Constitution of $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ and of $Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$ type solid solutions

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Abstract. Analytical explanation of an unexpected behaviour of sample densities is given. Three different types of construction of the investigated solid solutions have been recognised: normal for Z = constant versus increasing contribution of Sr substituent (X); atom-deficient for Z decreasing with X; atom-overcrowded for Z increasing with X.

The mechanism of mutual transformation of the 2201-type matrix to that of the 2212-type is proposed.

1. Introduction

In the preceding paper [1] strong evidence was obtained for the unusual construction of $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ type solid solutions. Accordingly, a postulation has been made on the ability of the 2201-type structure to exhibit a variable number of atoms (Z) in its elementary unit cell versus increasing concentration of the strontium substituent.

In this work we present an analytical confirmation of such behaviour, extended on similar solid solutions of the 2212 structure type. A mechanism of formation for all the Bi-based cuprates existing in the Bi_2O_3–SrO–CaO–CuO$_x$ system is proposed.

2. Experiment

The series of solid solutions available from [1] were enriched with some further samples, synthesised following the procedure described in [2]. However, this time the samples were subjected to additional heat treatment at different temperatures for different durations (see table 1):

Three parameters were the subject of careful control, namely phase composition and lattice constants (by x-ray powder diffraction method), density (picnometrically) and the average valency of copper (by the double titration of KI-reduced sample solutions)—the appropriate procedures being described in [2].

In addition, simulation type calculations of sample x-ray powder diffraction patterns have been performed to deduce the most probable distribution of structure component atoms in some chosen samples of the 2201-type structure.

3. Results and discussion

All the experimental data are summarised in table 1. The values Z_{calc} have been determined from general formulae presented below, specific for each series of solid solutions tested. The values Z_{obs} were obtained directly from sample density measurements.

In the case of $Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$ type solid solutions (see table 1) the Z_{calc} seem to vary in an irregular way. Nevertheless, through the series this parameter exhibits an evident tendency to decrease with reference to the maximum value (29) found for the terminal sample 4425 of $x = 0$. However, a few samples ($86610^{(2)}$ $x = 2/8$ and $84810^{(2)}$ $x = 4/8$) seem not to follow the general trend, and it is easy to notice that the accidental Z increase is closely connected with the sample history, mainly with the time of the heat treatment. What seems to be most important is that none of the samples of the series shows $Z > 29$. In this respect, our earlier prediction [1] concerning chemical compositions of the 85 K and 110 K phases, expected to be obligatory in the case of pure occupation of Me–O type layers, looks incorrect. This problem will be discussed again later on.

In the case of $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ type solid solutions (see also table 1), correct estimation of the Z_{calc} was more difficult. This was because of the multiphase nature of all the series as specified in [1]. Nevertheless, even if we consider the experimental values Z_{obs} as more adequate, their gradual increase through the series is quite evident.

Table 1. Solid solutions of the 2201 and 2212 structure types. Comparison of the experimental and the analytical results. Thermal treatments: a, 800 °C/24h; b, 800 °C/72h; c, 800 °C/96h; d, 830 °C/48h; e, 840 °C/24h; f, 850 °C/24h; g, 850–800 °C/24h.

General formula	x	Lattice constant (Å)		Thermal treatment	Average valence $(V_{Cu})_{obs}$	Densities (g cm^{-3})		Elementary sub-cell content		N	Δ
		a	c			d_{obs}	d_{cal}	Z_{obs}	Z_{calc}		
$Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$	0	5.382	24.655	a	2.25	6.90	6.938	20.88	21	0	0
	1/6	5.379	24.560	a	2.22	6.94	7.163	21.13	22	6	+1
	2/6	5.372	24.454	a	2.167	7.11	7.387	22.14	23	6	+2
	0.4	5.373	24.413	c	2.15	6.74	7.009	21.13	22	2.5	+1
	0.45	5.365	24.412	c	2.127	6.69	6.957	21.04	22	2.22	+1
	3/6	5.375	24.362	a	2.102	7.28	7.567	23.08	24	6	+3
$Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$	0	5.410	30.842	f + a	2.20	6.57	6.636	28.72	29	0	0
	1/8	5.403	30.745	f + a	2.17	6.26	6.353	27.60	28	−8	−1
	2/8	5.408	30.697	f + e + d	2.16	6.33$^{(1)}$	6.382	28.27	28.5	−2	−0.5
	2/8	5.404	30.683	b	2.17	6.52$^{(2)}$	6.505	29.07	29	0	0
	3/8	5.391	30.616	g	2.14	6.127	6.125	27.52	27.5	−4	−1.5
	4/8	5.397	30.558	d	2.12	6.00$^{(1)}$	6.043	27.3	27.5	−3	−1.5
	4/8	5.390	30.533	f + e + b + d	2.13	6.32$^{(2)}$	6.400	28.63	29	0	0

