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Feature Article

Properties and substitutional chemistry of layered lead cuprate superconductors

T. P. Beales

Metal Manufactures Ltd, High Temperature Superconductor Facility, Australian Technology Park, Eveleigh NSW1430, Australia

This article reviews the relationship between structure and properties for a series of layered Pb-containing superconducting cuprates from the research viewpoint of the solid state chemist or materials physicist. The 0211, 1201, 1212, 1222 and 2213 structures containing (Pb,M)O layers and their derivatives are considered with the emphasis on the general physiochemical relationships observed between crystal structure, allovalent ion chemical substitution, materials processing and optimisation of superconductivity.

It is now ten years since the discovery of high temperature superconductivity in cuprates. If these materials are to enjoy widespread application in high and low power electrical engineering, then they will need to function in devices operating at, or just below, 77 K. Experience shows that it is near to 20 years for a product engineered from a new material or process to enjoy commercial success from the point of innovation. If high temperature superconductors follow this pattern, we are already half way into the cycle. Our present state of understanding of the materials in the liquid nitrogen regime is that each of the known cuprate superconductors has specific strengths and weaknesses.

$YBa_2Cu_3O_{7-\delta}$ (Y-123) can be processed in bulk[1] and thin film form[2] to give high critical current densities (J_C) at 77 K in excess of 1×10^9 A m^{-2}. The drawbacks of Y-123 mainly arise from its crystal structure. The orthorhombic unit cell of Y-123 requires careful control during processing in both thin films and in bulk, as the biaxial alignment of Y-123 grains necessary for high J_C values is difficult to achieve. Labile oxygen on the CuO_2 chain site leads to Y-123 exhibiting an orthorhombic–tetragonal transition[3,4] and the CuO_2 chain site is also chemically reactive.[5]

The corresponding bismuth-, thallium- and mercury-containing layered cuprates all have highly anisotropic layered crystal structures with macroscopic plate-like crystals. As a consequence of this, they have been used to fabricate long conductors in the form of wires and tapes for high power applications.[6] These materials have an advantage over Y-123 in that they have melting points below 960 °C, allowing them to be sinter-processed in an inert metallic silver sheath. The higher order Bi-, Tl- and Hg-containing layered cuprates ($n>2$) also have higher superconducting transition temperatures (T_C) than Y-123 ($T_C=92$ K[7]) ($T_C=125$ K for Tl-2223[8] and 110 K for Bi-2223[9]). The volatility of Hg and Tl combined with their toxicity has made their use in these materials unattractive. Both the Bi- and Tl-containing superconductors are inferior to Y-123 in regards to their magnetic flux pinning capabilities at 77 K, which is weak, and small magnetic fields applied along the crystallographic *c* axis severely limit their current-carrying capability.[10]

The intrinsic flux pinning behaviour of layered high temperature superconductors can be understood in terms of their crystal structure.[11] In these materials, the magnetic flux lines resemble a set of cylinders with radius equal to the coherence length (λ) and height equal to the width of the CuO_5 planes in the unit cell. Below a temperature T^*, these cylinders are flux-pinned through the non-superconducting layers by a Josephson coupling interaction. Above T^*, the Josephson coupling breaks down and the flux cylinders move uncoupled through the CuO_5 planes. For practical applications, T^* needs to be close to 77 K.

To overcome the intrinsic problems of the known cuprate materials many groups across the world began to search for new materials that would keep the advantages of Y-123 *i.e.* good flux pinning and simple chemical structure but would also overcome its disadvantages *i.e.* oxygen non-stoichiometry, orthorhombic–tetragonal distortion and chemical reactivity. Any new material would also need to incorporate the advantages of the Bi- and Tl-containing superconductors *i.e.* at least two Cu—O layers containing the supercurrent (to ensure a T_C above 77 K) and should overcome anisotropy problems by resembling Y-123 in having an efficient non-superconducting dopant layer which was as atomically thin as possible (preferably a single non-superconducting oxide layer).[12]

Two likely candidate systems were discovered in the late 1980s: (Pb,Cu)-1212 with a general formula of $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ and Pb-2213, with a general formula of $Pb_2Sr_2(Y_{1-x}Ca_x)Cu_3O_{8+\delta}$ which partly fitted the desired material requirements in several areas and were closely allied to Y-123 in crystal structure. This review attempts to chart the progress since then in the layered Pb-containing cuprates. Other '1212' materials containing either Tl or Hg alone in the rocksalt structure and also other stoichiometries such as 2212 are not included in this review and are covered adequately elsewhere in the literature.[13,14]

$YSr_2Cu_3O_{7-\delta}$: the base unit for the layered Pb cuprates

$YSr_2Cu_3O_{7-\delta}$ is derived from the substitution of Sr into $YBa_2Cu_3O_{7-\delta}$. The smaller ionic radius of Sr^{II} (*cf.* Ba^{II}) prevents a stable $YSr_2Cu_3O_{7-\delta}$ structure forming when synthesised using normal solid state calcination procedures (maximum Sr substitution up to 60%)[15–18] and requires static high pressure synthetic techniques.[19] $YSr_2Cu_3O_{7-\delta}$ has a more tetragonal structure than $YBa_2Cu_3O_{7-\delta}$ with a shorter *a* and *c* axis.[19] The smaller $YSr_2Cu_3O_{7-\delta}$ unit cell volume reflects a more compressed structure with a corresponding higher Cu oxidation state. $YSr_2Cu_3O_{7-\delta}$ can be chemically stabilised by cationic substitution as explored by Slater and Greaves,[20] Sunshine *et al.*,[18] Den and Kobayashi[21] and others. These workers have shown that for two particular cases, four and six coordinate cations, the '123' structure obeys general substitutional rules. Four coordinate substitution is favoured in $YSr_2Cu_{3-x}M_xO_{7-\delta}$ for small M, *e.g.* Al^{III}, Ga^{III} or Cr^{VI}.

Six-fold coordinate substitution is favoured for larger M and for δ values near full oxygenation and represents the incorporation of MO_6 units into the CuO_2 chain sites *e.g.* Ti^{IV}, Mo^{VI} or W^{VI}. It is possible to obtain mixed coordination states in the same compound[20] *e.g.* in $YSr_2Cu_2FeO_{7.42}$, the formal Fe = 3.84 oxidation state implies a mix of Fe^{III}/Fe^{IV}, most probably in four and six oxygen co-ordination respectively.

It is possible to link the (Pb,M)-1212, Y-123 and Pb-2213 phases by comparing the unit cell structures and highlighting similar features. There is a common chemical block found in all three materials containing CuO_5 square basal pyramid units able to transmit the supercurrent. This is the CuO_5 plane or perovskite block, and is relatively stable to chemical attack. It also contains a group 2 ion astride the corner sharing CuO_5 pyramids and a layer of lanthanide or (Ln/group 2 ion solid solution) which has no oxygen layer associated with it. In Y-123, this layer contains Ba and Y ions respectively: in (Pb,M)-1212, it contains Sr and Ln/Ca ions respectively and in Pb-2213, it contains Sr/Ba and Y/Ca ions respectively. The perovskite unit is schematically shown in Fig. 1 and has the general chemical formula $YSr_2Cu_2O_6$.

The structural difference in each of the materials arises at the ends of the CuO_5 units, where a new block consisting of ions able to act as charge reservoirs for doping the CuO_5 planes is present. This block is unique to each structure. How successful this oxide layer is in accepting and accommodating electronic charge determines the overall degree of three dimensionality of the material.

Fig. 2 shows the connecting block for the '123' structure and is composed of CuO_2 chains. It is this block that effectively determines the properties of Y-123: its labile oxygen produces charge carriers from non-stoichiometry and its ability to undergo structural rearrangement is the root cause of the orthorhombic–tetragonal transition. The Cu ions in the CuO_2 site are also chemically different from those in the CuO_5 site and are more susceptible to chemical attack and substitution. The advantage of the CuO_2 chains is that they endow on Y-123 a higher dimensionality by allowing the flux cylinders in adjacent perovskite blocks to couple through them resulting in a high T^*. Fig. 3 shows a representation of how the CuO_2 units and $YBa_2Cu_2O_5$ units in Y-123 are arranged.

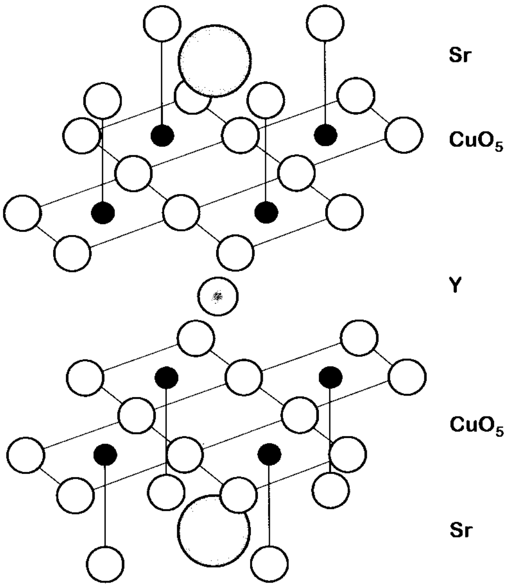

Fig. 1 Illustration of the $YSr_2Cu_2O_6$ chemically stable perovskite block found in the '123', '1212' '1222' and '2213' structures

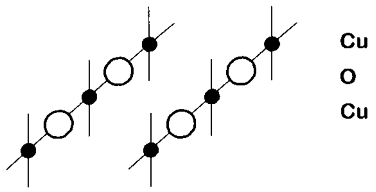

Fig. 2 Illustration of the CuO_2 chain block sited at the apical oxygen of the $YSr_2Cu_2O_6$ perovskite block in the '123' structure

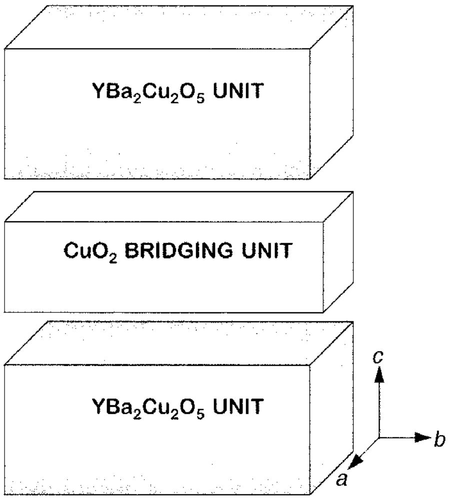

Fig. 3 Pictorial representation of the building block structure of the '123' phase

