on the cation and anion sub-lattices.[26] Fig. 5 shows the structure of $Gd_2Ba_2Ti_2Cu_2O_{11}$ which consists of a stack of four perovskite blocks; the central two units are TiO_6 octahedra while the stack is terminated by CuO_5 square pyramidal units. The distribution of A type cations is such that the site between the terminal CuO_5 polyhedra is fully occupied by the lanthanide ion which is in eight-fold coordination to oxygen, as is the site between the TiO_6 units. For the larger lanthanides, with a desire for high coordination numbers due to their increased ionic radius, occupancy of the site between the CuO_5 units is unfavourable and would demand or allow extra oxygen to be incorporated in this plane destroying the B cation ordering. For the smaller lanthanides the 12-fold coordination by the oxygen in the double titanium oxide blocks seemingly becomes unfavourable. As with many multiple perovskite structures, detailed structural studies show that tilting, twisting or distortion of the octahedra occurs in response to the various, competing structural demands.[27]

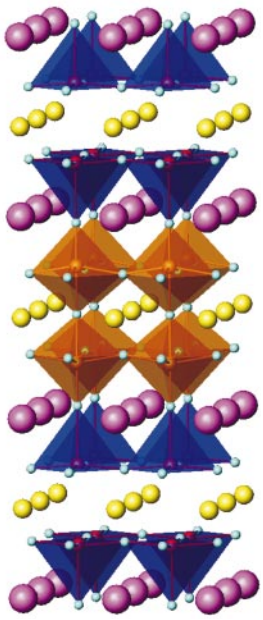

Fig. 5 The structure of $Ln_2Ba_2Cu_2M_2O_{11}$, M = Sn, Ti. CuO_5 square based pyramids — blue, Ti/SnO_6 octahedra — orange, Ln — yellow and Ba — magenta.

Even longer perovskite stacking sequences involving copper and titanium have been reported including 5 and 6 units as in $Gd_2Ba_2CaCu_2Ti_3O_{14}$[28,29] and $Dy_2Ba_2Ca_2Cu_2Ti_4O_{17}$,[30] Fig. 6. However, these materials become increasingly difficult to form with regular structures without defects or intergrowths that result in different repeat units along the *c*-axis.

In terms of cuprate-free chemistry the formation of perovskite stacking sequences with *n* greater than three is not, as yet, confirmed. Presumably this results from the need to have greatly differing coordination needs for the two or more B type cations. The preference of copper for square pyramidal over octahedral coordination coupled with the demand of titanium for octahedral coordination to oxygen drives the formation of oxygen defective units in combination with normal octahedral layers and segregation into a complex stacking sequence. The formation of similar units outside copper chemistry is only likely to occur for species which similarly prefer non-octahedral coordination and might occur for Ni^{3+}, Fe^{4+} and Mn^{3+}. The latter two are potentially the most interesting if their oxidation states, which have strong tendencies to reduce or oxidise respectively, can be controlled within the complex synthetic chemistry.

(2) CsCl and fluorite-type separating layers

One of the more unusual separating layers to have been utilised in cuprate chemistry is the Pb_2Cl layer with a CsCl type atomic

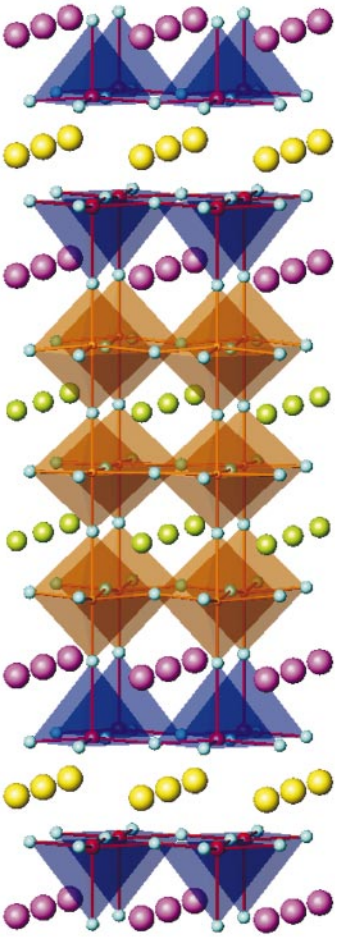

Fig. 6 $Gd_2Ba_2CaCu_2Ti_3O_{14}$. CuO_5 square based pyramids — blue, TiO_6 octahedra — orange, Ln — yellow, Ba — magenta, Ca — green.

arrangement. Originally observed in the antiferromagnetic mineral Hematophanite, $Pb_4Fe_3O_8Cl$,[31] Li successfully replaced the separating lanthanide ion within triple perovskites of the form $LnBa_2M^{5+}Cu_2O_8$, to give the materials, $Pb_2Ba_2Cu_2MO_8X$, M = Ta, Nb[32] (Fig. 7a) and subsequently, $Pb_2BaCuFeO_5X$, with X = Cl, Br.[33] The latter compounds are derived by removing the central $PbM^{5+}O_3$ perovskite unit to leave two vertically opposed $(Cu,Fe)O_5$ pyramids linked *via* an apical oxygen (Fig. 7b). The mixed iron/copper site weakens the magnetic interaction between the iron spins and antiferromagnetic order appears at $T_N \approx 120$ K, a value close to the structurally related $YBaCuFeO_5$.[34] The authors have extended the $Pb_2Ba_2Cu_2MO_8X$ series producing Sr analogues and introducing Sb^{5+} into the central MO_6 octahedral position to obtain a Cu–O environment compatible with superconductivity.[35] But so far it has not been possible to induce a superconducting transition within the materials through suitable doping, and so, like their $LnBa_2MCu_2O_8$ counterparts, they remain insulating.