It is interesting to note that, as in the series discussed previously, the 2201-type series also contains some samples which do not follow the general tendency. But again, no sample of the series showed $Z < 21$. In this respect, the results of Sonder et al [3] on the Sr-deficient nature of the 2201 structure type phase must be considered as incorrect.

The above remarks allow us to conclude that:

(i) The 2212-type series must be composed of somewhat deficient solid solutions ($Z = 29 - \Delta$), with a tendency to become normal ($Z = 29$). It is highly probable that the densification occurs as the result of a discharge of vacancies, present in each elementary unit cell, on grain boundaries.

(ii) The crystallochemical nature of the 2201-type solid solutions is quite different. As postulated in [1], they seem to be overabundant ($Z = 21 + \Delta$), but they also exhibit a tendency to transform to normal ones ($Z = 21$). However, contrary to the previous case, the transformation seems to result in some quantities of the 2212-type phase created due to an ordering of the matrix phase with the extra ions included. In this sense, the process probably has nothing to do with typical disproportion.

In order to verify these statements analytically we have to determine first if the crystal structure of the 2201-type contains any set of atomic positions (holes) that would be used to realise the case of the densified solid solutions mentioned above.

Such a possibility has been outlined in a previous paper [2]. Indeed, apart from the 4f positions existing within the Cu–O type layers, which are partly occupied with Cu^{3+} ions, crystal structure of the 2201-type (as well as of the two remaining homologues) offers another eight atomic sites situated in between the Bi–O double layers. They are the 4d and 4c in the space group Cccm of non-conventional setting. Except for about 1.5 atoms of oxygen, resulting from $\bar{V}_{Cu} > 2$, the positions are empty and large enough (each about 2.1 Å in diameter) to contain up to four MeO type molecules.

With the assumption that only these positions may be occupied, we can undertake an interpretation of the peculiar behaviour of densities noticed for both the series of solid solutions presented herein.

For this purpose general formulae, which in their present form (see the title) reflect only the case of normal (Z = constant) solid solutions of substitution type, have to be modulated in such a way to comprise an eventual variation of Z versus increasing contribution of strontium substituent x. This we can make following:

(i) For a solid solution of 2201-type structure

$$[Bi_{\%Bi^{(0)}}(Sr_{1-x}Ca_x)_{\%Sr^{(0)}}Cu_{\%Cu^{(0)}}]_{(21 \pm \Delta)} \qquad (1)$$

with the overall oxygen content corresponding to

$$O_{(21 \pm \Delta)}\left(1 + \frac{\%Bi^{(0)} + \%Cu^{(0)}(V - 2)}{2}\right).$$

(ii) For a solid solution of 2212-type structure

$$[Bi_{\%Bi^{(0)}}(Sr_{1-x}Ca_x)_{\%Sr^{(0)}}Ca_{\%Ca^{(0)}}Cu_{\%Cu^{(0)}}]_{(29\pm\Delta)} \quad (2)$$

with the overall oxygen content corresponding to

$$O_{(29\pm\Delta)}\left(1 + \frac{\%Bi^{(0)} + \%Cu^{(0)}(V-2)}{2}\right).$$

In the above $\%Bi^{(0)} \ldots \%Cu^{(0)}$ are the atomic contributions of the metallic structure components in the terminal sample of given series. Δ corresponds to the calcium-for-strontium · substitution-caused increase (decrease) of atomic content of the 2201- or 2212-type unit sub-cells, over (below) that characteristic of the terminal composition of the given series, directly obtainable from sample density. Δ may change within the interval $(-\Delta)_{min}$–$(+\Delta)_{max}$. x is the fraction of the overall content of calcium ($\%Ca^{(\Delta)}$), accepted by the crystal structure in replacement of part of the initial amount of strontium ($\%Sr^{(0)}$). So, for solid solution of 2201-type structure

$$x = \frac{\%Ca^{(\Delta)}}{\%Sr^{(0)}} \quad (3)$$

(a priori known from the experiment for each separate sample of given series) and for a solid solution of 2212-type structure

$$x = \frac{\%Ca^{(\Delta)} - \%Ca^{(0)}}{\%Sr^{(0)}} \quad (4)$$

(available from the experiment provided the $\%Ca^{(0)}$ is defined). V is the average valence of copper in each particular sample, available from the experiment.