The (Pb,Cu)-1212 phase: $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$

In chemical terms, one can envisage the doping of Pb into the Sr-containing Y-123 phase in an idealised formula of $YSr_2(Cu_{3-y}Pb_y)O_{7-\delta}$. When this type of chemical substitution was tried, it was found that the Pb did preferentially substitute into the CuO_2 site in the Y-123 structure as expected, but in doing so formed a new crystal structure. The Pb ions adopted a rocksalt arrangement rather than the perovskite structure favoured in the CuO_2 chains. This new phase was called the '1212' phase [usually written as $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ or (Pb,Cu)-1212]. It can be thought of as a shear translation of the chain site oxygen in Y-123 by (½, 0, 0) to form the new layer shown schematically in Fig. 4. (The '123' structure can really be thought of as a special case of the '1212' structure *i.e.* CuO-$YSr_2Cu_2O_6$). Fig. 5 shows how the rock salt and perovskite blocks fit together in the '1212' structure. (Pb,Cu)-1212 was first synthesised with nominal stoichiometries of $(Pb_{0.69}Cu_{0.31})Sr_2(Y_{0.85}Ca_{0.15})Cu_2O_{7-\delta}$[22] and $(Pb_{0.29}Cu_{0.71})Sr_2(Y_{0.73}Ca_{0.27})Cu_2O_{7-\delta}$[23] and was originally thought not to be superconducting.

A noticeable fact about the synthesis of (Pb,Cu)-1212 is that phase pure samples are difficult to prepare, and (Pb,Cu)-1212

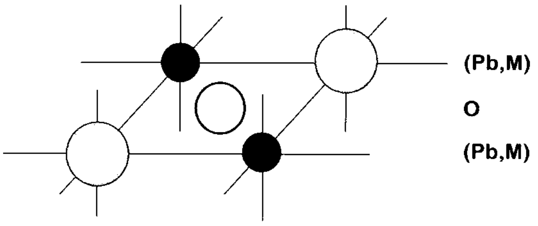

Fig. 4 Illustration of the (Pb,M)O rocksalt structure block sited at the apical oxygen of the $YSr_2Cu_2O_6$ perovskite block in the '1212' structure

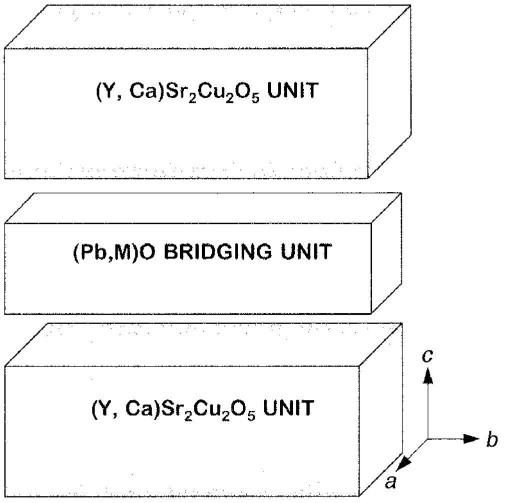

Fig. 5 Pictorial representation of the building block structure of the '1212' phase

samples have been reported for the nominal compositions $(Pb_{0.5}Cu_{0.5})Sr_2YCu_2O_{7-\delta}$,[24] $(Pb_{1-y}Cu_y)Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ $(0.2 \leqslant y \leqslant 0.5)$[25] and $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ $(x \leqslant 0.35)$[26] using conventional solid state synthesis techniques. The exact limits of the Ca solid solution range are difficult to define from the literature XRD patterns due to an ambiguity in the phase purity. High Ca substitution levels $(\geqslant 0.5)$ require both the increased substitution of Pb for Cu in the rocksalt layer and careful control of the overall oxygen stoichiometry (best achieved by quenching from high temperatures). Using this procedure Naqvii and Boyd,[27] synthesised reasonably phase pure XRD patterns for compositions of $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ $(0.25 \leqslant y \leqslant 0.35$ and $x \leqslant 0.8)$. Phase pure samples of (Pb,Cu)-1212 have been synthesised using a laser ablation technique,[28] which indicate that the Ca solid solubility limit is close to $x = 0.7$. Both the solid state and thin film synthetic procedures agree that the T_C value is related to the amount of Ca present. A T_C onset = 82 K in $(Pb_{0.75}Cu_{0.25})Sr_2(Y_{0.2}Ca_{0.8})Cu_2O_{7-\delta}$ produced by the solid state route[27] and a T_C onset = 86 K in $(Pb_{0.75}Cu_{0.25})Sr_2(Y_{0.3}Ca_{0.7})Cu_2O_{7-\delta}$ produced by laser ablation[28] are in good agreement and suggest that this is probably the maximum T_C value in this material. No evidence of superconductivity has been reported in the Ca-free compound $(Pb_{0.5}Cu_{0.5})Sr_2YCu_2O_{7-\delta}$.

In addition to the inducement of superconductivity by doping the Y site with Ca, the properties of (Pb,Cu)-1212 show a marked sensitivity in its oxygen stoichiometry, which can be readily altered by processing in high pressure O_2 gas, especially during post-synthesis annealing. For example, Tang *et al.*[29] showed that the resultant oxygen stoichiometry in $(Pb_{0.5}Cu_{0.5})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7-\delta}$ was dependent on the sample cooling rate after calcination (at 940 °C). T_C values below 10 K were observed for samples cooled at less than 10 K min^{-1} and T_C values up to 67 K were observed for samples cooled at a rate above 10 K min^{-1}. The low T_C value for the slow-cooled samples was attributed to labile oxygen loss during cooling. A Pb^{IV} oxidation state was calculated from iodometric titration for these samples, the high T_C samples exhibited a value of $\delta = 0.01$ and the lower T_C samples $\delta > 0.01$. A value of $\delta = 0.01$ in the above compound yields a net Cu valency = +2.2, which is close to the optimum value[30] of +2.15 (assuming an overall valency of the rocksalt layer = +3) and can explain the higher T_C value. Similar monitoring of the oxygen concentration by Kurusu *et al.*[31] using coulometric titration in $(Pb_{(1+x)/2}Cu_{(1-x)/2})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ $(x \leqslant 0.35)$ showed that samples quenched from 800 °C in air had $\delta = 0.0$, compared to $\delta = 0.1$ for slow cooled samples for all values of x. In this system, superconductivity was observed between the narrow ranges $0.3 \leqslant x \leqslant 0.35$ with T_C onset values between 20 and 40 K. Fig. 6 shows a 3D projection of the observed literature values of T_C onsets in $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ plotted against the Pb and Ca contents determined after using different processing conditions. The observed T_C values show a strong correlation with the Ca content of (Pb,Cu)-1212 in the excess Pb content region with the highest T_C onset values near to $x = 0.7$.

From the oxygen concentration measurements, it can be shown that increasing the Ca concentration alone is not solely responsible for increasing the hole concentration in (Pb,Cu)-1212, but samples do become more metallic and show an increase in both the Hall and Seebeck coefficients with increasing Ca concentration.[32] In quenched samples with fixed Ca contents, those with $\delta = 0.0$ show a lower resistivity and lower Hall and Seebeck coefficients than for samples with $\delta > 0.0$, indicating that quenching also increases the carrier density. These same samples also showed a positive magnetoconductance and a ln(T) behaviour at temperatures $\leqslant 4$ K. This is usually associated with the Kondo effect and can be explained as arising from localised cationic distributions. Neutron diffraction data[33] on $(Pb_{0.65}Cu_{0.35})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_{7-\delta}$ showed that oxygen vacancies were statistically located on the (0, ½, 0) site in the (Pb,Cu)O layer (*i.e.* equivalent to the O chain site in Y-123). The evidence from neutron diffraction data implies that it is these oxygen vacancies that cause a random potential to occur in the (Pb,Cu)O layer which in turn leads to a decrease in carrier concentration. At present, it is not possible to differentiate whether this arises from Anderson localisation or from disruption of the Pb^{IV}–Pb^{II} metavalence necessary to provide charge carriers in the self-doping mechanism in these materials.

Substitutions for Cu: the $(Pb_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ series

The '1212' lattice consists of stable perovskite $YSrCu_2O_6$ blocks surrounding rocksalt (Pb,Cu)O layers. The thermodynamic stability of these $YSrCu_2O_6$ blocks means that chemical substitution invariably takes place in the rocksalt layer [except in the case where M = Tl which commonly cross substitutes for Ca in the $(Y_{1-x}Ca_x)$ layer]. As will be described in more detail in this section, there is a strong correlation between the effective ionic radius of the M ion and the maximum T_C onset values in the $(Pb_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ series. Fig. 7 shows a plot of the maximum observed T_C values in selected (Pb,M)-1212 compositions *versus* the effective ionic radius of the M^{n+} substituted into the (Pb,M)O layer. The synthesis and

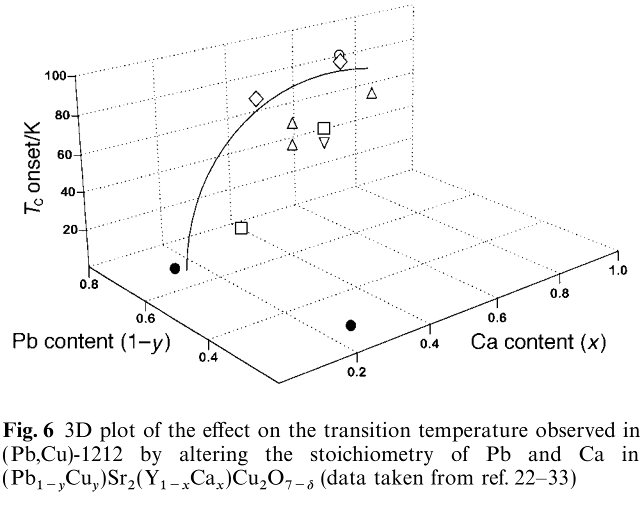

Fig. 6 3D plot of the effect on the transition temperature observed in (Pb,Cu)-1212 by altering the stoichiometry of Pb and Ca in $(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ (data taken from ref. 22–33)