The development of these materials exemplifies the transfer of structural chemistry from one transition metal oxide to another, in this case more unusually from iron to copper. It also represents an excellent example of where the solid state chemist has borrowed and developed structural ideas from nature.[36] Hematophanite itself displays interesting characteristics, with antiferromagnetic ordering of the Fe spins within the triple FeO_5–FeO_6–FeO_5 perovskite block at $T_N \approx 600$ K.[37] Similar behaviour was subsequently observed for the $RBa_2Fe_3O_8$ phases isolated following the synthesis of YBCO (see previous section). The layer of stoichiometry Pb_2X that interleaves the triple perovskite blocks is derived from the CsCl structure. Lead replaces caesium at the corners of an approximate cube, with four Pb–O bonds and four Pb–X interactions, Fig. 7a. Reaction temperatures in the range 650–700 °C are used in the preparation of the $Pb_2Ba_2Cu_2MO_8X$ compounds, considerably lower than those required to prepare the $LnBa_2MCu_2O_8$ oxides, which typically form at temperatures > 1000 °C. The ease of formation of the lead halide layer appears to be the controlling factor in this and shows that the triple perovskite block, whether it be a CuO_5–MO_6–CuO_5 or FeO_5–FeO_6–FeO_5 unit, can be stabilised using relatively mild conditions.

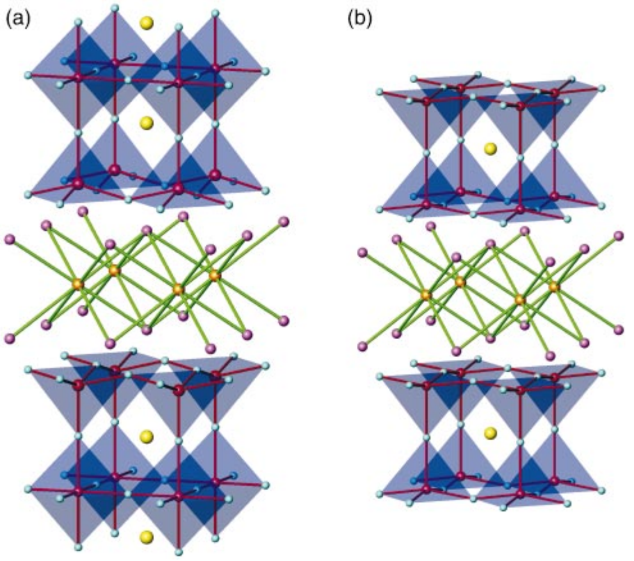

Fig. 7 The structures of (a) $Pb_2Ba_2Cu_2MO_8X$ (M = Ta, Nb) and (b) $Pb_2BaCuFeO_5X$, with X = Cl, Br. CuO_5 and $(Cu,Fe)O_5$ square based pyramids and MO_6 octahedra are shown in blue. Pb — orange, Ba — yellow and X — magenta.

Fluorite layer. Another, more commonly observed feature in cuprate chemistry is the fluorite type $(Ln,Ce)_2O_{2-x}$ layer. Superconductors such as $(Nd_{1.5}Ce_{0.5})Sr_2Cu_2NbO_{10-\delta}$[38] contain the familiar triple perovskite block but the single lanthanide has been replaced by a $(Nd_{1.5}Ce_{0.5})O_{2-x}$ layer thus shifting alternate perovskite blocks by $(a+b)/2$. A survey of the literature reveals that the addition of a fluorite block into layered perovskites based on a single B type cation is confined to cuprate chemistry. The formation of YBCO type iron based phases suggests that it may be possible to incorporate a fluorite $(Ln,Ce)_2O_{2-x}$ layer in an analogous fashion to cuprate chemistry to give phases of the general formula $(Ln,Ce)_2Sr_2Fe_3O_{10}$, Fig. 8.

Fluorite layers may also be introduced into the complex perovskite stacking sequences described earlier though in doing so they cleave these units in half. Hence the formal addition of a Ln,Ce unit into the quadruple perovskites, $Gd_2Ba_2CaCu_2Ti_2O_{12}$, yields phases such as $(Gd,Ce)_3Ba_2CaTi_2Cu_2O_{14}$.[39] The central fluorite unit cuts the quadruple perovskite block in two producing a structure that contains double TiO_6–CuO_5 perovskite blocks that have also been described as an intergrowth between 123 and 0201 structures. In such materials the titanium may be formally replaced by manganese as occurs in the previously mentioned $Eu_3Ba_2Mn_2Cu_2O_{12}$.[23] Such compounds therefore contain discrete layers of copper and, most interestingly, manganese, a structural unit not seen for simpler perovskite structures.

A further group of compounds worthy of mention in this section are the oxysulfides described by the general formula $(Cu_2S_2)(Sr_{n+1}M_nO_{3n-1})$, with $n = 1$ and 2. These materials, first reported by Zhu and Hor *et al.*,[40] form for a variety of transition metals, M = Zn, Mn, Co, Cr and Fe, and contain a Cu_2S_2 anti-PbO type separating layer closely related to the

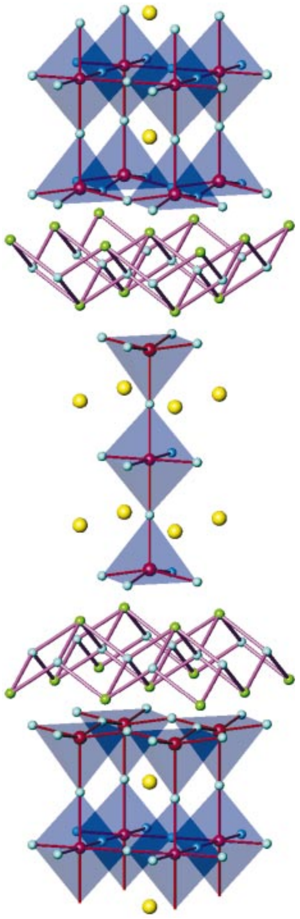

Fig. 8 The structure of the proposed phase $(Ln,Ce)_2Sr_2Fe_3O_{10}$. Iron centred square based pyramids and octahedra are shown in blue, the Ce (cyan) and oxygen (green) fluorite network is outlined with bonds. Sr — yellow.

fluorite type block.[40–42] The coordination of the transition metal varies, forming linked arrays of square planes in the $n=1$ compounds and square pyramids in the $n=2$ ferrate, $(Cu_2S_2)Sr_3Fe_2O_5$.[42] The series has recently been extended to include $(Cu_2S_2)(Sr_2CuO_2)$, which is a possible candidate for superconductivity.[43]

