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Crystallochemical characterization of $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ type solid solutions

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Abstract

A series of solid solutions of nominal composition $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ ($0 \leqslant x \leqslant 4$) have been prepared and characterized by X-ray diffraction, copper valency and density measurements. The series is characteristic of the 2212 structure type with a domain of homogeneity which at 860 °C only slightly exceeds $x_{Ca}=3$. Within the calcium concentration interval studied, the lattice parameters (mainly the c parameter), average valency of copper and sample density all exhibit a smooth decrease *vs.* x_{Ca}. The decrease in sample density is not as large as expected for the $(Sr_{1-x}Ca_x)$-type substitution performed. The series can be described analytically via a structural model in which the oxygen sublattice ($32+\delta$ atoms) remains practically intact throughout the range of homogeneity but the metallic sublattice exhibits an x_{Ca}-dependent deficiency. The total number of vacancies present in the 28-atom metallic sublattice decreases *vs.* x_{Ca} and at the terminal composition of the series ($x_{Ca}=3$) it becomes zero. The observed effect of a steady densification of the Me sublattice explains satisfactorily why even in the case of isoelectronic cation substitution a substantial decrease in the average valency of copper can be observed. The paper also contains some important conclusions concerning local charge imbalances existing in Bi-based cuprates and their role as the main source of the overall power factor for oxidation higher than 2+ observed in these phases irrespective of whether they exhibit superconducting or non-superconducting character.

1. Introduction

One of the most prominent results obtained in early studies of the 123-type cuprates, deduced from band structure calculations [1], concerns the existence of a strong hybridization between the Cu 3d and O 2p levels taking place in the CuO_2 planes. At present this feature seems to be common to all the high T_c cuprates, including those based on Bi and Tl. Moreover, in the Bi-based cuprates a strong hybridization between the Bi 6p and O 2p levels is also believed to exist within the Bi–O double layers.

The occurrence of superconductivity in all these cuprates is not connected solely with presence of CuO_2 planes. There are at least two other factors related to this property. The first of these is the valency of copper within the CuO_2 planes. Numerous experiments have shown that its average value is always higher than 2+, with an optimum level ensuring maximum T_c specific to each family of the high T_c cuprates. The second factor concerns the specific arrangement of other structural components inserted between the planes. The arrangement is such that the planes can communicate electrically, and this is the role played for instance by the Cu–O chains in 123s or by the double Bi–O layers in Bi-based cuprates.

Direct proof of the existence of Cu^{3+} ions is not possible because of the strong hybridization mentioned above. For this reason it is more sensible to express the presence of these ions in terms of the analytically available overall power factor for oxidation, denoted as the formal valency of either copper (214s and 123s) or, as some scientists prefer, copper + bismuth (Bi-based cuprates).

The formal valency of copper in all the high T_c cuprates can be chemically modified and controlled in several ways: (1) by deeper oxidation; (2) by removing from the crystal structure a part of its overall oxygen content; (3) through cation substitution. The last method offers various possibilities to affect the sample T_c, *e.g.* isoelectronic or non-isoelectronic cation substitution performed within the CuO_2 planes or out of them.

Indeed, according to numerous reports published in the literature on this topic (see *e.g.* the review article by Tarascon and Bagley [2]), the T_cs of these materials may exhibit variations which in the case of non-isoelectronic cation substitutions out of the CuO_2 planes are undoubtedly sensitive to the formal valency of

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copper, or at least to its variation caused by charge transfer (partial replacement of La by Sr in 214s, of Ba by La in 123s, or of Sr and/or Ca by rare earths (REs) in Bi-based cuprates). Moreover, there is even evidence [3] of a linear relation between T_c and the number of Cu^{3+} ions (*i.e.* the number of holes) created in the crystal structure of these materials.

The correlation outlined above seems to gain further confirmation in all out-of-CuO_2-plane substitutions of the isoelectronic type (partial replacement of La by REs in 214s, or of Y by REs or of Ba by Sr in 123s) [2]. In this case the formal valency of copper remains intact; therefore the sample T_cs are practically invariable if one ignores their slight increase or decrease caused by the cell volume variation effect.