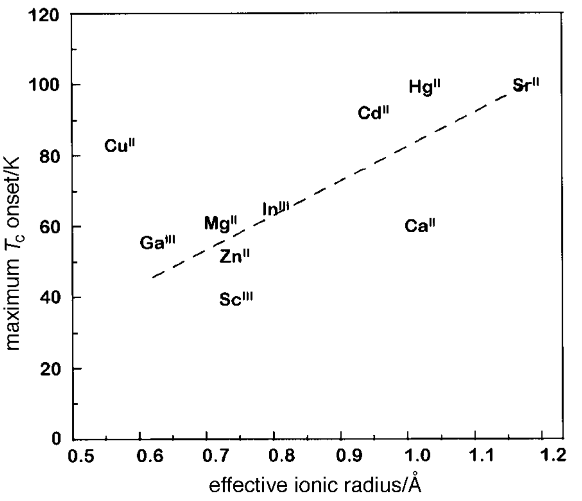

Fig. 7 A plot of the observed T_C onset value for a range of M ions substituted into the (Pb,M)-1212 structure *versus* the effective ionic radius of M^{n+} ions

properties of each group of the M^{n+} cations in the (Pb,M)-1212 structure, according to their position in the Periodic Table, are discussed in the following section.

Substitution by group 2 metals (M = Mg, Ca and Sr)

The earliest substitution work in the 1212 system was the substitution of Cu by the group 2 metals. As in (Pb,Cu)-1212, phase purity is difficult to achieve using conventional solid state synthetic techniques and secondary phases of $SrCuO_2$, Sr_2CuO_3 and $Sr_5Pb_3CuO_{12}$ regularly appear in the XRD patterns of published work. Maignan *et al.*[34] used TEM and EDAX to carry out detailed analysis of 1212 phases. They found that cross-site cation substitution was common, along with the presence of secondary phases calculated to be in the order of 10% per sample. For the (Pb,Sr)-1212 phase $(Pb_{0.5}Sr_{0.5})Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$, actual stoichiometries were found to be $(Pb_{0.64}Cu_{0.2}Sr_{0.16})Sr_2(Y_{0.6}Ca_{0.32}Sr_{0.19})Cu_2O_{7-\delta}$ and $(Pb_{0.66}Sr_{0.34})Sr_2(Y_{0.6}Ca_{0.21}Sr_{0.19})Cu_2O_{7-\delta}$, suggesting partial substitution of the Sr into the Y site and displacement some of the Ca. This is not entirely unexpected as similar cross-substitution is known in the bismuth cuprates where Pb, Sr and Bi form a solid solution.[35] The cross substitutional effect seems to be amplified when the M cation is particularly small, (as in Mg^{II}) where Maignan *et al.* found solid solutions of the nominal (Pb,Mg)-1212 phase[34] $(Pb_{0.5}Mg_{0.5})Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ to contain actual stoichiometries from the EDAX analysis of $(Pb_{0.6}Mg_{0.17}Cu_{0.21}Sr_{0.02})Sr_2(Y_{0.56}Ca_{0.44})Cu_2O_{7-\delta}$ and $(Pb_{0.61}Mg_{0.07}Cu_{0.28}Ca_{0.04})(Sr_{1.92}Ca_{0.04})(Y_{0.7}Ca_{0.3})Cu_2O_{7-\delta}$. This implies that Mg really does not substitute at all and that a rather random cationic composition of the rocksalt layer occurs, and can explain the poor XRD phase purity shown by samples in this system. An independent report of the preparation of the (Pb,Mg)-1212 phase was given by Liu *et al.*,[36] who used an additive of 10 mass% silver oxide and processed in 10 MPa of high pressure O_2 at 950 °C but only managed to see a very weak superconducting signal at 60 K.

This latter point emphasises that aside from cation inhomogeneity, the group 2 substituted materials also suffer from oxygen non-stoichiometry. Both (Pb,Sr)-1212 and (Pb,Ca)-1212 can be made superconducting as-synthesised, but the superconducting properties are improved by post-synthesis annealing in high pressure O_2. The presence of Ca on the Y site is essential for superconductivity in these materials. The complex cross-substitutional and phase equilibria of these materials is reflected in the fact that T_C is seen to increase even after the nominal XRD phase solid solution limit of Ca substitution is reached. This suggests that the mechanism for superconductivity in the group 2 1212 phases is due mainly to the doping effect of Ca^{II} for Y^{III} and not to an ability to self-dope as in (Pb,Cu)-1212. The mixed ion rocksalt layer induces a random oxygen stoichiometry which can be, in part, compensated for by a post synthesis high pressure O_2 anneal. Oxygen vacancies have been directly observed in both (Pb,Ca)-1212 and (Pb,Sr)-1212 where values of $\delta = 0.3$ were determined for stoichiometries of $(Pb_{0.5}M_{0.5})Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ (M = Sr or Ca),[37,38] showing highest T_C onset temperatures of 104 and 80 K, respectively. Single crystals of (Pb,Sr)-1212 have been grown from a self-flux, but only show a T_C onset of 50 K.[39] In low oxygen content (Pb,Sr)-1212 and (Pb,Ca)-1212, non-commensurate satellite reflections are observed in the electron diffraction data which are attributed to oxygen vacancies at the apical CuO_5 rocksalt site. These features were seen to reduce in intensity after high pressure O_2 annealing. (Pb,Sr)-1212 also displays further reflections arising from an $n \times a$ superstructure along the a axis attributed to Pb and Sr cation disordering.[40] Similar cation disorder phenomena have been observed in the optical spectroscopy data from (Pb,Sr)-1212 single crystals.[41]

Substitution by the d block elements

Transition metals have been substituted into the (Pb,M)O layer to completely replace the Cu ions. Beales *et al.*[42] synthesised a series of samples with the nominal stoichiometry $(Pb_{0.5}M_{0.5})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ (M = Cd, Zn, Cu and $0.0 \leqslant x \leqslant 0.5$). They found that pure '1212' samples were formed at $750 \leqslant T/°C \leqslant 900$ when $x = 0.0$ but that only the $(Pb_{0.5}Cd_{0.5})Sr_2YCu_2O_{7-\delta}$ samples were superconducting as synthesised with T_C onset = 60 K. They concluded that the (Pb,Cd)O layers were able to spontaneously create charge carriers in the CuO_5 layers, probably *via* a Pb^{II}–Pb^{IV} redox reaction. $(Pb_{0.5}Cu_{0.5})Sr_2YCu_2O_{7-\delta}$ and $(Pb_{0.5}Zn_{0.5})Sr_2YCu_2O_{7-\delta}$ did not superconduct even with high pressure O_2 anneals, suggesting that interstitial oxygen is not generating charge carriers in these materials. As x was increased, the phase purity of the samples began to fall and Sr_2CuO_3, $SrCuO_2$ and $Cd_{1-x}Ca_xO$ impurity phases began to form. The highest $T_C = 92$ K in (Pb,Cd)-1212 was found for $x = 0.3$.[43] When the stoichiometry of the (Pb,Cd)O layer in $(Pb_{1-y}Cd_y)Sr_2YCu_2O_{7-\delta}$ $(0.25 \leqslant y \leqslant 0.75)$ was varied it was found that the phase purity and T_C onset temperature of the samples began to decrease as y deviated from 0.5, with Sr_2CuO_3, $SrCuO_2$, $Sr_5Pb_3CuO_{12}$ present for $y < 0.5$ and CdO identified for $y > 0.5$. Beales *et al.*[42] found that the change in both the a and c lattice parameters was proportional to the effective ionic radius of M^{n+}, providing strong indirect evidence that transition metal ions directly substitute into the (Pb,M)O layer. Liu *et al.*[44] also synthesised $(Pb_{0.5}Cd_{0.5})Sr_2(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ and found $T_C = 70$ K. X-Ray emission spectrometry determined that the Cd was mainly present in the (Pb,Cd)O layer. Other workers have investigated substitution of Y for lanthanide ions.[45,46] The (Pb,Cd)-1212 phase can be synthesised phase pure for $Y_{1-x}Ln_x$ for $x \leqslant 1$, for all lanthanide ions except for La and Ce. Yu *et al.*[47] investigated the properties of the solid solution series $(Pb_{0.5}Cd_{0.5})(Sr_{2-x}Ba_x)(Y_{0.5}Ca_{0.5})Cu_2O_{7-\delta}$ for $0 \leqslant x \leqslant 0.5$, and from XPS measurements concluded that the apical oxygen on the CuO_5 pyramids plays an important part in the superconductivity in this system. Table 1 summarises the findings of Yu *et al.*[47]

Widder *et al.*[48] reported on the substitution of V^{II} in $(Pb_{1-y}V_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ $(0.1 \leqslant y \leqslant 0.7$ and $0 \leqslant x \leqslant 1)$. They found that none of the samples were superconducting as synthesised, but the composition $(Pb_{0.7}V_{0.3})Sr_2(Y_{0.6}Ca_{0.4})Cu_2O_{7-\delta}$ showed a T_C onset = 40 K when annealed in Ar at 500 °C after synthesis. The behaviour of this compound again

Table 1 Listing of experimentally determined lattice parameters and transition temperatures for some $(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7-\delta}$

formula	y	z	volume/Å^3
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.0	173.5
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.1	173.4
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.2	174.2
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.3	174.7
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.4	175.7
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-z}Ba_z)Cu_2O_{7+\delta}$	0.5	0.5	176.3

is evidence that the smaller metavalent transition metal ions in the (Pb,M)O layer lead to oxygen and/or cation disorder and are deleterious for superconductivity.