It is necessary to state here that by terminal sample or terminal composition of the series of solid solutions under discussion, we understand the chemical composition of the sample the series originated from. So, in the case of the 2201-type structure, this can be any composition of the B phase [2], i.e. any Ca-free sample of the 2201-type structure. In reference to the 2212-type structure, however, this problem needs more detailed explanation. The reason is simple and it is connected with the crystal structure of the 2212-type, which requires the presence of a certain minimum content of calcium ($\%Ca^{(0)}$) as the structure constituent but not as any atom substituent. Besides, it is unknown at present if the domain of existence of the 2212-type phase in the quaternary system Bi$_2$O$_3$–SrO–CaO–CuO (no matter how large it is) represents a surface situated on the level of $\%Ca^{(0)} = 1/7$ parallel to the ternary system Bi$_2$O$_3$–SrO–CuO. The case presented herein ($\%Ca^{(0)} = 2/15$), as well as in [4] ($\%Ca^{(0)} = 0.8/7$), may indicate the original domain of the phase to be slightly deviated. That is why the 85 K phase, considered from early on to have the chemical composition 2212, at this composition point represents a solid solution of the real phase, the latter having the stoichiometry 2, 2.2, 0.8, 2 [4].

All this makes it necessary to determine ($\%Ca^{(0)}$) separately for each particular series of solid solutions of

the type Sr$_{1-x}$Ca$_x$. This can be done by x-ray diffraction. The maximum value of the lattice parameter c within the series tested unequivocally indicates the correct $\%Ca^{(0)}$.

Note that each of the formulae given above comprises all possible variations of solid solutions available within given series, namely: overabundant when $Z = (21 + \Delta)$ or $(29 + \Delta)$; deficient for $Z = (21 - \Delta)$ or $(29 - \Delta)$; and normal with $\Delta = 0$.

The formulae will get their final shape if we replace Δ with the following factor containing x, namely

$$|\Delta| = |Nx|. \quad (5)$$

Here N is a coefficient, whose physical meaning is the deviation of density of given sample up or down from that characteristic for the variant of the normal solid solution of the same x. In this sense N represents a direct measure of the overabundance or of the deficiency caused by the substitution and existence in the crystal structure of each separate sample. So, within any series of solid solutions, defined as characteristic of common ($\%Sr^{(0)}$), ($\%Ca^{(0)}$) and of constant ratio (Bi/Cu), all possible levels (variants) of structure densification can be characterised, each one with a common N.

In a recent paper [1] we have shown that, independent of the structure type, the maximum solubility of calcium in appropriate matrices corresponds to $x = 1/2$. This means that no more than 50% of the strontium present in Sr–O type layers (in the ideal case, four of the eight atoms) can be replaced by calcium. From equation (5) one can deduce that the extreme value of N cannot exceed $2\Delta_{ext}$.

Now, considering that no matter what the crystal structure, the capacity of the (4d + 4c) type interstitials corresponds to four molecules of MeO, we have the maximum value of $+\Delta = 4$ and the upper slope N of the most dense solid solutions equal to $+8$ (by analogy we expect that for the most deficient solid solutions, N can not be smaller than -8).

Other relations are necessarily the same as for any series of solid solutions of the substitution type, namely

$$\%Bi^{(\Delta)} = \%Bi^{(\Delta-1)} = \%Bi^{(\Delta-2)} = \ldots = \%Bi^{(0)} \quad (6)$$

$$\%Cu^{(\Delta)} = \%Cu^{(\Delta-1)} = \%Cu^{(\Delta-2)} = \ldots = \%Cu^{(0)} \quad (7)$$

$$\%(Sr + Ca)^{(\Delta)} = \%(Sr + Ca)^{(\Delta-1)}$$
$$= \%(Sr + Ca)^{(\Delta-2)} = \ldots = \%Sr^{(0)} \quad (8)$$

$$\%Sr^{(\Delta)} = (1-x)\%Sr^{(0)}. \quad (9)$$

$\%Ca^{(\Delta)}$ is obtainable from either equation (3) or (4), depending on the structure type of the solid solution considered.