Considering, however, the Bi-based family, this rule seems not to be fulfilled, at least in relation to invariability of the valency of copper. This problem has already been partly evidenced in a previous paper [4] in which we tried to explain analytically the crystallochemical nature of the unexpected behaviour of both the sample density and the formal valency of copper within the series of isoelectronic-cation-substituted (Ca for Sr) solid solutions of the 2201 and 2212 structure types. We showed that no matter what the structure type, this simple substitution is usually accompanied by a significant variation in the metallic component content of the elementary unit cell (Z) up or down from the values of 20 and 28 atoms characteristic of the ideal 2201- and 2212-type structures respectively. Accordingly, and in spite of the absence of any charge transfer, the formal valency of copper in these solid solutions undergoes a substantial variation too, to say nothing about the sample T_cs whose slight variation may be connected with the cell volume decrease.

The aim of this work was to study isoelectronic-cation-substituted solid solutions of the 2212 structure type in order to get a more detailed explanation of the problem outlined above. Bi-based cuprates are not chemical compounds of fixed stoichiometry [5, 6]. They occur as real phases, *i.e.* chemical entities of variable composition and defined domains of homogeneity within the Bi_2O_3–Sr–CaO–CuO system. The proper meaning of the commonly used formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ corresponds to a code according to which the compounds are constructed (number of separate Me–O-type layers) but not composed. Occupation of the separate structural layers may be deficient, random or even somewhat "overcrowded", which is why we have chosen to work with slightly copper-enriched solid solutions of the 2212 type.

2. Experimental details

Samples with the general formula $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ and a total weight of about 3 g each were prepared from Bi_2O_3, CuO, $SrCO_3$ and $CaCO_3$ components, all of 99.9% purity. Appropriate mixtures of these reagents were pressed into pellet form and sintered in air at 750 °C for 24 h and then at 800 °C for 6 days. The sintering was considered to be finished after 3–4 cycles of 24 h exposure to 800 °C with subsequent re-grinding and pressing. The last sintering cycle consisted of heating at 860 °C.

The phase composition of each sample was verified with the aid of a DRON-type X-ray diffractometer and Cu Kα radiation. The X-ray patterns served also for evaluation of the lattice parameters of the major phase. All single-phase samples were subjected to deeper characterization with respect to the overall power factor for oxidation (V_{Cu}) and the phase density, both *vs.* x_{Ca}.

The densities were determined pycnometrically at 25 ± 0.1 °C using CCl_4 as the immersion medium. Finely powdered samples of about 2 g in weight were subjected to outgassing (10^{-4} Torr) and then to saturation with CCl_4 via condensation of its vapour.

The procedure for determining the overall power factor for oxidation consisted of double iodometric titration as described in ref. 7, modified slightly by the addition of ammonium rhodine (NH_4SCN) before titration. This was done in order to "fix" all Cu^{+1} ions created during the reduction with KI so that they could not be oxidized with the oxygen of air.

3. Results and discussion

According to the X-ray phase composition analysis, all the samples (except that with $x_{Ca}=4$) prepared in this work were single phase. They represent solid solutions of the 2212 structure type with the domain of homogeneity slightly exceeding $x_{Ca}=3$. In Fig. 1. we present the X-ray powder diffraction diagram for the solid solution with $x_{Ca}=2$. We do not observe any traces of CuO.

In Fig. 2 we present the variations in the lattice parameters and the overall power factor for oxidation found for each sample. As can be seen, in spite of the isoelectronic cation substitution performed, the formal valency of copper (V_{Cu}) clearly decreases within the series *vs.* increasing concentration of calcium. The lattice parameters behave as expected.