At approximately the same time that the mercury cuprates were discovered,[49] (Pb,Hg)-1212 phases were reported. Early reports showed[50] a T_C onset = 90 K for the composition $(Pb_{0.5}Cd_{0.5})Sr_2(Y_{0.7}Ca_{0.3})Cu_2O_{7-\delta}$. Chmaissen and Sheng[51] reported a $T_C = 100$ K for (Pb,Hg)-1212 and suggested that there was evidence for partial cation disorder in the (Pb,Hg)O layer and that, like Tl, Hg can cross-substitute onto the Ca site. The determined stoichiometry for a nominal composition of $(Hg_{0.7}Pb_{0.3})Sr_2(Y_{0.3}Ca_{0.7})Cu_2O_{7-\delta}$ by Chmaissen *et al.* using Rietveld refinement was actually $(Hg_{0.651}Pb_{0.3}Cu_{0.049})Sr_2(Y_{0.264}Ca_{0.616}Hg_{0.12})Cu_2O_{6.84}$. Table 2 summarises the results from a series of transition metal doped (Pb,M)-1212 materials processed under different synthetic conditions.

Substitution by the p block elements (M = Sb, In, Bi and Tl)

(Pb,In)-1212 was first reported by Liu *et al.*[52] who substituted In for Tl in $(Tl_yPb_{1-y})Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$. Bulk superconductivity[53] in this system occurs at 60 K with T_C onset at 80 K for the composition $(Pb_{0.7}In_{0.3})Sr_2(Y_{0.2}Ca_{0.8})Cu_2O_{7-\delta}$. Superconductivity in the (Pb,In)-1212 phase was also confirmed by other authors.[54,55] However, the small size of In^{III} and its mixed valence causes problems with cation disorder and oxygen non-stoichiometry. Liu *et al.*[56] found that Cu can form a solid solution in the rocksalt layer and that (Pb,In)-1212 samples are not phase pure. For a nominal starting composition of $(Pb_{0.55}In_{0.2})Sr_2(Y_{0.5}Ca_{0.5})Cu_{2.25}O_{7-\delta}$ (showing the highest T_C onset), the phase composition by EDAX was found to be $(Pb_{0.69}In_{0.06}Cu_{0.25})Sr_{1.99}(Y_{0.53}Ca_{0.47})Cu_{2.25}O_{7-\delta}$. Evidence of corresponding oxygen non-stoichiometry comes from the enhancement of T_C by Ohta *et al.*[57] who increased T_C onset values to near 90 K by processing a composition of $(Pb_{0.7}In_{0.3})Sr_2(Y_{0.2}Ca_{0.8})Cu_2O_{7-\delta}$ at 1150 °C in 6 GPa of O_2.

(Pb,Sb)-1212 has been reported by Widder *et al.*[58] but these samples were not superconducting and no single phase materials could be made. Given the very small size of Sb^{III} and the impure XRD data, it is not clear if Sb enters this structure at all, especially as (Pb,Cu)-1212 and Pb-2213 impurity phases were also found to be present.

It is possible however to synthesise (Pb,Bi)-1212. Bauernfeind *et al.*[59] for instance, looked at the partial substitution of Bi for Pb in (Pb,Cu)-1212. For a nominal starting stoichiometry of $(Cu_{1-(x+y)}[Pb_xBi_y])Sr_2YCu_2O_{7-\delta}$, near phase pure samples were obtained for compositions where the average valency in the rocksalt layer was +3. They found that for samples containing Pb, only partial Bi substitution was possible in the range $0.25 \leqslant x \leqslant 0.5$ and that all samples were semiconducting despite a range of annealing conditions at different temperatures and atmospheres. This was attributed once again to a random oxygen stoichiometry caused by cation disorder in the rocksalt layer leading to localised trapping of holes. Superconductivity in (Pb,Bi)-1212 has also been reported at 94 K by Bauer *et al.*[60] in $(Pb_{0.45}Bi_{0.4})Sr_{1.9}(Y_{0.7}Ca_{0.4})Cu_{2.25}O_{7-\delta}$ using a melt process route followed by a rapid cool. It is likely that the composition reported by these authors also has a mixed Pb–Cu–Bi rocksalt layer but that the processing conditions has resulted in a more uniform oxygen distribution and that partial substitution of Y by Ca has added additional charge carriers for superconductivity.

The (Pb,Tl)-1212 materials have been extensively investigated and are worthy of a review in themselves. In the context of this article, it is worthwhile to summarise the properties of these materials. Both Pb[61] and Bi[62] can be substituted into the rocksalt layer along with Tl^{III}. The Y site can also be substituted with Ca and other lanthanides.[63,64] The highest T_C value of 108 K in this system is found in $(Pb_{0.5}Tl_{0.5})Sr_2(Y_{0.2}Ca_{0.8})Cu_2O_{7-\delta}$. The substantial difference between the Tl-containing systems and the (Pb,M)O systems is that in the former, complete Ca replacement for Y is possible and Tl-containing materials can be made to undergo metal–semiconductor transitions concomitant with the level of Ca doping.[65]

As a summary of the effects of cation substitution in (Pb,M)-1212 materials Fig. 8 shows the correlation of *a* axis decrease with increasing effective ionic radius of the M^{n+} ion and as an alternative way of representation, Fig. 9 shows the correspond-

Table 2 Listing of experimentally determined lattice parameters and transition temperatures for some $(Pb_{1-y}M_y)Sr_2(Ln_{1-x}Ca_x)Cu_2O_{7-\delta}$ series materials

formula	y	x	T_C/K	volume/Å^3	ref.
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.25–0.75	0.0–0.5	92	173.4	42
$(Pb_{1-y}Zn_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.5	0.0–0.5	50	173.6	42
$(Pb_{1-y}Cu_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.5	0.0–0.5	—	173.6	42
$(Pb_{1-y}Cd_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.5	0.5	70	174.4	44
$(Pb_{1-y}Cd_y)Sr_2(Lu_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.5	0.5	—	173.8	45
$(Pb_{1-y}Cd_y)Sr_2PrCu_2O_{7+\delta}$	0.5	0.0	—	179.6	46
$(Pb_{1-y}Cd_y)Sr_2NdCu_2O_{7+\delta}$	0.5	0.0	—	179.0	46
$(Pb_{1-y}Cd_y)Sr_2SmCu_2O_{7+\delta}$	0.5	0.0	—	177.9	46
$(Pb_{1-y}Cd_y)Sr_2EuCu_2O_{7+\delta}$	0.5	0.0	—	177.1	46
$(Pb_{1-y}Cd_y)Sr_2GdCu_2O_{7+\delta}$	0.5	0.0	—	176.6	46
$(Pb_{1-y}Cd_y)Sr_2TbCu_2O_{7+\delta}$	0.5	0.0	—	174.6	46
$(Pb_{1-y}Cd_y)Sr_2DyCu_2O_{7+\delta}$	0.5	0.0	—	174.8	46
$(Pb_{1-y}Cd_y)Sr_2YCu_2O_{7+\delta}$	0.5	0.0	—	174.7	46
$(Pb_{1-y}Cd_y)Sr_2HoCu_2O_{7+\delta}$	0.5	0.0	—	174.1	46
$(Pb_{1-y}Cd_y)Sr_2ErCu_2O_{7+\delta}$	0.5	0.0	—	173.6	46
$(Pb_{1-y}Cd_y)Sr_2TmCu_2O_{7+\delta}$	0.5	0.0	—	172.9	46
$(Pb_{1-y}Cd_y)Sr_2YbCu_2O_{7+\delta}$	0.5	0.0	—	173.8	46
$(Pb_{1-y}Hg_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.5	0.7	90	174.3	50
$(Pb_{1-y}Hg_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.7	0.7	100	174.1	51
$(Pb_{1-y}V_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7+\delta}$	0.3	0.4	40	172.6	48

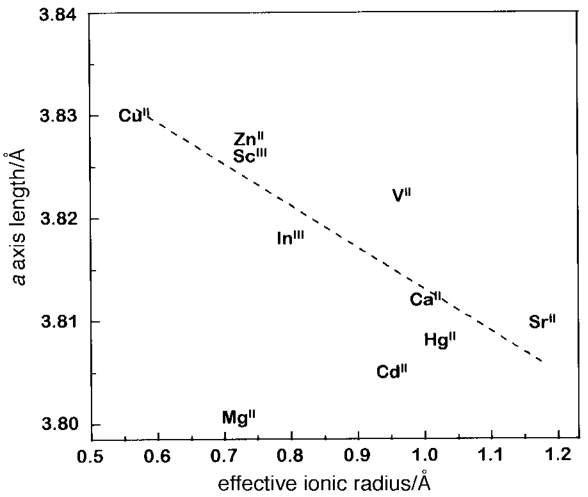

Fig. 8 A plot of the observed shift in the a axis lattice parameter *versus* the effective ionic radius of M^{n+} ions in the substituted (Pb,M)-1212 structure

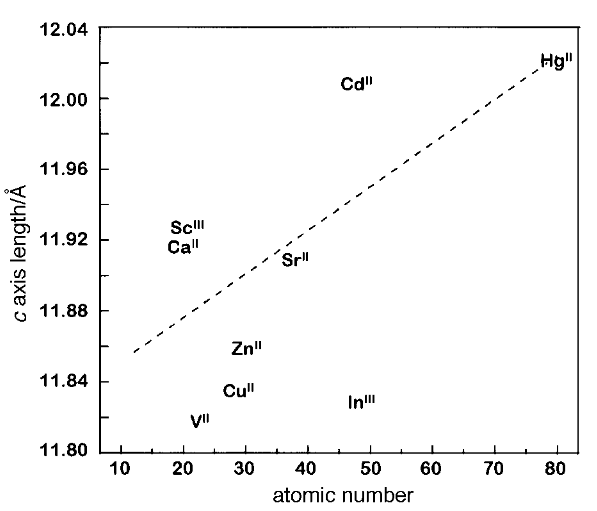

Fig. 9 A plot of the observed shift in the c axis lattice parameter *versus* the atomic number of the M^{n+} ion in substituted (Pb,M)-1212 compounds

ing increase in c axis length with increasing M atomic number. Both these phenomena reflect the move towards a higher oxidation state of the Cu in the '1212' lattice perovskite blocks resulting in an increase in T_C as highlighted in Fig. 7.