(3) Thallium, bismuth, lead and mercury layers

Thallium–oxygen layers. The thallium copper oxide superconductors exhibit some of the highest critical temperatures and contain the familiar cuprate perovskite blocks interleaved by either one or two rock salt-like Tl–O layers. The single thallium–oxygen layer family is represented by the formula, $TlBa_2Ca_{n-1}Cu_nO_{2n+3}$, $n=1$–5, and the double thallium oxygen layer compounds by, $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$, $n=1$–4. Full discussion of these can be found in several review papers.[44,45] The copper oxidation states in the stoichiometric materials of these two series are very different; in the double thallium series the valence of copper is 2+ irrespective of the number of CuO_2 planes whereas in the single layer materials values range from 3+ to 2.25+ for $n=1$–4. It is the requirement for a copper oxidation state significantly >2+ that makes the single thallium layer materials suitable candidates for other first row transition metals that generally favour higher oxidation states.

Trivalent copper is present in the simplest, $n=1$, stoichiometric member of the single thallium layer family, $Tl(Ba,Sr)_2CuO_5$, and Co[46] and Ni[47] analogues of this material have been reported. The general structure of the compound may be viewed as repeat layers of corner sharing, CuO_6 octahedra separated by a single rock salt TlO sheet, Fig. 9. Unusually, $TlSr_2CuO_{5-\delta}$ exists in both tetragonal and orthorhombic forms depending upon the synthesis conditions. The tetragonal phase was reported in a single crystal study[48] and becomes superconducting when suitable doping of the phase is performed, *e.g.* $TlSrLaCuO_5$, which has a $T_c \approx 40$ K.[49] The polycrystalline orthorhombic form exhibits a significant oxygen deficiency within the infinite CuO_{2-y} planes, that precludes superconductivity and leads to the reduced symmetry, *e.g.* $a=3.66$ Å, $b=3.79$ Å due to an uneven distribution of the oxygen vacancies.[50]

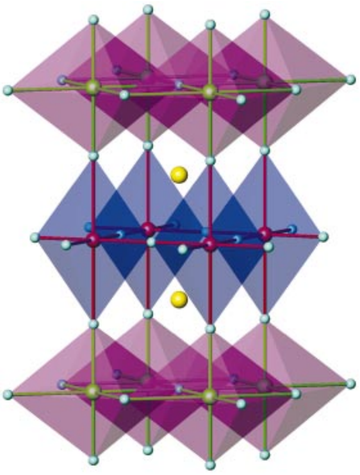

Fig. 9 The structure of $TlSr_2CuO_5$. CuO_6 octahedra are shown in blue, TlO_6 octahedra in magenta, Sr in yellow.

Structurally the nickelate $TlSr_2NiO_{4+\delta}$ is very closely related to bulk $TlSr_2CuO_{5-y}$, sharing an orthorhombic structure due to oxygen defects located in the basal plane of the nominal NiO_6 octahedra. Neutron diffraction studies have shown that the vacancies in both materials are partially ordered along the *b*-axis leading to a 2*b* supercell and an unusual arrangement of alternating MO_6 octhadedra/MO_4 square planes, Fig. 10.[51,52] The Ni oxidation state at ≈2.7+ is considerably higher than the copper oxidation state of 2.1+ in the analogous cuprate. This is consistent with the greater, Jahn–Teller induced, distortion of the Cu–O coordination. For example the apical M–O interaction within the CuO_6 octahedra of $TlSr_2CuO_{5-y}$ is 2.41(2) Å, 0.12 Å longer than the equivalent Ni–O distance.

In contrast, $TlSr_2CoO_5$, reported by Countanceau and coworkers[46] adopts a tetragonal structure. The lack of significant oxygen deficiency, due to the preference of Co for a 3+

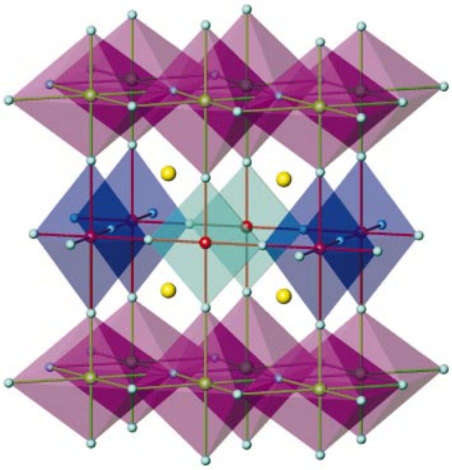

Fig. 10 The structure of $TlSr_2NiO_{4+\delta}$ showing the alternating square planar and octahedral geometries for nickel. NiO_6 octahedra are shown in blue, NiO_4 square plane in cyan, TlO_6 octahedra in magenta and Sr in yellow.

oxidation state, is a likely reason for the absence of an orthorhombic distortion. However, detailed structural analysis of the compound is complicated as the reported synthetic method yields a mixture of two structurally similar phases, *i.e.* a low and high temperature form, which have slightly different cell parameters. The material exhibits interesting electrical and magnetic properties, undergoing a structural change and a correlated metal–insulator transition at room temperature.

Another closely related single layer thallium cuprate, $TlBa_{1.6}La_{2.4}Cu_2O_{9\pm\delta}$ with a $T_c \approx 35$ K,[53] has also been shown to be able to accommodate other transition metals. The parent structure consists of a regular 1 : 1 intergrowth of La_2CuO_4 and $TlBa_2CuO_5$ structural units, Fig. 11. In 1994 the series of Fe oxides $(Pb_{1-x}Tl_x)Sr_4Fe_2O_9$ $(0 \leqslant x \leqslant 1)$ were isolated and the presence of a mixed Fe^{3+}/Fe^{4+} valence for the thallium containing phases was confirmed by Mössbauer and susceptibility techniques.[54] More recently the authors have succeeded in synthesising the isostructural nickelate family, $Tl(Ln_2Sr_2)Ni_2O_9$, with Ln = La, Pr, Nd, Sm, Eu and Gd.[55] These oxides consist of layers of stoichiometric NiO_6 octahedra connected by a TlO layer with a mixed Ni valence of 2.5+ and exhibit paramagnetic behaviour. In both cases the replacement of Ba by Sr has been necessary to produce the Fe and Ni 1201–0201 phases, possibly reflecting the smaller M–O bonds resulting from higher oxidation states of the transition metal in these compounds than in the cuprate. Another well known example of a mono-layer thallium oxide is the ferrite $TlSr_3Fe_2O_8$ which adopts the 1212-type YBCO structure.[56] A common structural feature of all these materials is the disorder they exhibit in the Tl–O plane arising from the requirement of the rock salt TlO layer to register with the larger MO_2 layer.