The last value, i.e. the atomic contribution of calcium in a given sample ($\%Ca^{(\Delta)}$) can be used as an universal variable (X), common for any series of solid solutions of any structure type and thus valuable for comparisons. In this case, the equations (1) and (2) will change as follows:
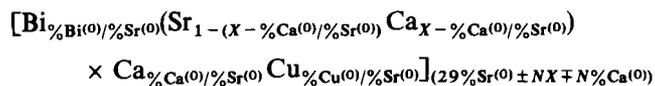
(i) For a solid solution of 2201-type structure

$$[Bi_{\%Bi^{(0)}/\%Sr^{(0)}}(Sr_{1-X/\%Sr^{(0)}}Ca_{X/\%Sr^{(0)}})$$

$$\times Cu_{\%Cu^{(0)}/\%Sr^{(0)}}](21\%Sr^{(0)} \pm NX)$$
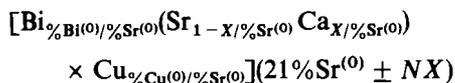
with the overall oxygen content equal to

$$O_{(21\%Sr^{(0)} \pm NX)}\left(1 + \frac{3\%Bi^{(0)} + V\%Cu^{(0)}}{2\%Sr^{(0)}}\right). \quad (10)$$

(ii) For solid solution of 2212-type structure

$$[Bi_{\%Bi^{(0)}/\%Sr^{(0)}}(Sr_{1-(X-\%Ca^{(0)})/\%Sr^{(0)}}Ca_{X-\%Ca^{(0)}/\%Sr^{(0)}})$$

$$\times Ca_{\%Ca^{(0)}/\%Sr^{(0)}}Cu_{\%Cu^{(0)}/\%Sr^{(0)}}]_{(29\%Sr^{(0)} \pm NX \mp N\%Ca^{(0)})}$$

the appropriate term connected with the oxygen content corresponding to

$$O_{(29\%Sr^{(0)} \pm NX \mp N\%Ca^{(0)})}\left(1 + \frac{3\%Bi^{(0)} + V\%Cu^{(0)}}{2\%Sr^{(0)}}\right) \quad (11)$$

[handwritten annotation:] $+2\%Ca^{(0)}$

all valid within the range:

$$\%Ca^{(0)} \leqslant X \leqslant \frac{\%Sr^{(0)}}{2}.$$

The formulae (10) and (11) served us for calculation of densities, their graphical illustration and for comparison with the experimental data. Note that the terms in large parentheses, when added together, give us the molecular weight of the monoatomic $MeO_{1+\delta}$ type formula, necessary for the determination of sample Z_{obs} that stays in the equation for sample density.

3.1. Comparison of the formulae with the experimental data

3.1.1. Calcium-for-strontium substitution-type solid solutions of the 2201 structure.
Figure 1 presents the variation of densities versus X calculated for both the series

of solid solutions presented in this work. The full lines represent densities calculated for the case of zero and the extreme values (see the text) of the parameters Δ and N. In this sense, they fix the range (the frame) within which the densities of real samples can be found.

As can be seen, densities of our multiphase samples of nominal composition $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ and of the 2201-type structure seem to reflect the case resulting from $N = +6$. A slight deviation from the theoretical line is due to some traces of the 2212-type phase, created via the internal ordering of the matrix as suggested in [1]. With increasing duration of the heat treatment, the ordering proceeds deeper (see samples with $x = 0.4$ and 0.45), the quantity of the 2212-type secondary phase increases, and the average density of the sample tends to reach the level of the appropriate solid solution with $Z = 21$. Concerning chemical composition of the resulting 2212-type phase, it is too early to state anything definite. Based on some preliminary considerations we are convinced the phase should have the same composition as its parent of the 2201-type structure. This means the presence of some Bi ions in both Sr-O and Ca-O type layers, if normal ($Z = 29$) structure occurs or, the equivalent number of vacancies therein if the deficient structure occurs. In any case, the phase will belong to quite a different series from the series presented in this paper. This problem will be the subject of a separate paper in which we are also going to verify the variation of the densities versus external pressure of oxygen.