Alternatives to Pb: $(A_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$

The $(Bi_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ series: (Bi,M)-1212

(Bi,Cu)-1212 was first reported by Ehmann *et al.*[66] who found that using solid state calcination procedures a higher synthesis temperature [compared to that for (Pb,Cu)-1212] of at least 970 °C was required to form relatively clean XRD patterns. They found that the highest T_C of 68 K occurred in a sample of nominal composition $(Bi_{0.5}Cu_{0.5})Sr_2Y_{0.8}Cu_{2.2}O_{6.95}$ including a post-calcination anneal in flowing O_2 at 500 °C. TEM on the samples[67] did not show the presence of any intergrowths. Since the as-synthesised samples were not superconducting, a non-optimised (Bi,Cu)O layer was implied. Later samples with stoichiometry $(Bi_{0.3}Cu_{0.7})Sr_2YCu_2O_{7.125}$ were prepared by Wang *et al.*[68] and although they were phase pure, the T_C onset value of samples prepared in high pressure O_2 was low at 18 K with a small Meissner fraction. The T_C onset value was found to increase significantly by Zoller and co-workers[69] by using a post-calcination anneal in Ar gas rather than in O_2 and also by partially substituting Pb for Cu to form $(Bi_{0.45}Pb_{0.35})Sr_2(Y_{0.5}Ca_{0.5})Cu_{2.15}O_{7-\delta}$. This material showed a T_C onset of 110 K and Meissner volume fraction = 50%. A neutron diffraction study by Gopalakrishnan *et al.*[70] on $(Bi_{0.5}Cu_{0.5})Sr_2Y_{0.8}Cu_{2.2}O_{7-\delta}$ identified that it was *via* the removal of oxygen that (Bi,Cu)-1212 achieved superconductivity. The (Bi,Cu)O layer did act as an effective charge reservoir (from the relatively elongated Cu—O bond length along the bridging oxygen), but unusually this system suffered from having excess oxygen vacancies in both the rocksalt layer and the perovskite CuO_5 layers. A similar conclusion was arrived at by Kambe *et al.*[71] who measured the hole density in (Bi,Cu)-1212 samples from the Hall effect and concluded that the observed figure of $3.6 \times 10^{20}\ cm^{-3}$ was too low to induce superconductivity.

Beales *et al.*[72] reported on the synthesis and properties of a series of (Bi,M)-1212 materials with M = Cd, Zn and Cu, $0.0 \leqslant x \leqslant 0.5$ and $0.5 \leqslant y \leqslant 0.75$. Ca-free samples ($x = 0$) could only be prepared for samples with $y = 0.7$ suggesting that the optimum composition for phase stability in the rocksalt layer is the $(Bi_{0.3}M_{0.7})$ composition. Virtually phase-pure (Bi,Cd)-1212 phases were formed in air at calcination temperatures $850 \leqslant T/°C \leqslant 975$, (Bi,Zn)-1212 formed at slightly higher calcination temperatures between $900 \leqslant T/°C \leqslant 975$ and the (Bi,Cu)-1212 phase required higher calcination temperatures around 975 °C. The a axis increased from Cd, Zn to Cu as 3.802, 3.814 and 3.814 Å and the c axis decreased from Cd, Zn to Cu as 11.96, 11.75 and 11.72 Å. No superconductivity was observed in (Bi,M)-1212 samples as synthesised, but (Bi,Cd)-1212 annealed in high pressure O_2 showed a T_C onset of 40 K. No (Bi,M)-1212 samples with Y substituted by Ca ($x > 0$) could be synthesised by Beales *et al.* (Bi,Cd)-1212 was also reported by Tang *et al.*[73] and Qian *et al.*[74] The former workers only found semiconducting behaviour, while the latter reported a T_C of 26 K after processing in 10 MPa of O_2 at 800 °C. Very few transport measurements have been performed on the (Bi,Cd)-1212 materials. Beales and Parberry[75] performed thermoelectric power measurements on $(Bi_{0.33}Cd_{0.67})Sr_2YCu_2O_{7-\delta}$ yielding a value of $S_{290\ K} = 50\ \mu V\ K^{-1}$ and a hole concentration = 0.08 per planar Cu atom. This value of p suggests a theoretical maximum $T_C = 85$ K for the (Bi,Cd)-1212 system. As even high pressure O_2 annealing only obtains a maximum T_C of 40 K, it implies that $(Bi_{0.33}Cd_{0.67})Sr_2YCu_2O_{7-\delta}$ is highly intrinsically underdoped.

Other (Bi,M)-1212 phases that have been reported are $(Bi_{0.3}Hg_{0.7})Sr_2(Pr_xCa_{1-x})Cu_2O_{7-\delta}$ [(Bi,Hg)-1212] for $0.25 \leqslant x \leqslant 1.0$ which showed the highest T_C onset at 91 K,[76] the highly non-stoichiometric (Bi,In)-1212 phase[77] $(Bi_{0.21}In_{0.33}Pb_{0.25})Sr_2(Gd_{0.89}Ca_{0.11})Cu_{2.21}O_{7-\delta}$ with T_C onset at 70 K and the (Bi,Mo)-1212 phase[78] in which the Cu and Mo are in solid solution in the rocksalt layer. The highest T_C in the series $(Bi_{1-x}Mo_x)_{0.33}Cu_{0.67})Sr_2YCu_2O_{7-\delta}$ $(0.0 \leqslant x \leqslant 1.0)$ was 37 K. Table 3 summarises the results obtained from several authors on the crystal parameters and properties of the (Bi,M)-1212 series.

The $(Ce_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7\pm\delta}$ series: (Ce,M)-1212

Phases with this composition were first synthesised by Beales *et al.*[72] for M = Cd, Zn and Cu with ($0.0 \leqslant x \leqslant 0.5$ and $0 \leqslant y \leqslant 0.5$). For Ca-free samples ($x = 0$), virtually phase-pure (Ce,Cd)-1212 was formed in air between $850 \leqslant T/°C \leqslant 975$. (Ce,Zn)-1212 also formed at slightly higher calcination temperatures between $900 \leqslant T/°C \leqslant 975$ and (Ce,Cu)-1212 phase required higher calcination temperatures around 975 °C to form a reasonably phase pure sample. Phase purity decreased as y deviated from 0.5 suggesting that the $(Ce_{0.5}M_{0.5})$ composition was the optimum in the rocksalt layer for phase stability. The a axis increased from Cd, Zn to Cu as 3.808, 3.824 and 3.823 Å and the c axis decreased from Cd, Zn to Cu as 12.10,

Table 3 Listing of experimentally determined lattice parameters and transition temperatures for some of the $(Bi_{1-y}M_y)Sr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ series materials

formula	a/Å	c/Å	T_C/K	ref.
$(Bi_{0.5}Cu_{0.5})Sr_2Y_{0.8}Cu_{2.2}O_{7+\delta}$	3.815	11.73	68	66
$(Bi_{0.3}Cu_{0.7})Sr_2YCu_2O_{7+\delta}$	3.816	11.71	18	68
$(Bi_{0.45}Pb_{0.35})Sr_2(Y_{0.5}Ca_{0.5})Cu_{2.15}O_{7+\delta}$	3.819	11.81	102	69
$(Bi_{0.33}Cd_{0.67})Sr_2YCu_2O_{7+\delta}$	3.802	11.96	40	72
$(Bi_{0.33}Zn_{0.67})Sr_2YCu_2O_{7+\delta}$	3.814	11.75	—	72
$(Bi_{0.33}Cu_{0.67})Sr_2YCu_2O_{7+\delta}$	3.814	11.72	—	72
$(Bi_{0.5}Cd_{0.5})Sr_2YCu_2O_{7+\delta}$	3.812	11.91	—	73
$(Bi_{0.5}Hg_{0.5})Sr_2(Pr_{0.5}Ca_{0.5})Cu_2O_{7+\delta}$	3.863	12.09	91	76
$(Bi_{0.5}In_{0.5})Sr_2YCu_2O_{7+\delta}$	3.838	11.84	70	77

11.92 and 11.88 Å. Magnetisation measurements showed that none of the (Ce,M)-1212 samples were found to exhibit superconductivity as synthesised, but after annealing in high pressure O_2 for 16 h at 900 °C, a weak superconducting transition with a T_C onset = 30 K was observed in (Ce,Cd)-1212. For samples containing Ca, the phase purity of (Ce,Cd)-1212 samples decreased with increasing x and the impurity phases Sr_2CuO_3, $SrCuO_2$ and $Cd_{1-x}Ca_xO$ appeared in the XRD data. Magnetisation measurements showed none of these samples were superconducting, even after annealing in high pressure O_2.[79]

Other (A,M)-1212 series

Tl has long been a favourite ion to substitute for Pb in the (Pb,M)O layer, and the M ion in (Tl,M)-1212 materials has been subjected to substitution from all over the Periodic Table, with often haphazard logic. Liu *et al.*[80] substituted a number of group 4 and 5 elements into the Tl layer of $TlSr_2(Y_{1-x}Ca_x)Cu_2O_{7-\delta}$ and obtained a range of T_C onset values from 40 to 100 K. Ce[81] (T_C onset values around 66 K), Mo[82,83] (T_C onset = 70–100 K), Cr,[83,84] Bi[85] and Hg[86] (T_C onset = 92 K) have all similarly been substituted into the Tl layer. However, the tendency of Tl to cross-substitute onto the Y site and also the tendency of Ca to cross-substitute onto the Tl site means that the exact relationship between (Tl,M)O and the optimisation of T_C in these materials is nearly always impossible to determine, as extra doping effects will certainly be present from the cation disorder. The overall tendency of these materials is to behave similar to the parent Tl-1212 phase.

The most common other substituted element for Pb forming a rocksalt layer (aside from thallium) is mercury. (Hg,M)-1212 structures have been reported for M = Nb and Ta[87] (T_C onset = 80 K), Pr,[88] Re,[89] Cr,[90] Ga[91] (T_C onset = 80 K) and Mo[92] (T_C onset = 98 K). However, indications are that these materials owe little to the unique nature of the (Hg,M)O layer and act more like the parent HgO-layered phases (of which these can be considered as sub-sections). The T_C value in (Hg,M)-1212 compounds seems dependent more on the processing method to yield T_C values similar to the corresponding Hg-1212 phase rather than any particular unique chemical properties of the (Hg,M)O layer.