Figure 3 shows the atomic occupancy of the structural elementary unit cell (Z_{exp}) evaluated for each sample from the experimental densities ($Z_{exp}=d_{exp}\ 6.02a^2c/10A_{MeO}$). Note that for the ideal 2212 structure type this occupancy should be equal to 28, which means 28 molecules of the MeO_δ type, where Me represents the sum of atomic fractions of each metallic component (all available from the general formula $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$) and the overall oxygen content

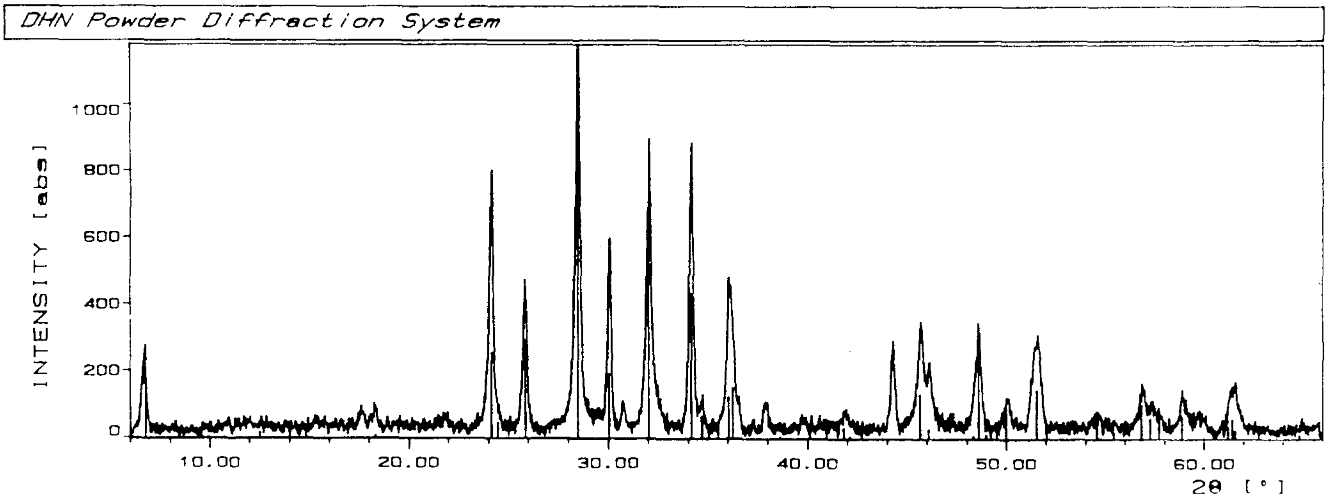

Fig. 1. X-ray powder diffraction pattern for $Bi_8Sr_6Ca_6Cu_9O_{33-y}$ sample.

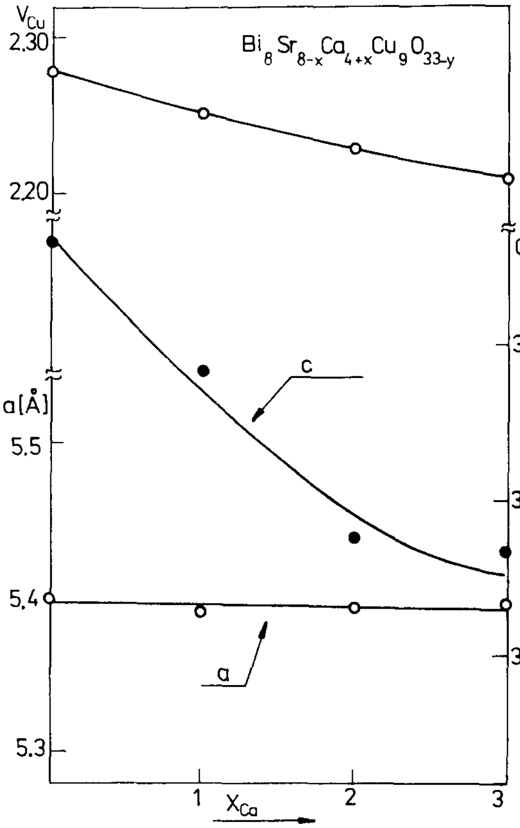

Fig. 2. Lattice parameters (a, c) and formal valency (V_{Cu}) of copper within the series of solid solutions of the $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ type.