In our opinion, the given level of sample density should depend much more on the external pressure of oxygen then on the temperature and time of thermal treatment applied. To us, sintering under 1 atm of oxygen will stabilise both the 2201-type structure and also the upper limit of sample densification. The latter is
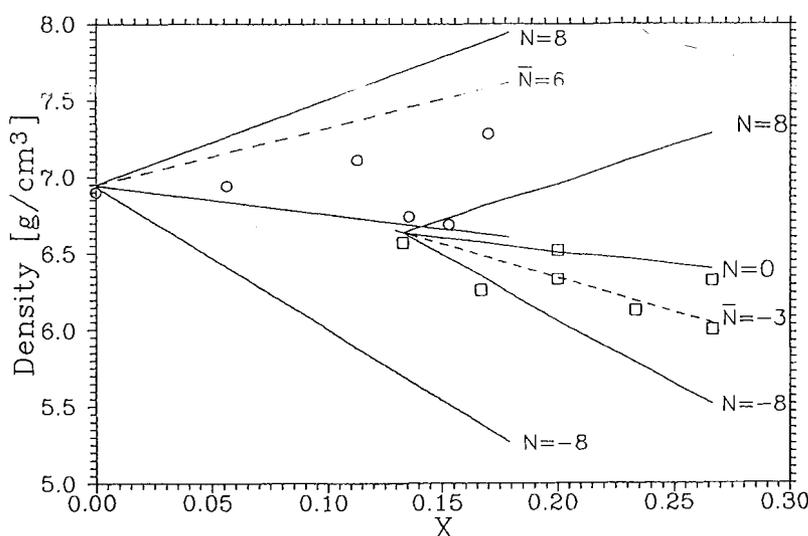
Figure 1. Densities versus the total concentration of calcium (X) for the series of solid solutions of the 2201- and 2212-type structure. Graphical comparison of experimental and calculated results: circles, samples of 2201-type; squares, samples of 2212-type; full and broken lines, calculated values.

closely connected with the increasing occupation of the (4d + 4c)-type interstitials. As soon as the external pressure of oxygen diminishes (sintering in air or under a stream of an inert gas), extraction of oxygen from the interstitials can occur and, as a consequence, the Me type ions present therein, start to diffuse out to form, admittedly deficient, but separate layers of the Me–O type. Here we have the reason for the presence of some quantities of 2212-type phase in our solid solutions of 2201-type structure. Recent results of Perrin et al [5] on reversible transformation of these two structure types versus partial pressure of oxygen in thin layers with 2212 stoichiometry, may demonstrate the correctness of the predictions proposed above.

As already stated, the independent variables found for the series discussed above are $N = 6$ and $\Delta_{max} = 3$. The other ones, such as $\%Sr^{(0)}$, $\%Bi^{(0)}$ and $\%Cu^{(0)}$, as corresponding to chemical composition of the B phase in the 2202-type sample [2], are 0.34, 0.35 and 0.31 respectively.

3.1.2. Calcium-for-strontium substitution-type solid solution of the 2212 structure.

According to the x-ray data reported in [1], a sample of stoichiometry 88410 exhibits a maximum c-lattice constant. This determines the terminal composition of the series $Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$. On the other hand, and as already stated earlier, no sample of the series showed $Z > 29$. This indicates a somewhat different principle, according to which the $n = 2$ representative of the family realises the ideal case of its crystal structure, i.e. the state characteristic of Me–O type layers free of any substitution. It looks as if crystal structure of the 2212-type would contain two different sorts of the Cu–O layers—the old one, characteristic of the $n = 1$ representative, i.e. slightly overcrowded [2], and the freshly created one, as normal.