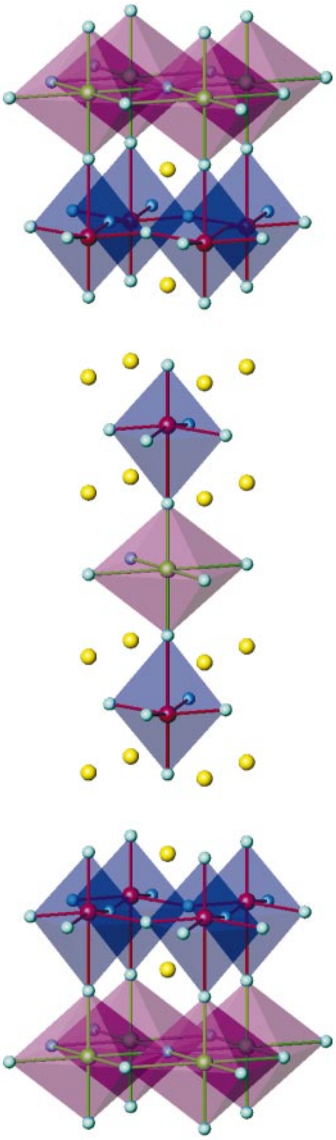

Fig. 11 The structure adopted by $TlBa_{1.6}La_{2.4}Cu_2O_{9\pm\delta}$, $Tl(Ln_2Sr_2)Ni_2O_9$ and $(Hg,Pr)Sr_4Fe_2O_9$. Cu, Ni and Fe based octahedra are shown in blue, TlO_6 octahedral coordination in magenta and Ba/Sr in yellow.

Synthetically the production of thallium containing oxides presents its own set of challenges. Firstly, the high toxicity of Tl_2O_3 demands stringent working protocols and secondly the high volatility of the oxide which decomposes at ≈770 °C to give Tl_2O (g) and oxygen. This necessitates the use of isolated reaction vessels, most frequently sealed gold tubes or pellets wrapped in gold/silver foils, to prevent or at least reduce the loss of thallium at the elevated temperatures required for reaction. Excess thallium within the starting mixtures is also commonly used to compensate for its loss during synthesis. The expansion of thallium oxide chemistry to non-cuprate systems has also required the use of metal precursors, *i.e.* $Sr_2Co_2O_5$ and $Sr_2Ni_2O_5$ are used in the synthesis of $TlSr_2CoO_5$ and $TlSr_2NiO_{4+\delta}$, whilst $TlSr_2CuO_{5-y}$ may be obtained by reacting Tl_2O_3, SrO and CuO. This is a reflection of the higher reactivity of CuO when compared with other binary oxides, especially NiO. Reaction temperatures in the region of 900 °C are routinely employed in the syntheses to yield typically black crystalline products.

The complications of synthesising thallium oxides are now well understood as a result of the intensive effort in the development of high T_c cuprates and the number of non-cuprate thallium oxides is steadily growing. One specific challenge within this area is to extend the number of repeat $MO_{5/6}$ units to the quadrupled and quintupled level observed for the cuprates, *e.g.* $TlBa_2Ca_4Cu_5O_{13}$,[57] particularly for M = Ni and Co. However the phase stability ranges for these materials are likely to be extremely small and isolation of pure phases extremely difficult. In contrast to the increasing number of single thallium layer materials the first non-cuprate double thallium layer material remains to be discovered. This probably reflects the difficulty of stabilising a pure 2+ oxidation for transition metals other than copper with thallium oxide.

Bismuth layer oxides. Developed alongside the thallium cuprates, the bismuth superconductors have also demonstrated the potential to produce new isostructural complex transition metal oxides. Unlike their thallium counterparts the bismuth cuprates only form with double rock salt layers, represented by the formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$, $n = 1$–4. Within a few years of the discovery of the cuprate superconductors, related iron and cobalt based materials were reported; their synthesis motivated by the need to gain an understanding of the relationship between magnetism and the superconducting state within the structurally related copper oxides. These materials correspond to the generic formula, $Bi_2(Sr,Ca)_{n+1}M_nO_{3n+3\pm\delta}$, with $n = 1$, 2, 3 for M = Fe[58–60] and $n = 1,2$ for M = Co.[60,61] Structurally, they share the same unusual feature of incommensurate modulation within the rock salt Bi–O layers as exhibited by the cuprates. However, important structural differences between the cuprates and the other transition metal compounds exist. The main one is linked to the lower oxygen content of the cuprate phases, arising from the lower copper oxidation state, which leads to the appearance of ordered oxygen vacancies within the $(Sr/Ca)CuO_{3-x}$ perovskite blocks, Fig. 12.