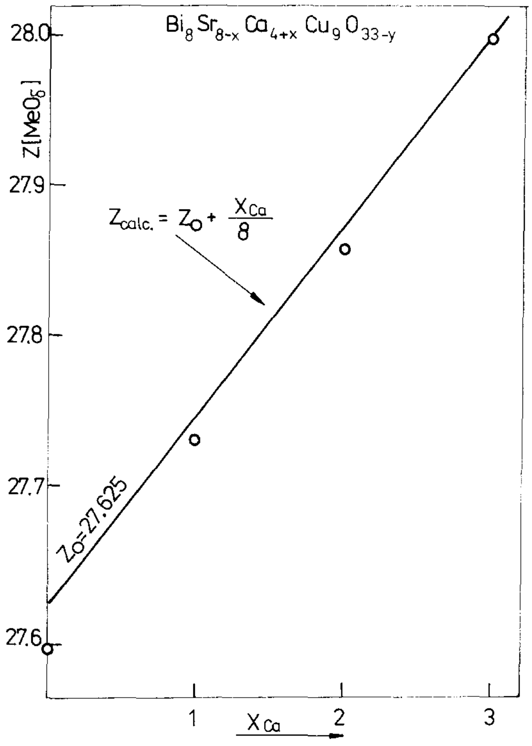

Fig. 3. Atomic occupancy (Z in MeO_6 units) of the 2212-type elementary unit cell $vs.$ concentration of calcium (x_{Ca}) in $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ samples. Solid line – analytical function $Z_{calc} = (Z_0 + x_{Ca}/8)$; $Z_0 = 27.625$. Circles – appropriate values taken from the experimental densities.

is given by $\delta = [33 + (V-2)9/2]/29$, *i.e.* corrected for the observed valency of copper higher than 2+. As can be seen, the occupancy factor Z_{exp} increases linearly $vs.$ x_{Ca}, with an evident tendency to reach the expected value $Z = 28$ just at the terminal composition of the series, *i.e.* at $x_{Ca} = 3$. With some degree of certainty, this tendency can be expressed by the analytical formula $Z_{calc} = Z_0 + x_{Ca}/8$ (solid line in Fig. 3), where $Z_0 = 27.625$ is the starting occupancy of the elementary cell in the matrix sample of the series, *i.e.* for $x_{Ca} = 0$.

Direct proof of the x_{Ca}-dependent densification of the elementary unit cell observed to accompany the Ca-for-Sr substitution is clearly seen in Fig. 4, which illustrates the variations in the calculated densities $d_{calc} = Z_{calc} 10A_{MeO}/6.02a^2c$ and those measured pycno-

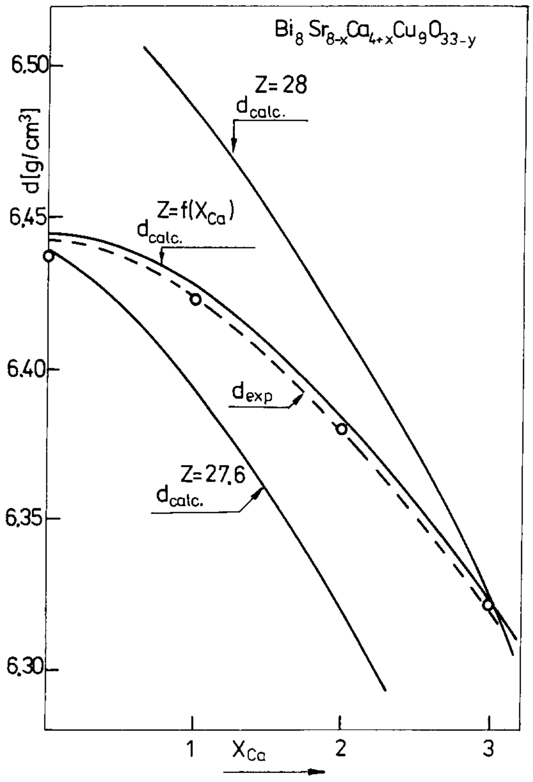

Fig. 4. Experimental (d_{exp}, broken curve) and calculated (solid curve) densities for the series of solid solutions of the $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ type: solid curves $d^{Z-27.6}$ and d^{Z-28}, densities calculated for the structural models of constant (x_{Ca}-independent) atomic occupancy of the 2212-type elementary unit cell, for the model of $Z=27.6$ molecules of MeO_δ as found in the $x_{Ca}=0$ starting sample and for the model of $Z=28$ molecules of MeO_δ, reflecting the case of the ideal structure, respectively; solid curve $d^{Z-f(x_{Ca})}$, densities calculated for the model of x_{Ca}-dependent occupancy, $Z=Z_0+x_{Ca}/8$, with $Z_0=27.625$.