Other layered cuprate materials containing (Pb,M) layers

The $(Pb_{1-y}M_x)(La_{2-x}Sr_x)CuO_{5-\delta}$ series: (Pb,M)-1201

It was Mochiku *et al.* who first reported the 1201 structure[93] in 1989 for $Tl(La,Sr)_2CuO_{5-\delta}$ and noted that for a series of compositions, the highest T_C onset observed was close to 40 K. Shortly afterwards, a (Pb,Cu)O rocksalt layer in place of the Tl layer was reported by Adachi *et al.*[94] in (Pb,Cu)-1201 for a nominal composition of $(Pb_{0.6}Cu_{0..5})(La,Sr)CuO_{5-\delta}$, with an observed T_C onset near to 28 K. This material was easily synthesised using the conventional solid state method of mixing stoichiometric quantities of oxides and/or carbonates and calcining at temperatures near to 900 °C for up to 90 h. Martin *et al.*[95] reported the synthesis and structure of $(Pb_{0.5}Tl_{0.5})Sr_2CuO_{5-\delta}$ but did not detect superconductivity in as-synthesised or O_2 annealed samples. However superconductivity at T_C (onset) = 40 K, with approx. 2% Meissner fraction, was reported by Bourgault *et al.*[96] in the structurally and chemically related $(Tl_{0.8}Pr_{0.2})(Sr_{1.6}Pr_{0.4})CuO_{5-\delta}$.

The (Pb,M)-1201 structure is schematically shown in Fig. 10. The Cu occupies a typical perovskite site in an octahedral oxygen geometry, with the larger Sr and La ions located at the apical oxygen ions of the CuO_6 octahedra. In (Pb,M)-1201, this is the equivalent of the stable perovskite $YSrCu_2O_6$ unit found in (Pb,M)-1212. As in the (Pb,M)-1212 structure, the rocksalt (Pb,Cu)O units simply sit on the outside of this base unit, attached at the apical oxygen of the CuO_6 octahedra.

The phase stability of the (Pb,Cu)-1201 phase has been determined[97,98] for the series $(Pb_{0.5}Cu_{0.5})(La_{1-x}Sr_{1+x})CuO_{5-\delta}$ $(0.0 \leqslant x \leqslant 0.1)$. The (Pb,Cu)-1201 phase has many similarities to the corresponding (Pb,Cu)-1212 phase. It is difficult to prepare phase pure and Beales *et al.*[42] have pointed out the presence of impurity phases such as $Sr_5Pb_3CuO_{12}$ in the XRD patterns during synthesis. Also the physical properties are strongly dependent on the processing: the T_C onset value of (Pb,Cu)-1201 can be increased to 36 K[97] by quenching from 900 °C or by annealing at 500 °C for 24 h in N_2.[99] In addition, a post synthesis high pressure anneal at 600 °C in 50 MPa O_2, was shown to both decrease T_C and increase the normal state resistivity. This suggests that the material is either in, or close to, the overdoped state as synthesised. Very little work has been done on determining the oxygen stoichiometry of the (Pb,Cu)-1201 phase, compared to that carried out on the (Pb,Cu)-1212 phase. Recent results determining the oxidation state of the Pb and Cu in the (Pb,Cu)O layer by Shida *et al.*[100] in $(Pb_{0.5}Cu_{0.5})(Sr_{2-x}La_x)CuO_{5-\delta}$ $(1.0 \leqslant x \leqslant 1.2)$ and $(Pb_{0.6}Cu_{0.4})(Sr_{2-x}La_x)CuO_{5-\delta}$ $(0.9 \leqslant x \leqslant 1.2)$ prepared in flowing O_2 at 1010 °C, show that the T_C onset value is related to δ. As the structure loses oxygen, the T_C onset value rises. However, the T_C onset value was found to be insensitive to both substitution of Sr^{II} by La^{III} and to increases in Pb^{IV}

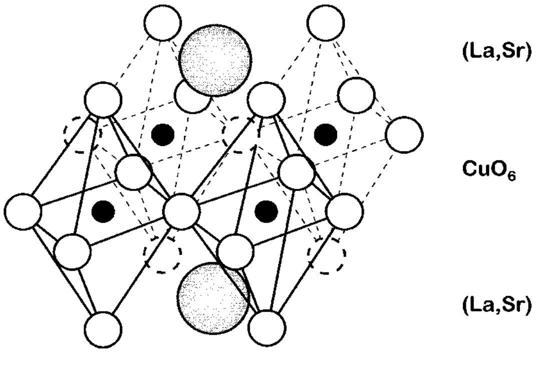

Fig. 10 Idealised crystal structure of the $(Pb_{1-y}M_x)(La_{2-x}Sr_x)CuO_{5-\delta}$ phase

concentration, suggesting that interstitial oxygen is mainly responsible for superconductivity in this phase. Shida *et al.* believe that the Cu ions in the rocksalt layer charge compensate for the electrochemical changes caused by the chemical substitution or changes in δ.

Like for the corresponding '1212' structure, the '1201' phase preferentially substitutes on the rocksalt layer rather than into the thermodynamically stable perovskite layer. Beales *et al.*[42] reported the formation of the (Pb,Cd)-1201 and (Pb,Zn)-1201 phases as well as (Pb,Cu)-1212 for $(Pb_{0.5}M_{0.5})(La_{2-x}Sr_x)CuO_{5-\delta}$ ($1.0 \leqslant x \leqslant 1.25$). Between $750 \leqslant T/°C \leqslant 900$, virtually phase-pure samples of (Pb,Cd)-1201 were formed for all values of x. (Pb,Zn)-1201 also formed in this temperature range but only for compositions with $x \approx 1$. (Pb,Cu)-1201 needed a higher calcination range of $850 \leqslant T/°C \leqslant 900$ to form a reasonably phase-pure material but again, only for compositions with $x \approx 1$. The elemental substitution into the rocksalt layer was reflected in the decreasing a axis lengths of 3.784, 3.776 and 3.757 Å and increasing c axis lengths of 8.627, 8.659 and 8.891 Å for M = Cu, Zn and Cd respectively. Beales *et al.* found that only the (Pb,Cd)-1201 phase could be made phase pure, with the (Pb,Zn)-1201 and (Pb,Cu)-1201 phases forming impurities of $Sr_5Pb_3(Cu,Zn)O_{12}$ and $Sr_5Pb_3CuO_{12}$ respectively. (Pb,Cd)-1201 had a T_C onset = 40 K for the $x = 1$ composition, which deteriorated with decreasing x. The corresponding (Pb,Cu)-1201 and (Pb,Zn)-1201 phases with $x = 1$ were found to have T_C onsets of 28 K and 15 K, respectively. These results confirm the beneficial effect of Cd in the rocksalt layer as was also found in the '1212' materials and suggests for the 1201 phase, the $(Pb_{0.5}Cu_{0.5})$ composition in the rocksalt layer is near optimised for superconductivity in the nominally undoped compositions ($x = 1.0$).

Several other (Pb,M)-1201 structures have been reported in the literature, notably $(Pb_{0.5}Tl_{0.5})(Sr_{2-x}La_x)CuO_{5-\delta}$ ($T_C = 40$ K[101]), $(Pb_{0.5}Hg_{0.5})(Sr_{2-x}La_x)CuO_{5-\delta}$ ($T_C = 32$ K[102]), $(Hg_{0.5}Bi_{0.5})(Sr_{2-x}La_x)CuO_{5-\delta}$,[103] $(Bi_{0.2}Hg_{0.8})Ba_2CuO_{5-\delta}$ (T_C onset = 75 K[104]), and finally $(Hg_{0.7}V_{0.3})(Sr_{2-x}La_x)CuO_{5-\delta}$; ($T_C = 50$ K[105]). Very little physical characterisation has been performed on these interesting materials. Recently, Beales *et al.* reported on the magnetisation data for $(Pb_{0.5}Cd_{0.5})(La_{2-x}Sr_x)CuO_{5-\delta}$ ($x = 1.0 \pm 0.2$).[106] The strongest Meissner signal occurred at the $x = 1.0$ composition, with an intragrain J_C calculated to be in the order of 1×10^9 A m^{-2} at 4 K. The London penetration depth, λ_L, was found to be the smallest for the $x = 1.0$ composition with $\lambda_L = 3.8$ µm and 4.4 µm for H $\perp$ and $\parallel$ to the c axes, respectively. The anisotropy ratio (λ_{ab}/λ_c) for all samples was found to be close to 1 reflecting a more 3D nature than in the '1212' phase. Resistivity and thermopower power measurements confirmed that the '1201' phase is intrinsically highly overdoped with high hole concentrations $\geqslant 0.2$ as synthesised and is close to the theoretical maximum T_C value.

$(Pb_{1-z}M_z)(AE_{1-x}Ln'_x)_2(Ln''_{1-y}Ln'_y)_2Cu_2O_{9-\delta}$: (Pb,M)-1222

Higher order members incorporating Pb-containing rocksalt layers have been synthesised. The (Pb,M)-1222 lattice contains bridging layers of fluorite-structure lanthanide ions of similar configuration to those found in the T′ [$(Nd,Ce)CuO_4$] structure.[107] The (Pb,M)-1222 structure can be mentally constructed by splitting the (Pb,M)-1212 structure shown in Fig. 5 in half at the Y site, and then inserting a bridging fluorite layer as shown schematically in Fig. 11.