Unlike the non-cuprate thallium oxides, bismuth manganese derivatives have also been isolated, although until fairly recently only the simplest $n = 1$ member of the series, $Bi_2Sr_2MnO_{6+\delta}$, had been reported.[62] The discovery of

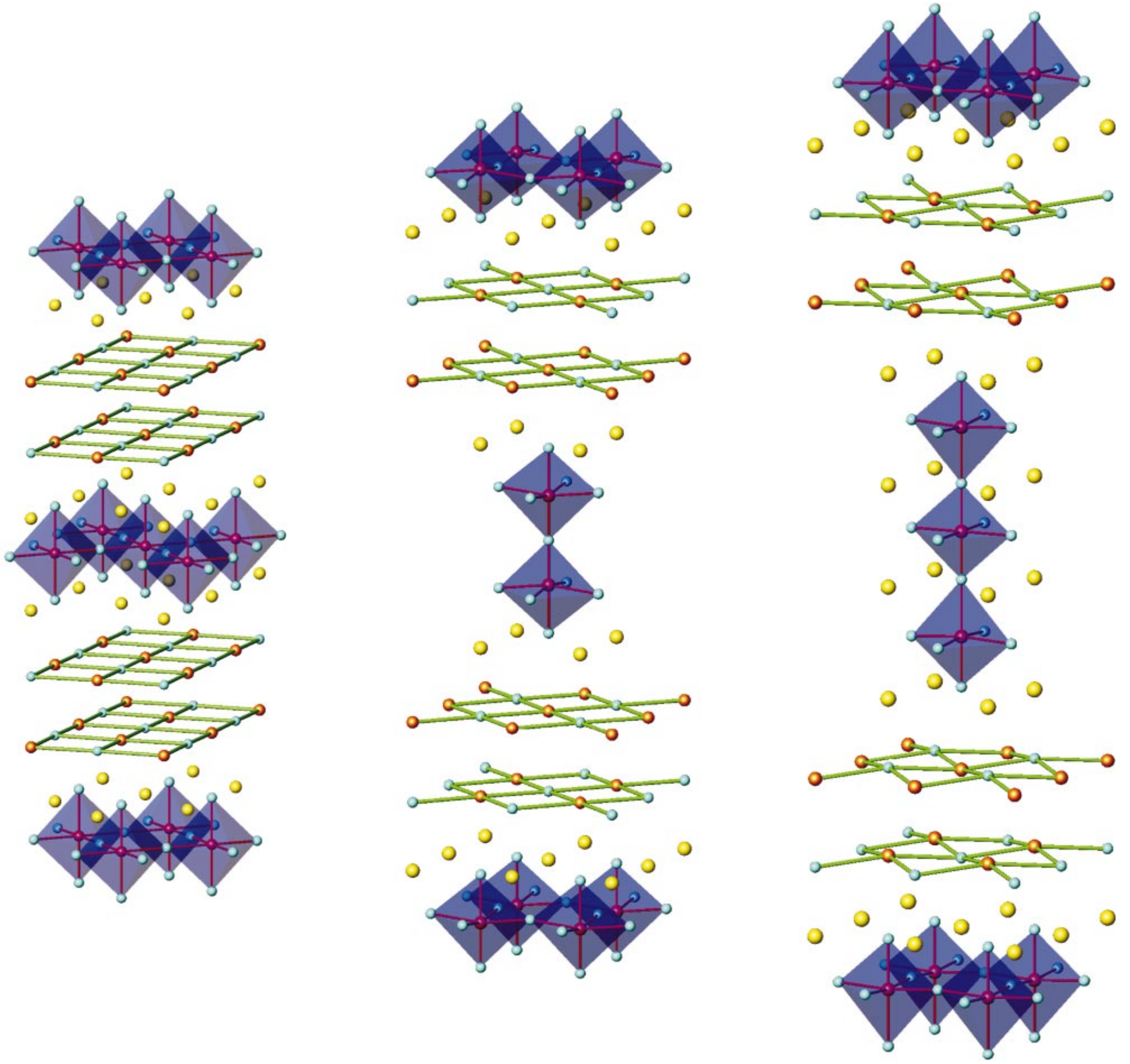

Fig. 12 $Bi_2(Sr,Ca)_{n+1}M_nO_{3n+3\pm\delta}$, with $n=1, 2, 3$ for M = Fe and $n=1,2$ for M = Co. Fe and Co based polyhedra are shown in blue, the Bi(orange)–O(cyan) net is outlined, Sr/Ca in yellow.

CMR within layered manganese oxides has prompted fresh interest and in 1997 Hervieu and co-workers[63] synthesised the second bismuth manganite, $Bi_{2-x}Pb_xSr_{1.5}Ca_{1.5}Mn_2O_{9-\delta}$, which adopts the 2212 structure. Nonetheless a significant level of Pb ($x=0.5$) is required to stabilise the phase, which crystallises in an orthorhombic unit cell, $a=5.3594$ Å, $b=5.3443$ Å and $c=30.976$ Å. More recently the same group have reported three new strontium rich phases, the 1201 $Bi_{0.4}Sr_{2.6}MnO_{5-\delta}$ and the 2201 compounds $Bi_{0.9}Sr_{3.1}MnO_{6-\delta}$[64] and $BiSr_3CoO_{5.8}$;[65] the former compound is the first to stabilise a manganite within a single rock salt layer structure, and the latter two are noteworthy for the absence of a modulated structure. Furthermore the Bi_2O_2 layer may be combined with an ordered tripled perovskite block as in $Bi_2Sr_2Nb_2MnO_{12-\delta}$; in this material the niobium and manganese are believed to segregate into distinct layers with MnO_6 octahedra sandwiched between the niobium-based layers.[66]

To date there is no reported bismuth nickel oxide. The authors have attempted to introduce $Tl_{1-x}Bi_xO$ units into nickelate structures but this has been unsuccessful, a possible reason is that phases such as the cubic nickel doped bismuth oxide materials, *e.g.* $Bi_{18}Ni_8O_{36}$, which have no cuprate analogue, readily form in this system.

Pb and HgO Layers. Lead oxide and mercury oxide layers are the two other common rock salt structure type separating blocks present within a large number of high T_c cuprates, whether as the only constituent of the layer as for $HgBa_2CuO_{4+\delta}$, or in conjunction with thallium or Bi, *e.g.* $(Bi_{0.8}Pb_{0.2})_2Sr_2Ca_2Cu_3O_{10-\delta}$.[67] It is not surprising, therefore, to find a number of Pb substituted Bi and Tl superconductor analogues, such as the previously mentioned $BiPbSr_2MnO_6$ and $PbSr_4Fe_2O_9$, although the latter compound is unusual in that it contains solely Pb. In comparison the number of mercury containing phases is limited to ferrites containing small amounts of Hg. This may be partially explained by the difficulty of isolating Hg–Sr cuprates, which always require the introduction of either lead or bismuth, or a lanthanide or a transition metal to stabilise the structure. The 1201–0201 phase $(Hg,Pr)Sr_4Fe_2O_9$ was the first to demonstrate that these mixed (Hg,M)–$O_{1-\delta}$ could be transferred outside cuprate chemistry,[68] Fig. 11.