metrically (circles), both *vs.* x_{Ca}. The steady movement of these mutually satisfactorily fitted values towards the model for ideal occupancy ($Z=28$) is unquestionable.

It now becomes clear that our solid solutions are characteristic of x_{Ca}-dependent deficiency in the cationic sublattice, steadily disappearing *vs.* x_{Ca}. A question arises: what about the atomic occupancy of the anionic sublattice and its eventual evolution *vs.* x_{Ca}? The answer lies in the δ values of the MeO_δ formula given above and we can get it by multiplication of the appropriate sample δs by $Z=f(x_{Ca})$. The final result is given in Fig. 5 as $(\Sigma O_2)_{exp}$. There is also a reference line $(\Sigma O_2)_{ref}$ obtained for the case of $V_{Cu}=2$, which represents non-oxidizing sintering conditions.

The first observation that emerges from Fig. 5 is the excess of oxygen in $(\Sigma O_2)_{exp}$ which exists throughout the range of homogeneity in spite of the deficiency in the cationic sublattice. Note that for the ideal 2212 structure type the overall oxygen content should correspond to no more than 32 atoms per elementary unit cell. The second point that arises from Fig. 5 is the very weak dependence of $(\Sigma O_2)_{exp}$ on x_{Ca}. To some extent, we can consider it as constant or independent of x_{Ca}. This would indicate a strong tendency of the structure to have its anionic sublattice intact or even "overcrowded" irrespective of the deficiency of the cationic sublattice.

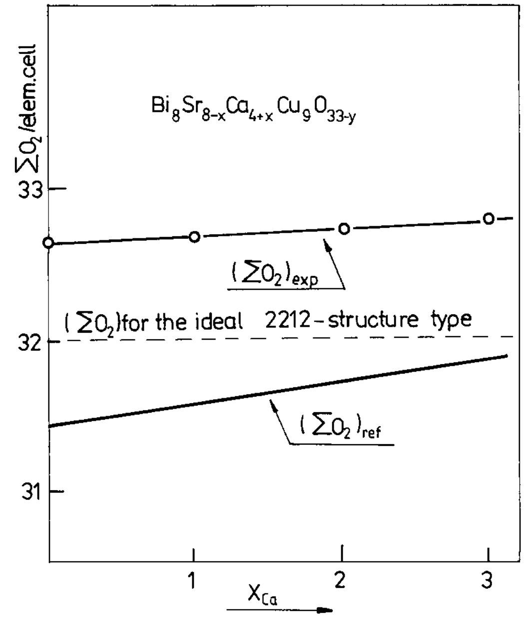

Fig. 5. Atomic occupancy of the 2212-type anionic sublattice *vs.* x_{Ca} in $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ samples: $(\Sigma O_2)_{exp}=(Z_0+x_{Ca}/8)-(24+9V/2)/29$; $(\Sigma O_2)_{ref}=(Z_0+x_{Ca}/8)(33/29)$.

Now the problem of the power factor for oxidation and its variation within the single-phase region of $Bi_8Sr_{8-x}Ca_{4+x}Cu_9O_{33-y}$ solid solutions is more or less clear. These solutions are characteristic of somewhat deficient cationic sublattice. The specificity of the substitution performed is such that it proceeds *vs.* x_{Ca} with a simultaneous densification of the structural unit cell. Thanks to this, the deficiency within the cationic sublattice disappears.