This suggests that, in any case, formation of the 2212 phase is preceded by the formation of crystal structure of the simplest representative, i.e. $n = 1$, which occurs first and which, via the net of 4d and 4c holes, mentioned above, is able to dissolve additional portions of CaO and CuO. As a result, a solid solution of the 2201-type structure can be realised. Now, dependent on chemical composition of the starting sample, or in other words on the given level of oversaturation with CaO and CuO (with the 'dirty' component such as PbO as well), the process of internal ordering can proceed with time and temperature, leading to a final product which can be one of the structure types under discussion or their mixtures. It should be emphasised that because of the diffusional character of the process, real equilibrium is difficult to achieve. In other words, despite a 'highway' being available, the speed of the 'cars' is still not high enough. Hence, the multiphase nature and the exceptional sensitivity of superconducting properties of the Bi based cuprates to temperature and duration of heat treatment applied (the multistep T_c curves changing versus sample history). This problem has already

been discussed in [1] and is fully confirmed in real samples.

Concerning chemical compositions that would reflect the case of ideal distribution of atoms through the Me–O type structure layers, our actual prediction is as follows:

$n = 1$ 8 8 0 5 —21 metal component atoms

$n = 2$ 8 8 4 9 —29 metal component atoms

$n = 3$ 8 8 8 13—37 metal component atoms.

Considering the densities of samples of nominal composition $Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$, and of the 2212-type structure (see again figure 1) it looks as if they are much more chaotically spread within the range of densities available. Indeed, while still belonging to the series of common origin, i.e. of the terminal compositions 4425, they represent very different levels of temperature and time-dependent densification (different N and Δ for constant X of the same series). In our opinion, at the moment of creation (very difficult to define), the series is characterised by maximum deficiency $(Z = 29 - \Delta)$ with the basic parameters $N = -8$ and $\Delta_{max} = -4$. As seen, the original deficiency is still present in one of the samples, namely in 87510 ($x = 1/8$). However, with increased duration of heat treatment (consult table 1), densification has caused the primary deficiency to be accidentally changed in some of them, and finally the actual deficiency existing in samples $86610^{(4)}$ ($x = 2/8$), 85710 ($x = 3/8$) and in $84810^{(1)}$ ($x = 4/8$) is determined by the intermediate parameters N and Δ_{max}. To some degree of certainty one can consider that these three samples contain a comparable deficiency reflected by an average value of $\bar{N} = -3$ with $\Delta_{max} = -1.5$. Two remaining samples, i.e. $86610^{(2)}$ and $84810^{(2)}$, have no deficiency at all as the appropriate Δ found are close to zero.

At present we do not know if the densification can proceed further, leading to an 'oversaturation' similar or identical to that found in the preceding series. In such a case, creation of some quantities of the 110 K phase within the range of calcium content given above, would be quite understandable. Whether densification can proceed or not, the domain of existence of the 110 K phase can reasonably be expected to start from $X = 0.216$ (see figure 1).

A large range of coexistence of the 2201- and 2212-type structures versus the overall calcium content (X) (see figure 1), together with the unique ability of these phases to exist independently of the level of ordering, must be taken into account when trying to explain more quantitatively the very often multiphase constitution of the appropriate samples, the high sensitivity of their physical properties to temperature and duration of heat treatment, and so on.

With respect to this let us have a look again at figure 1. It looks as if, independent of structure type, the density behavior of 'normal' ($\Delta = 0$) variants of solid

Table 2. Solid solutions of $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ and $Bi_8(Sr_{1-x}Ca_x)_8Ca_4Cu_{10}O_y$; the most probable distribution of atoms within the Me–O type layers. Values given for x, Z_{calc} and $(V_{Cu})_{obs}$ are taken from table 1.