One of the first (Pb,M)-1222 phases to be reported was $(Pb,Cu)(Sr,Pr)_2Pr_2Cu_2O_{9-\delta}$ or (Pb,Cu)-1222 by Adachi *et al.*[108] (this phase is isostructural with $TlSr_2(Nd,Ce)_2Cu_2O_{9-\delta}$).[109] As synthesised, $(Pb,Cu)(Sr,Pr)_2Pr_2Cu_2O_{9-\delta}$ is non-superconducting. The idealised bridging fluorite layer found in (Pb,Cu)-1222 structure is shown in Fig. 12. The Sr site in (Pb,M)-1212 connects to the first fluorite layer (designated as an M′ ion site) and can contain a mixture of either lanthanide or Sr/Ln ions. This sits astride a central fluorite layer of M″ lanthanide ions which also contains CuO_5 square-basal pyramids and rocksalt (Pb,Cu)O monolayer. Maeda *et al.*[110] found that elemental substitution on the Ln sites could induce superconductivity in (Pb,Cu)-1222 with a T_C onset of 25 K for the composition $(Pb_{0.5}Cu_{0.5})(Sr_{0.875}Eu_{0.125})_2(Eu_{0.75}Ce_{0.25})_2Cu_2O_{9-\delta}$ annealed in O_2 at 400 °C for 10 h. Rietveld refinement of the XRD data by Maeda *et al.*[111] found that the M′ and the M″ sites are crystallographically distinct with the M′ site = (Sr,Eu) and the M″ site = (Eu,Ce). The Eu could be replaced by either a single lanthanide *e.g.* Pr, Sm, Gd, Dy, Ho and Y or by a mixture of lanthanides *e.g.* (La,Eu), (Nd,Eu), (Nd,Dy), (Nd,Y), (Nd,Eu), *etc.* When a mixture of lanthanides was used, it was found that the larger ions (La, Sm and Nd) preferentially substituted onto the M′ site and the smaller lanthanides onto the M″ site. Superconductivity could only be induced in samples in which the average cation radius on the M″ site was close to 0.104 nm. Using the above, Maeda *et al.* were able to increase T_C onset to 32 K. Further

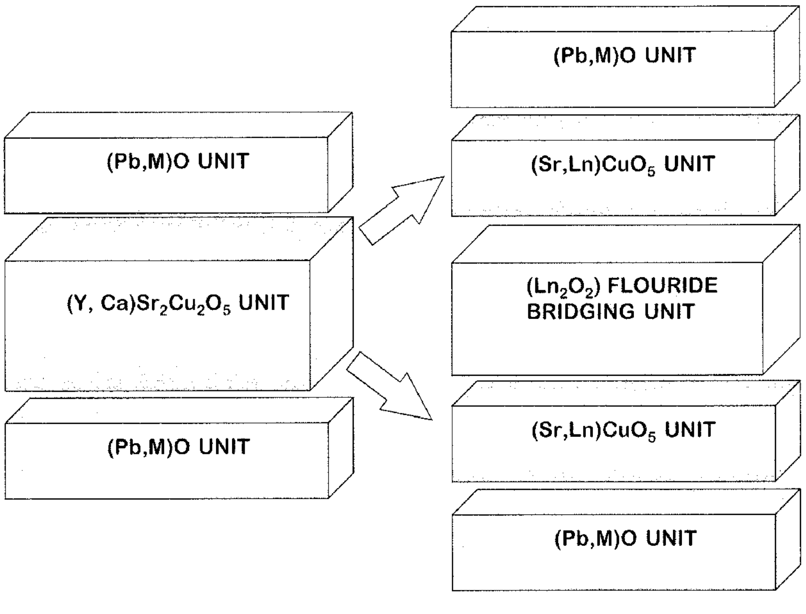

Fig. 11 Pictorial representation of the building block structure of the '1222' phase by incorporating a fluorite block into the '1212' structure

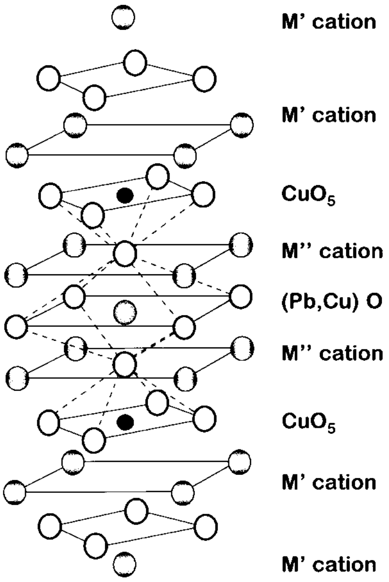

Fig. 12 Idealised crystal structure of the fluorite block found in $(Pb_{1-z}M_z)(AE_{1-x}Ln'_x)_2(Ln''_{1-y}Ln'_y)_2Cu_2O_{9-\delta}$

Rietveld refinement of the X-ray diffraction data by Maeda *et al.*[112] of $(Pb_{0.5}Cu_{0.5})(Sr_{0.875}Nd_{0.125})_2(Ho_{0.69}Ce_{0.31})_2Cu_2O_{9-\delta}$ revealed that the (Pb,Cu)O layer was highly disordered [similar to the (Pb,Cu)-1212 materials] with 13% oxygen deficiency at the apical oxygen site connecting the outer rocksalt (Pb,Cu)O layer and the CuO_5 square basal pyramids in the (Pb,M)-1212 derived unit. The origin of this disorder was attributed to the lattice mismatch between the (Pb,Cu)O and CuO_5 layers and that this in turn caused hole localisation and a corresponding low T_C value. Saskura *et al.*[113] synthesised $(Pb_{0.5}Cu_{0.5})(Sr_{1-x}Ln_x)_2(Sr_{1-y}La_y)_2Cu_2O_{9-\delta}$ (Ln = Gd, Dy, Ho, Er; $x=$ 0.975, 0.9, 0.875, 0.875 and $y=0.3$, 0.45, 0.325, 0.3, respectively) which showed similar results to those obtained by Maeda *et al.* on materials that contained tetravalent ions. Only the Gd-containing composition was superconducting showing a weak magnetic T_C onset at 20 K.

Beales *et al.*[42] synthesised a series of samples with the nominal stoichiometry $(Pb_{0.5}M_{0.5})(Nd_{1+x}Ce_{1-x})Cu_2O_{9-\delta}$ (M = Cd, Zn, Cu and $0.0 \leqslant x \leqslant 0.5$). They found that moderately phase pure samples of (Pb,Cd)-1222, (Pb,Zn)-1222 and (Pb,Cu)-1222 phases were formed at 750 °C for $x \approx 0.3$. The samples were indexed with a tetragonal structure, space group *I*4/*mmm*. The lattice parameters were observed to change with substitution into the rocksalt layer, the *a* axis increasing as 3.856, 3.874 and 3.880 Å and the *c* axis shortening from 29.7, 29.4 and 29.4 Å for M = Cd, Zn and Cu, respectively. Compared with their work on corresponding 1201 and 1212 phases, Beales *et al.* found that the 1222 phase was more difficult to form and that calcination at higher temperatures induced phase decomposition inducing disorder along the *c* axis from the presence of intergrowths of thicker fluorite-type blocks of (Nd,Ce) ions and (Pb,M)-1212 layers. None of the (Pb,M)-1222 phases synthesised by Beales *et al.* were found to be superconducting. A similar semiconducting (Pb,Cd)-1222 structure was reported by Min *et al.*[114] with a composition of $(Pb_{0.5}Cd_{0.5})(Sr_{0.9}Eu_{0.1})_2(Eu_{0.7}Ce_{0.3})_2Cu_2O_{9-\delta}$ who found by Rietveld refinement that the (Pb,Cd)O layers are displaced from their ideal crystallographic sites.

It is possible to substitute for Pb in the '1222' structure and semiconducting compositions of (M,Cu)-1222 substituted materials have been reported by Wada and colleagues[115,116] for $(Fe_{0.75}Cu_{0.25})Sr_2(Y_{0..5}Ce_{0.5})_2Cu_2O_{9-\delta}$, and for $(Ce_{1-z}Cd_z)$-$Sr_2(Ln_{2-x-y}Ce_xSr_z)Cu_2O_{9-\delta}$ (Ln = Nd, Y; $0.797 \leqslant z \leqslant 0.844$; $0.676 \leqslant x \leqslant 0.743$ and $0.076 \leqslant y \leqslant 0.101$) by Shizhong *et al.*[117] The low T_C onset values in the (Pb,Cu)-1222 series and lack of superconductivity in the (Pb,M)-1222/(M,Cu)-1222 series can be explained as being due to a combination of, or all of, the following: random cationic site substitution; oxygen disorder in the (Pb,Cu)O layers and non-stoichiometric intergrowths. In addition, Beales *et al.*[42] pointed out that the fluorite layer favours n-type superconductivity while the (Pb,M)O layer favours p-type superconductivity which can lead to an electrochemical mismatch. However, one can point to potentially higher T_C values in this system. The oxygen stoichiometry may well be optimised by processing in high pressure O_2 and the work of Beales *et al.*[42] showed that the *a* axis length in (Pb,Cd)-1222 material was the shortest found in the (Pb,M)-1222 series, approaching that found in (Pb,Cu)-1212. This suggests that the (Pb,Cd) rocksalt mixture combined with annealing in high pressure O_2 could provide a Cu valence nearer to that required for superconductivity and push T_C onset temperatures to much higher values in the '1222' materials.

Other layered Pb-containing materials

It is possible to incorporate an additional fluorite layer into the (Pb,Cu)-1222 materials, acting as another bridging unit to that described in the previous section to form the (Pb,Cu)-1232 phase. Fig. 13 shows the idealised structure of the fluorite block in (Pb,Cu)-1232 materials. Wada *et al.*[118] managed to synthesise $(Pb,Cu)Sr_2(Ln,Ce)_3Cu_2O_{11-\delta}$ but this material was not found to be superconducting. Rietveld analysis of the neutron diffraction data[119] of a (Pb,Cu)-1232 material of composition $(Pb_{0.5}Cu_{0.5})Sr_2(Ho_{0.33}Ce_{0.67})_3Cu_2O_{11-\delta}$ again showed a highly disordered (Pb,Cu)O monolayer similar to those seen in (Pb,Cu)-1212 and (Pb,Cu)-1222. It is probable that this is the prime cause of the lack of superconductivity in these materials (a net Cu oxidation state of +2.12 in the CuO_5 planes is calculated if one assumes cationic valencies of Pb^{IV}, Sr^{II}, Ho^{III} and Ce^{IV} in the above composition).