At the same time the anionic sublattice remains entirely occupied with oxygen atoms. Moreover, throughout the interval of homogeneity this sublattice is even somewhat overcrowded, with the excess oxygen presumably located in the interstitial positions between Bi–O layers [8]. Of course, the full occupancy of the anionic sublattice is not due to the densification mentioned above but to the ability of copper to exhibit oxidation state higher than 2+. The densification of the cationic sublattice results only in the requirement concerning full occupancy or, as in the case presented herein, over-occupancy of the anionic sublattice (the difference between $(\Sigma O_2)_{exp}$ and $(\Sigma O_2)_{ref}$ in Fig. 5) becoming smaller and smaller *vs.* x_{Ca}. Since the latter is equivalent to the percentage of Cu^{3+}, the x_{Ca}-dependent decrease of the overall power factor for oxidation in these isoelectronic-cation-substituted solid solutions becomes well understood.

At this point another problem arises, namely: why, in all the Bi-based cuprates, both superconducting and non-superconducting (here we have in mind numerous substitution-type derivatives of the matrix cuprates such as reported in ref. 9), is the overall power factor for oxidation much higher than necessary to ensure full occupancy of the appropriate anionic sublattice? Moreover: why, for the $n=1$ representative of the family is this factor always higher than the corresponding factors for the $n=2$ and 3 representatives, the latter two being comparable with each other but still higher than necessary?

At present we cannot answer the questions precisely but we can speculate somewhat. Considering the 2201 structure type, one can observe that within the Cu–O layers there is an excess negative charge of four electrons per layer, namely $[Cu_2{}^{2+}O_4]^{4-}$. At the same time each of the two Bi–O double layers exhibits an equivalent deficiency of electrons which we can express as $[Bi_4{}^{3+}O_4]^{4+}$. Taking into account the large mutual separation of the layers, it is quite logical to expect that the structure will act in some way to compensate this local charge imbalance. For this purpose there are several possibilities, all more or less equivalent.

(a) Partial substitution of the inner type, resulting in mixed occupancy of the Bi sites by copper ions and of the Cu sites by bismuth ions.

(b) A shift in the domain of homogeneity of the structure towards higher concentrations of copper with activation of the 4f interstitial positions in the CuO planes, and towards lower concentrations of bismuth with creation of local vacancies in the Bi–O layers. The famous paper by Michel *et al.* [10] on the chemical composition of the 2201-type phase as well as our recent results on phase equilibria in the Bi_2O_3–SrO–CuO system [5] both strongly support this explanation as the actual one.

(c) The ambient-conditioned oxidation of copper within the CuO_2 planes, leading to an excess of oxygen within the Bi–O double layers. The latter is closely connected with the chemical nature of bismuth, which as we know cannot exhibit an oxidation state lower than 3+. If it could, then no excess oxygen would be necessary to compensate the local chage imbalance in the Bi–O layers, since the Bi^{3+} ions themselves would accept all the electrons released by copper and transferred through the structural cell. In our opinion all the oxidation power which the Bi-based cuprates possess comes from higher than 2+ valency of copper alone, and in this respect we agree with the earlier results of Poter *et al.* [11] which exclude the existence of Bi^{5+} ions in the 2201 structure.

In conclusion we can say that there is probably no chance for a successful synthesis of the structures under discussion if other than an oxidizing atmosphere is applied, *e.g.* a vacuum of a flow of an inert gas. This means that the excess oxygen (overcrowded anionic sublattice) in Bi-based cuprates is necessary mainly to compensate local charge imbalances existing in the various structures in order to improve their stability. If so, then the superconductivity of these phases is in fact a secondary effect which comes to true *vs.* formal valency of copper not cessary at maximum value of V_{Cu}. Note that although having a lower formal valence of copper, the $n=2$ and 3 representativves of the family exhibit superconductivity at much higher temperatures than the $n=1$ representative. Here we have an additional indication confirming the supposition given above.

Returning to the point, we would like to answer our second question given above concerning the equivalent but evidently lower values of normal valency of copper in the 2212- and 2223-type phases as compared with the 2201-type phase.