In summary a number of non-cuprate transition metal oxides adopting structures directly related to the well established single and double rock salt layer high T_c families have been considered. Metals that show the ability to expand this particular area are the neighbouring first row elements, manganese, iron, cobalt and nickel, which, with the exception of nickel, are commonly found in octahedral coordination and trivalent oxidation states within perovskite-like structures. Fortuitously, the oxygen deficiency of the cuprate superconductors facilitates the introduction of the higher oxidation state of these elements. Structurally this often results in the replacement of CuO_5 square pyramids by MO_6 octahedra, as for example occurs in the 1212-type $TlSr_3Fe_2O_8$. Also particularly striking is the absence of a material containing barium as the perovskitic A cation. This highlights one difficulty in transferring the cuprate chemistry as it is not possible to recreate the large number of thallium barium cuprates, *e.g.* the 1201 phase $TlBa_2MO_5$, M = Ni, Co. The larger barium cation appears to be incompatible with the crucial RS–O to M–O interface.

(4) Anions in complex oxides

The incorporation of anions into complex oxide structures is another area that has received much more attention since the advent of high temperature superconductivity. In general the high temperatures used to generate complex oxide structures from their component oxides leads to the destruction of complex anions producing further oxide ions with the elimination of simple gaseous species. Hence, most simple compounds containing ions such as carbonate, phosphate, sulfate, borate *etc.* decompose at temperatures below 700–800 °C, that is at lower temperatures than those where many simple oxides react together.

However, a few compounds containing such simple anions in combination with complex oxide structural motifs were reported in the literature prior to the discovery of high temperature superconductivity, for example barium nickel oxide carbonate reported by Gottschall and Schöllhorn.[69] Even rarer within this category are structures containing infinite structure oxide elements in combination with the anions. In terms of high temperature superconducting cuprate chemistry many such phases have been developed with a realisation that particularly in combination with alkaline earth elements simple anionic species, such as carbonate and borate, may be stabilised in complex oxides at reaction temperatures to 1000 °C. The simplest compounds are the strontium cuprate carbonates, *e.g.* $Sr_2CuO_2CO_3$, first investigated in detail by Greaves *et al.*[70] The structure of this phase is related to that of perovskite, containing planes of the stoichiometry CuO_2 separated by strontium and carbonate ions; strontium may be partially replaced by barium in this structure, Fig. 13. Barium cuprate "$BaCuO_2$", a common impurity that develops in superconductor synthesis, due to the use of barium carbonate as a reactant or by uptake of carbonate from air, is in fact an oxide carbonate.[71] The structure, which has been studied in detail using both X-ray and neutron diffraction techniques, contains very unusual sphere-like polyhedral units constructed from CuO_4 square planes and CuO_5 square pyramids separated by barium and carbonate ions; the structure is similar to that of barium nickel carbonate originally reported by Gottschall and Schöllhorn.[69]

Later, carbonate was found to be a significant unit in a number of superconducting phases such as $Bi_2Sr_{6-x}Cu_3O_{10}(CO_3)_2$,[72] $Y_4Sr_8Cu_{11}CO_3O_{25}$,[73] $Pb_{0.7}Hg_{0.3}Sr_4Cu_2(CO_3)O_7$[74] and $Bi_{0.5}Hg_{0.5}Sr_4Cu_2(CO_3)O_{7-\delta}$[75] where the CO_3 group replaces CuO_4. Orientational disorder of the carbonate anions adds structural complexity. Carbonate is also believed to be incorporated in the YBCO structure under some conditions. In order to control the electronic properties of cuprate carbonates and induce superconductivity the CO_3^{2-} unit may be replaced by BO_3^{3-} in compounds such as $Sr_2CuO_2((CO_3)_{0.85}(BO_3)_{0.15})$ and $LnBaCuO_2BO_3$,[76] Fig. 14. Other anions that have been incorporated into cuprate structures include sulfate and phosphate. For example the series of oxyphosphate superconductors $(Cu_{0.5}P_{0.5})Sr_2(Ca,Y)_{n-1}Cu_nO_y$, with $n = 3$–6, has been prepared under high pressure, see following section, by Isobe and co-workers.[77] They show superconductivity with various critical temperatures in the range of 64–112 K depending on n and the yttrium and oxygen contents. Electron diffraction and HRTEM observations revealed that compounds of this series have mixed copper and phosphorus sites in an ordered way within the (Cu,P) plane forming a superstructure of $2a \times b \times 2c$ with respect to a basic tetragonal lattice, a, b, c.

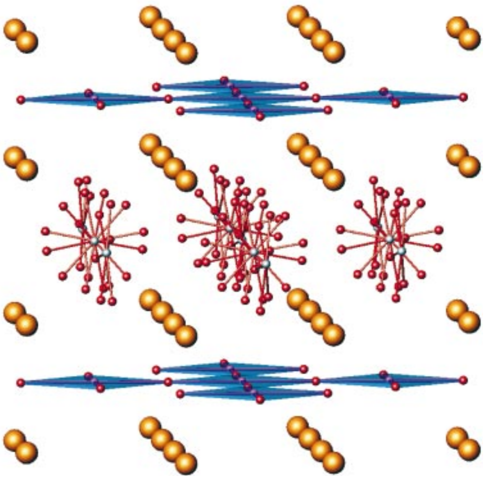

Fig. 13 The structure of $Sr_2CuO_2CO_3$. CuO_4 square planes are shown in blue, Sr in orange. The carbonate units (carbon — grey, oxygen — red) are disordered over several directions and all possible orientations are shown.