Structure type	x	Z_{calc}	Distribution of the metallic elements through the structure layers [...] and the interstitials (...) available	$(V_{Cu})_{calc}$	$(V_{Cu})_{obs}$
2201	0	21	$[Bi_{7.35}Cu_{0.65}^{3+}][Sr_{7.14}Cu_{0.86}][Cu_4(Cu_1^{3+})]$	2.253	2.25
	1/6	22	$[Bi_{7.70}Cu_{0.30}^{3+}(Cu_1)][Sr_{6.23}Ca_{1.25}Cu_{0.52}][Cu_4(Cu_1^{3+})]$	2.191	2.22
	2/6	23	$\left[Bi_{7.82}Cu_{0.18}^{3+}\binom{Bi_{0.05}}{Cu_{1.95}}\right][Sr_{5.21}Ca_{2.61}Bi_{0.18}][Cu_4(Cu_1^{3+})]$	2.163	2.167
	3/6	24	$\left[Bi_8\begin{pmatrix}Bi_{0.40}\\Cu_{2.44}\\Sr_{0.08}\\Ca_{0.08}\end{pmatrix}\right][Sr_{4.00}Ca_{4.00}][Cu_4(Cu_1^{3+})]$	2.134	2.102
2212	0	29	$[Bi_{7.33}Cu_{0.67}^{3+}][Sr_{7.73}Bi_{0.27}][Ca_{3.87}Bi_{0.13}][Cu_8(Cu_1^{3+})]$	2.173	2.20
	1/8	28	$[Bi_{7.47}Cu_{0.33}^{3+}][Sr_{6.53}Ca_{0.93}][Ca_{3.73}][Cu_8(Cu_1^{3+})]$	2.143	2.17
	2/8	28.5	$[Bi_{7.50}Cu_{0.50}^{3+}][Sr_{5.70}Ca_{1.90}Bi_{0.07}][Ca_{3.80}Bi_{0.03}][Cu_8(Cu_1^{3+})]$	2.158	2.16
	2/8	29	$[Bi_{7.33}Cu_{0.67}^{3+}][Sr_{5.80}Ca_{1.95}Bi_{0.27}][Ca_{3.87}Bi_{0.13}][Cu_8(Cu_1^{3+})]$	2.172	2.17
	3/8	27.5	$[Bi_{7.33}Cu_{0.17}^{3+}][Sr_{4.58}Ca_{1.93}][Ca_{3.67}][Cu_8(Cu_1^{3+})]$	2.127	2.14
	4/8	27.5	$[Bi_{7.33}Cu_{0.17}^{3+}][Sr_{3.67}Ca_{3.67}][Ca_{3.67}][Cu_8(Cu_1^{3+})]$	2.127	2.12
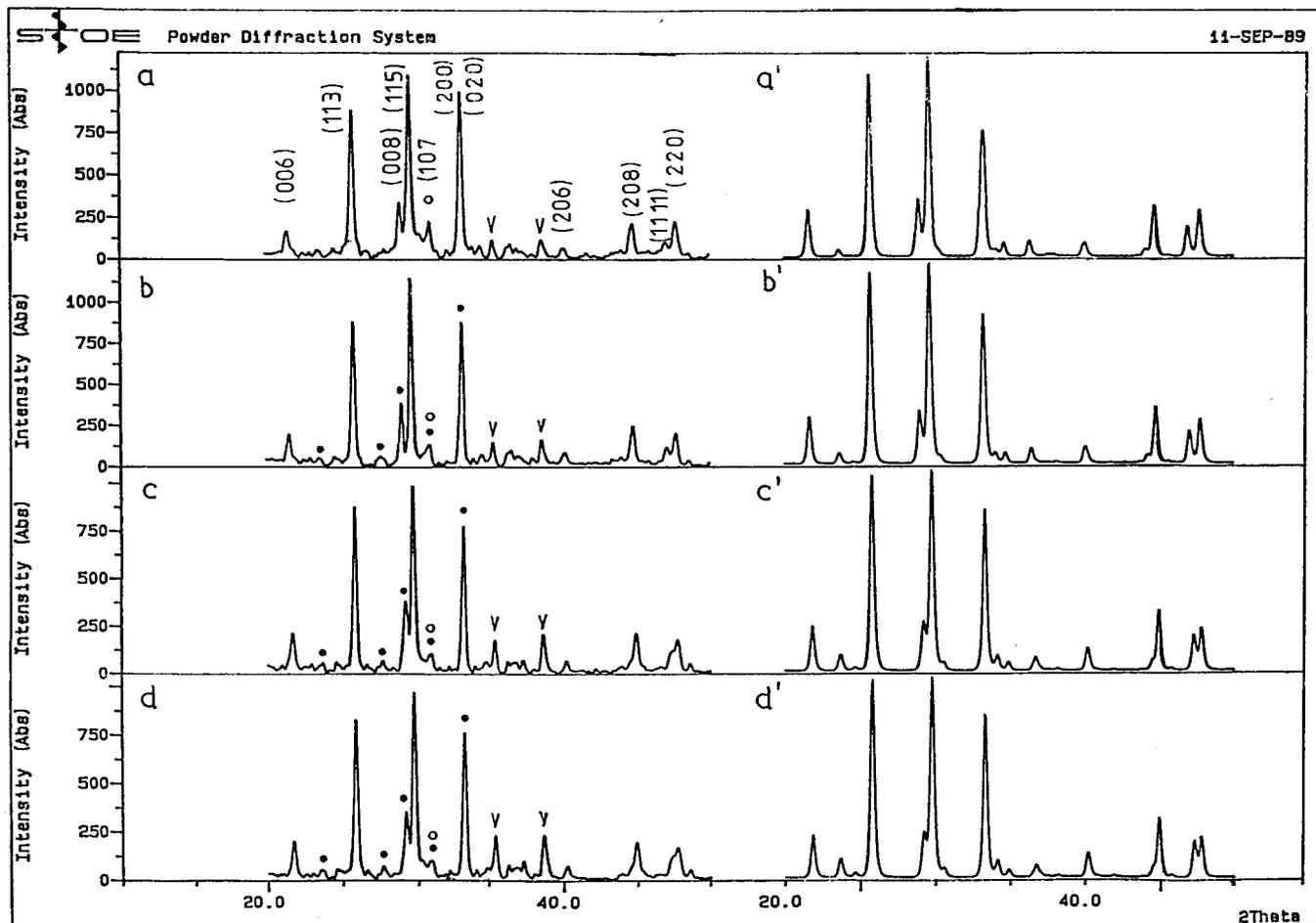
Figure 2. X-ray diffraction patterns for the series of solid solutions of $Bi_2(Sr_{1-x}Ca_x)_2Cu_2O_y$ type a, b, c, d, real samples with $\Delta = 0$, $+1$, $+2$, $+3$ respectively; a', b', c', d', x-ray spectra calculated for the appropriate models in which atomic positions within separate layers are taken from Torardi et al [6]; occupation of the interstitials 4d, 4e and 4f corresponds to the distribution given in table 2. For all the structure component atoms the Debye–Waller isotropic temperature factor $B = 0.8 \text{Å}^2$ was applied. V, CuO; $\bigcirc$, $Sr_4Cu_7O_{12}$; $\bullet$, 2212-type structure phase.