Considering the appropriate structure types, it is easy to see that on going from the 2201 to the 2212 type the excess of negative charge within the CuO_2 planes decreases to two electrons per layer, *i.e.* $[Cu_2{}^{2+}O^3]^{2+}$. This is because of partial compensation of the original charge imbalance ($[Cu_2{}^{2+}O_4]^{4-}$) by each of the two oxygen-free two-Ca-ion layers located between the CuO_2 planes. Admittedly, the absolute value of the charge imbalance in these structures remains the same ($[Cu_2{}^{2+}O_4]^{4-} \equiv 2[Cu_2{}^{2+}O_3]^{2-}$); however, it is easy to see that its compensation, via *e.g.* oxidation of copper, is much "easier" in the 2212 structure type than in the 2201 type, since irrespective of the level of compensation considered, it always requires a lower formal valency of coppe to be reached.

Finally, taking into account the 2223 structure type, one can find that each of the two additional CuO_2 planes, *i.e.* those at $c=\frac{1}{4}$ and $\frac{3}{4}$, is fully neutralized by the neighbouring Ca layers. The four remaining CuO_2 planes are the subject of a partial charge compensation identical to that which takes place in the 2212 structure type. As a result, each of them exhibits charge imbalance equivalent to $[Cu_2{}^{2+}O_3]^{2-}$, *i.e.* the same as in the case of the 2212 structure type. Thus it becomes obvious that energetically, compensation of these charge imbalances represents the same problem for both structure types, always easier than that for the 2201 type, irrespective of the way (or ways) through which it passes. The latter can be a combination of the possibilities listed above. One of them is presented below and refers to the sample with $x_{Ca}=3$.

As already shown, this sample exhibits a power factor for oxidation of $V=2.2112$ and is characteristic of a vacancy-free elementary unit cell consisting of $Z=28$

molecules of $MeO_{1.1707}$, $((\Sigma O_2)_{exp}=32.7796)$, where $Me=0.2759Bi+0.1724Sr+0.2414Ca+0.3103Cu$. The distribution of these molecules through particular structural layers can be given as in Table 1.

As can be seen, the structure compensates the imbalance of the local charges all together, by the partial oxidation of copper, by a small shift in the overall stoichiometry towards a higher concentration of copper and by the creation of some deficiency within the Bi–O layers, fully compensated with an equivalent number of Bi ions in interstitial positions of the CuO_2 planes.

TABLE 1. Optimum distribution of atoms through the 2212-structure-type layers in a $Bi_8Sr_5Ca_7Cu_9O_{33-y}$ sample, ensuring local charge balance (a tentative approach)

Atom	Atomic contribution of structural components within particular structure layer			
	Bi–O	Sr–O	Ca	Cu–O
Bi^{3+}	5.7241	–	–	2.0000[d]
Sr^{2+}	–	4.8276	–	–
Ca^{2+}	–	2.8965	3.8621	–
Cu^{3+}	–	–	–	1.8352
Cu^{2+}	0.2759	0.2759	0.1379	6.1647
ΣMe	6.0000	8.0000	4.0000	8.0000 + 2.0000[d]
Positive charge[a]	17.7241	16.0000	8.0000	23.8353
Negative charge[b]	16.0000 + 1.5592[c]	16.0000	0	24.0000 + (8.0000)[e]
Charge imbalance	+0.1649	0	0	−0.1650

[a] Equivalent to ΣMe × valence.
[b] Equivalent to real oxygen occupancy through the layers.
[c] Equivalent to the excessive oxygen $((\Sigma O_2)_{exp}-(\Sigma O_2)$ ideal $=0.7796)$ in (4d+4c)-type interstitial positions.
[d] In 4*f*-type interstitial positions.
[e] Negative charge fully compensated by the neighbouring Ca layers.

Further studies of the series, mainly focused on the electronic transport properties, are under way and their results will be published separately [12]. We hope to show therein a minor decrease in sample T_cs *vs.* x_{Ca} as just resulting from the cell volume decrease. On the other hand, a much stronger variation of this parameter is expected *vs.* the overall oxygen index decrease, when intentionally created by *e.g.* sample deoxidization.

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