In terms of complex anion incorporation more generally into oxide structures few compounds had been reported prior to the development of cuprate carbonate superconductors. However, research in this area has also been propelled by the discovery of new superconducting structure types. In terms of simple materials strong analogies exist in the structural chemistry of copper(II) and palladium(II) but the discovery of barium palladium oxide carbonate is noteworthy.[78] This material adopts the same structure as barium copper oxide carbonate with the complex polyhedral units based on linked PdO_4 square planes, Fig. 15. This compound is extremely unusual for

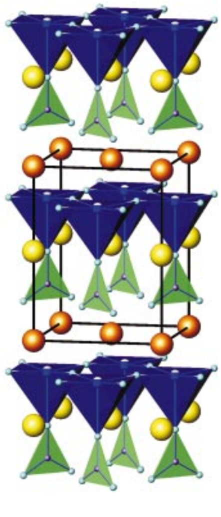

Fig. 14 The structure of the cuprate-borate $PrBaCuO_2BO_3$. CuO_5 square pyramids are shown in blue, borate groups in green, Pr in orange and Ba in yellow.

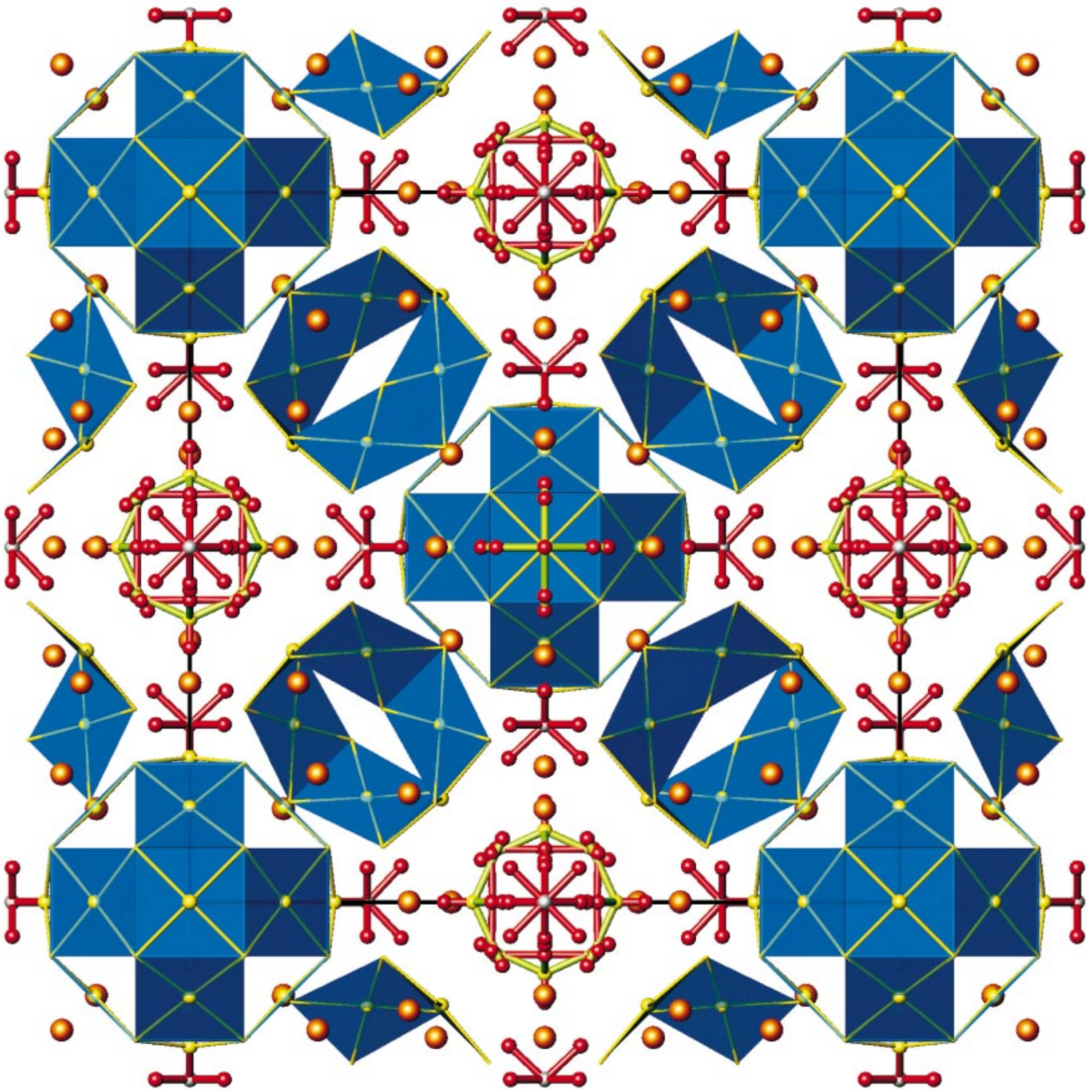

Fig. 15 The structure of barium palladium oxide carbonate "$BaPdO_2$". PdO_4 square planes are shown in blue (Pd in yellow), carbonate groups (partially disordered) with carbon in grey and oxygen in red. Barium ions are shown in orange.

palladium(II) in oxide materials as the Pd(II) centres are usually present as *discrete* PdO_4 square planes.

More recently the formation of perovskite-like analogues of cuprate carbonates but with ferrate has been reported by Yamaura and co-workers,[79] Fig. 16. Reaction of strontium carbonate and Fe_2O_3 at 1100 °C in 10% CO_2 leads to the formation of $Sr_4Fe_2O_6CO_3$ whose structure can be considered as related to that of a 4 : 3 : 10 Ruddlesden–Popper phase with carbonate units replacing the central octahedral MO_6 site. The use of a relatively high CO_2 pressure to help stabilise the carbonate ions in the structure at the high reaction temperature is noteworthy and is, perhaps, a technique that could be applied to many other transition metal systems. At around the same time Raveau *et al.* succeeded in introducing a smaller level of carbonate into the same parent structure using $SrCO_3$ as the source of CO_2 within an evacuated ampoule to produce $Sr_4Fe_{2.6}O_{8.2}(CO_3)_{0.4}$.[80] Carbonate and borate have also been incorporated into manganate structures as shown in $Sr_5Mn_4CO_3O_{10}$ and $Sr_4Mn_3(B_{1-x}Mn_x)O_{10}$.[81,82]

(5) High pressures

The application of high pressure methods in the synthesis of high temperature superconductors has led to the development of many new materials, several of which have been described above. Some of the most notable are the very complex layer structures such as the five cuprate layer, mercury containing, superconductor $(Hg_{0.58}Pb_{0.42})Ba_2Ca_4Cu_5O_{12.52}$,[83] Fig. 17. The use of high pressure in the synthesis of such materials probably has many purposes, as well as overcoming the volatility of the mercury and lead oxides it also helps stabilise the complex layer sequence with respect to decomposition to simpler structures. Similarly, high pressure can reduce the volatility of other oxides such as those of the alkali metals for example in the synthesis of the superconducting phase $Ca_{2-x}Na_xCuO_2Cl_2$.[84] A series of polycrystalline samples with $0 \leqslant x \leqslant 0.20$ were prepared at 6 GPa and 1173 K. The compound contains CuO_2 planes as in La_2CuO_4, but with apical chloride ions. A systematic variation of T_c, with a maximum value of 28 K, has been found as a function of sodium content.