The Pb-0201 structure, formed by doping lead into the non-superconductor $La_2CuO_{4-\delta}$ to form $(La_{2-x}Pb_x)CuO_{4-\delta}$, was synthesised by Maignan *et al.*[120] for $0.5 \leqslant x \leqslant 0.5$. This had a K_2NiF_4-related structure with lattice parameters of $a=5.3481(4)$, $b=5.3367(4)$ and $c=13.2186(6)$ Å. A T_C (onset) close to 15 K was achieved with a Meissner fraction of *ca.* 25% after a post-synthesis annealing at 450 °C in high pressure O_2. Similarly, the Pb-0212 structure, $Pb_{0.5}La_{1.4}Sr_{1.1}Cu_2O_{6-\delta}$, has been reported by Seling *et al.*[121] with a maximum T_C onset of 75 K. Fig. 14 shows an idealised crystal structure for the Pb-0212 phase. This material contains eight co-ordinate Sr atoms sandwiched between the CuO_5 planar units. These are then surrounded by the La ions and the Pb-0212 structure therefore contains no rocksalt layers. Doping the La sites with Pb induces superconductivity in this system *via* a Pb^{IV}/Pb^{II} charge transfer mechanism in contrast to the $La_2(Sr,Ca)Cu_2O_6$ system which requires processing under high pressure O_2 to induce superconductivity.[122]

Mateev *et al.*[123] managed to synthesise a (Ge,Cu)-1223 phase

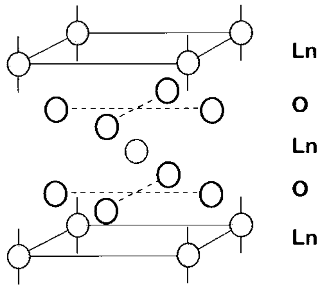

Fig. 13 Idealised crystal structure of the fluorite block found in $(Pb,Cu)Sr_2(Ln,Ce)_3Cu_2O_{11-\delta}$

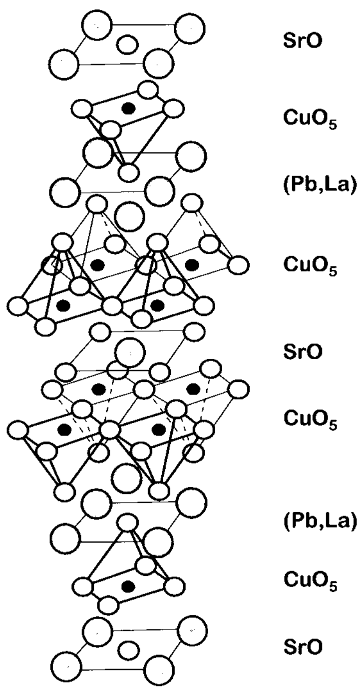

Fig. 14 The idealised $Pb_{0.5}La_{1.4}Sr_{1.1}Cu_2O_{6-\delta}$, Pb-0212 crystal structure

using powders encased in Au capsules synthesised in a belt apparatus at 6 GPa and 1300 °C. The composition was found to be slightly Cu-rich at $(Ge_{0.4}Cu_{0.6})Sr_2(Y_xCa_{1-x})Cu_3O_{9.3}$ $(0.1 \leqslant x \leqslant 0.3)$ and showed a T_C onset = 90 K. The 1223 phase is similar in structure to the corresponding 1212 phase but has an extra $(Y_xCa_{1-x})CuO_2$ plane in between the CuO_5 layers.

$Pb_2Sr_2(Y_{1-x}Ca_x)Cu_3O_{8-\delta}$: the Pb-2213 phase

Superconductivity in $Pb_2Sr_2(Y_{1-x}Ca_x)Cu_3O_{8\pm\delta}$ was first reported in 1988 by Cava *et al.*[124] and shortly after by other groups.[125,126] This material is best treated as a sub-set of the layered Pb cuprates. It has the same perovskite block seen in the '1212' phase but instead of a rocksalt bridging unit, a $(Pb_2Cu)O$ unit, shown in Fig. 15 is present.

The preparation of Pb-2213 using conventional powder metallurgical routes requires rather more care than that needed for preparing Y-123. This requires a multi-step process involving mixed oxide precursors. Cava *et al.*[124] found that the best method was to mix pellets of $YSr_2Cu_3O_7$ and calcine at temperatures between 920 and 980 °C for 16 h (with a single intermediate grinding stage) and then mix in PbO. The new powder mix was then re-calcined at temperatures between 860 and 925 °C for 16 h in a reducing atmosphere of 1% O_2 in N_2. Ca doping to synthesis $Pb_2Sr_2(Y_{1-x}Ca_x)Cu_3O_{8\pm\delta}$ can be achieved by using an appropriate $Y_{1-x}Ca_xSr_2Cu_3O_7$ precursor.[127] It is also possible to synthesis Pb-2213 directly from a stoichiometric mixture of oxides and carbonates, but this requires some care to obtain phase-pure material. Kadowski *et al.*[128] subjected the starting mixture to repeated firing and grinding at temperatures between 800 and 850 °C to prevent Pb loss. This mixture was then pelletised and heated between 900 and 930 °C for 1 to 2 h before being quenched. The pellet was made superconducting by annealing in N_2 at 800 °C for up to 5 h, cooled to 700 °C, and held at that temperature for about a day.

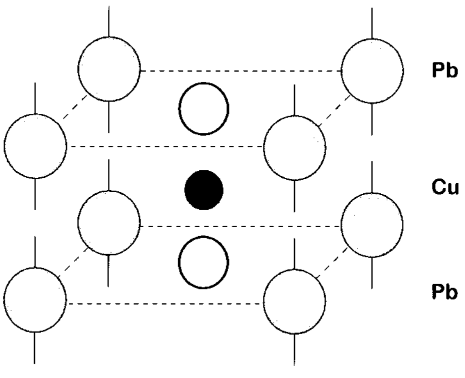

Fig. 15 Illustration of the $(Pb_2Cu)O$ block sited at the apical oxygen of the $YSr_2Cu_2O_6$ perovskite block in the '2213' structure

Pb-2213 is thermally unstable. At temperatures above 850 °C serious Pb volatilisation occurs (if the synthesis temperature is too low than scavenging phases such as $SrPbO_3$ and unreacted binary oxides occur in the product). Partial decomposition of Pb-2213 to $YSr_2(Pb,Cu)_3O_{7-\delta}$ and other complex oxides occurs at temperatures above 900 °C and the material melts just above 1000 °C: the melt can be cooled to form a mixed reaction product of Pb-2213 crystalline plates and complex mixed oxides.

Plate-like Pb-2213 crystals measuring up to $2 \times 2 \times 0.1$ mm^3 have been made using a PbO/PbF_2 flux.[129] The same group have also tried fluxes composed of CuO, PbO and PbF_2 as well as pure PbO and PbF_2. The flux solvent was mixed with Pb-2213 and heated in an Au crucible to 980 °C and held there for 20 to 50 h. The crucible was then cooled at 1–5 K h^{-1} to temperatures between 850 and 600 °C and furnace cooled in 1 to 2% O_2 in N_2 gas. Other groups have used Pb-2213 precursor mixtures rich in CuO, SrO and PbO, cooling the melt from 1025 to 1050 °C in corundum crucibles held in a nitrogen atmosphere. Superconducting crystals of $1 \times 1 \times 0.5$ mm^3 were reported using this synthesis route.[130]

A more novel route to synthesise $Pb_2Sr_2(Y_{1-x}Ca_x)Cu_3O_{8\pm\delta}$ films using laser ablation has also been used. Naqvi *et al.*[131] achieved this successfully on MgO substrates using stoichiometric targets without *ex situ* annealing, provided that a reducing atmosphere in the growth chamber was present. They also grew multilayered $Sr_2(Y_{0.5}Ca_{0.5})Cu_3O_\delta$: PbO structures by ablation using a Nd : YAG laser and then annealed these *ex situ* at 864 °C in air for 3 h. Four point resistivity measurements showed the samples to have a T_C onset of 83 K. Hughes *et al.*[132] also attempted to grow Pb-2213 films using laser ablation, but using a heavily Pb-compensated target. They reported preparing predominantly '1212' films grown *in situ* on (100) $LaAlO_3$ substrates with a T_C onset temperature of 90 K.

Pb-2213 can undergo substitution on the Pb site by Bi,[133] on the Sr site by Ba[134,135] and extensive substitution by lanthanides on the Y site.[136–139] However, the material still suffers from extensive charge localisation causing detrimental effects to any gains from cation doping[140] and structural similarities to the '1212' and '123' lattices often lead to intergrowths and stacking faults, especially in bulk prepared samples.[141] The Pb-2213 phase has been the subject of several reviews, see for example Naqvi *et al.*[142]

Conclusions

The layered curates incorporating a (Pb,M)O rocksalt layer, or its analogues, are a remarkably versatile chemical system to study the effects of chemical substitution on superconductivity in oxides. Despite having large numbers of constituent cations, these systems are thermodynamically stable, and more often than not form the major phase during conventional solid state calcination synthesis. This method of fabricating such complex systems does have its drawbacks, the main ones being non-stoichiometric cationic site substitution (outside the stable perovskite blocks), anionic oxygen disordering, intergrowths (for the higher order members) and the tendency to form scavenging impurity phases usually composed of simpler ternary and binary oxides of the cations.

These can be overcome by using a more sophisticated fabrication technology such as laser ablation or other thin film growth techniques which should lead to pure single crystal quality samples being synthesised. These synthetic methods have not been widely employed at all at present on the layered Pb cuprates with the exception of a few groups who have produced laser ablated films of Pb-2213 (and managed to produce some (Pb,Cu)-1212 impurities as well). Since the potential application of these materials is clearly in the electronics industry, this fabrication route is compatible with that employed in present day semiconductor manufacturing. High temperature superconducting electronics is in its infancy and we have only scratched the surface. The lesson from semiconductors is that as devices become smaller, materials issues come to the fore. Layered cuprates may well prove useful in the future as alternatives to Y-123 and may have more versatility in future devices. The non-superconducting forms may even provide ready-made lattice-matched substrates. The crystal chemistry still needs much investigation before economic exploitation can fully arise. Unfortunately in today's commercial climate, this is unlikely to be undertaken by industry. However, this area can and should be researched by academia. The field is still wide open and the potential rewards very great indeed.

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