solutions is defined by a common linear function. A slight shift between the appropriate density lines of the 2201- and 2212-type structures can be neglected. This may indicate that the diffusion-type transformation of one structure to the other occurs without any strains. In other words we can say that the formation energies of these structure types are very similar if not identical. Here we have an additional reason for the multiphase nature reported for some Bi_2O_3–SrO–CaO–CuO type samples of stoichiometric composition. The latter reason is especially probable in the case of local inhomogeneities caused, for example, by improper mixing of sample components.

3.2. Tests on the most probable distribution of structure component atoms within the series of solid solutions obtained

The analytical description presented above concerning the constitution of the two series of solid solutions served us as a basis for determination of the most probable distribution of atoms through the Me–O type layers in each separate structure type. This was done on the basis of experimental results concerning the average valence of copper and its variation versus x, reported in [1], and on simulation calculations of x-ray powder diffraction spectra of some chosen samples. Our computation was used to obtain the most satisfactory agreement with the experimental data. In this work, we restricted the x-ray calculations to the case of the overabundant solid solutions only.

The results obtained are presented in table 2 and in figure 2(a)–(d). The following remarks are worthy of note:

(i) No matter what the structure type and level of deficiency, the Cu–O type layers, i.e. the original Cu_5O_4

type planes as well as those resulting from the 2201 structure transformation (Cu_4O_4), both remain intact. This undoubtedly suggests that the Cu–O type configuration is the most stable.

(ii) With increasing deficiency the Me vacancies occur in Ca– and Sr–O type layers first. This may indicate that the Bi–O layers are the most stable in after those of Cu–O type.

(iii) Excess of copper, if present, may occupy any of the Me type atomic positions, but preferably those of bismuth in Bi–O type layers.

(iv) Of all the extra atoms of copper, only those which occupy atomic positions of bismuth, and 25% of those present in original Cu–O layers, are in the $+3$ state of oxidation.

(v) The overabundant variant of solid solution is realised owing to the net of 4d and 4c type holes existing in between the Bi–O layers.

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