Such high pressure synthesis methods have again been widely applied to cuprate synthesis and many of the most recently reported, since 1992, high temperature superconducting materials have been prepared using various solid state presses. The application of such methods to non-cuprate systems would presumably extend the structural chemistry of other transition metals still further and recent results support this view. For example the simple perovskite $TlNiO_3$, synthesised at 7 GPa and 680 °C, has recently been reported.[85] This material adopts the $GdFeO_3$ type perovskite structure and orders antiferromagnetically below 105 K.

Work in the area of manganate materials demonstrating

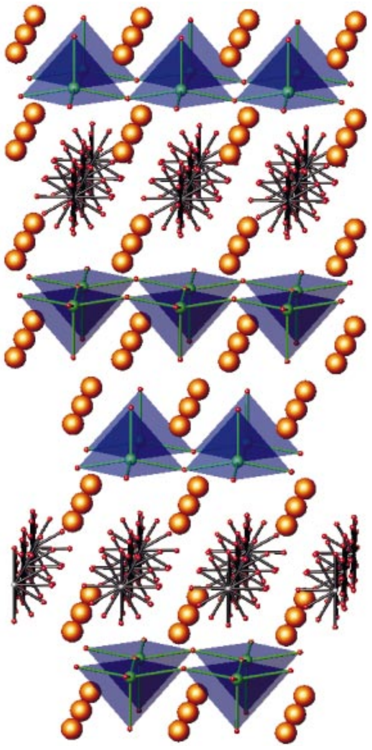

Fig. 16 The structure of $Sr_4Fe_2O_6CO_3$. FeO_5 square based pyramids are shown in blue. Carbonate groups (carbon — grey, oxygen — red) are disordered. Sr atoms are shown in orange.

magnetoresistance has also been extended through the use of high pressures; for example the syntheses of the pyrochlore $Tl_2Mn_2O_7$ and its doped derivatives are undertaken at high pressure.[86] The parent manganate demonstrates a magnetoresistance ratio of −86% at 7 T and 135 K; the doped derivatives with cadmium and scandium partially replacing thallium show even greater effects. Further syntheses of perovskite manganates such as $Bi_{1-x}A_xMnO_3$ have also been carried out under high pressure conditions (4 GPa) but without generating new structure types.[87]

Outside cuprate, nickelate and manganate chemistry the application of high pressure synthesis methods to transition metal oxides has been less extensive though of course such methods are routinely used for the synthesis in the field of geochemistry. One notable recent example in solid state chemistry has been the preparation of the first alkaline-earth mercurato(II)–palladate(II,IV).[88] Single crystals of $Ba_2Hg_3Pd_7O_{14}$ were prepared under high pressure oxygen (3.9 GPa) — similar conditions to those used for producing and annealing many superconductor phases. The Hg^{2+} ions show 2-fold dumb-bell-like and 3-fold coordination while the Pd^{4+} and Pd^{2+} centres show an octahedral and square planar coordination, respectively, in this material.

Discussion

In this article several areas of synthetic and structural solid state chemistry have been reviewed in terms of progress over the last decade as a consequence of results emerging from the worldwide interest in high temperature superconductor cuprate chemistry. In four areas, (i) structurally complex multilayer perovskites, (ii) materials containing layers of volatile metal oxides/halides such as thallium, bismuth, mercury and lead, (iii) compounds containing complex anionic species and (iv) synthesis under high pressure, there has been radical progress in synthetic and structural solid state chemistry. However, this effort has been directed almost totally at copper chemistry, which, while suited to the development of superconducting phases, has really limited the impact in terms of delivering new materials. Recent application of these new methodologies and structural insights to non-cuprate systems, as discussed in this article, has demonstrated that they have just as much to offer but in a much wider range of materials.

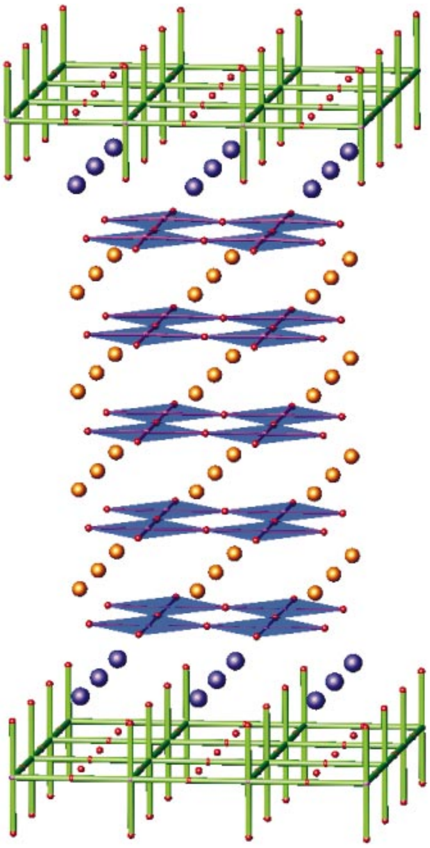

Fig. 17 The structure of the five layer cuprate $(Hg_{0.58}Pb_{0.42})Ba_2Ca_4Cu_5O_{12.52}$. CuO_4 square planes are shown in blue, the Hg/Pb–O network is outlined in green, Ba in purple and Ca in orange.

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