

# Domains of existence and physical properties of the 2201- and 2202-type structure phases in the $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ quaternary system

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**Abstract.** The domains of existence of the 2201- and 2202-type structures in solid solutions of the  $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$  quaternary system are investigated from the powder x-ray diffraction, density and resistive transition measurements. It is shown that the general formula of Torardi should not be identified as describing fixed stoichiometry of Bi-based compounds but as a code according to which the unit cells are to be constructed. We have also shown that the composition of the investigated phases can vary within some region of homogeneity. The 2201-type structure acts as a matrix for the formation of new phases by addition of some quantities of calcium and copper, which are known as 80 K and 110 K superconductors. The influence of oxygen on the properties of Bi-based compounds is also evaluated.

## 1. Introduction

As we have shown in the preceding paper [1], the general formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n = 1-3$ ), describing the crystallochemical nature of the Bi-based series of superconducting cuprates [2], is somewhat deceptive. Its original sense is such that it reflects just the number and sequence of separate layers of Me-O type, such as Bi-O, Sr-O, Cu-O etc, existing in the crystal structure of the particular member (phase) of the series, but not the exact chemical composition of the phases.

It happens, however, that the actual and commonly accepted interpretation of the formula identifies it with the chemical composition of a typical compound of stoichiometry with fixed  $n$ . As a consequence, there is no possibility for the existence of phases with variable composition although, in practice, they are very often seen. There is also no possibility of giving a reasonable explanation of the numerous experimental results concerning the chemical composition of these phases. The results often contradict the formula and seem to be mutually exclusive. For illustration we recall the settlements of Tarascon *et al* [3] and Zandbergen *et al* [4] concerning the 2212-type phase composition which are (2, 1.5, 1.5, 2) and (2, 1.7, 0.8, 2), respectively, and also those of Zandbergen *et al* [4] and Shi *et al* [5] referred to the 2223-type one, which according to their measurements are (2, 1.4, 1.2, 3) and (2, 2, 3, 4), respectively, differences which are very significant.

If we treat the formula as a code, according to which the phases are constructed and not composed, then the occupation of each individual layer of the structure becomes free and may vary. The layers may be deficient, randomly filled with atoms of at least two structure components or, as it is suggested in [1] for the Cu-O layers of the B-phase, somewhat 'overcrowded' compared with what one could infer from the formula. It is quite evident that this can explain all the discrepancies mentioned above. For example the problem: 'Why does the first member of the series, i.e. the B-phase [1], exhibit such a large domain of existence, and why do no compositions of its domain have the stoichiometry 2201?', now looks reasonably clear.

Mixed occupation, which undoubtedly takes place within the structure layers of each representative of the series, is so full of consequence that instead of irrational efforts to follow the general formula in the preparation of single-phase samples of a particular member of the series, we should rather be determining the borders of their domains of existence.

We are convinced that, including the 2201-type structure phase, all these phases occupy quite a considerable volume of the quaternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ , and that their superconducting properties must be the subject of some substantial variations with composition. The mentioned penetration of the  $n = 1$  member of the series into the quaternary system with calcium, arises from the substitution of

$(\text{Sr}_{1-x}\text{Ca}_x)$ -type layers that may probably occur within the Sr-O layers of the calcium-free matrix.

Thus, this paper opens our programme of research on the problems outlined above.

## 2. Experiment

The starting materials and the preparation procedure applied in this work were the same as those described in [1]. However, whenever possible reagents other than  $\text{CaCO}_3$  and  $\text{SrCO}_3$  served as the source of calcium and/or strontium, to make samples of appropriate composition. In fact the majority of them have been prepared with the use of  $\text{Ca}_2\text{CuO}_3$  and/or  $\text{Sr}_2\text{CuO}_3$  binary compounds, separately made in advance in sufficient amounts.

The final products of  $800^\circ\text{C}$  annealing, were analysed by x-ray powder diffraction. As in [1], all the single-phase (or almost single-phase) samples were further characterised by determination of their densities and the average valence of copper. Finally, the samples were used for low-temperature resistivity measurements.

For resistivity measurements the samples were cut in the form of the rods with approximate dimensions  $1 \times 2 \times 10 \text{ mm}^3$ . The resistivity was measured by the standard four-point probe DC and AC methods. The results for both methods are reproducible within about 1%.

## 3. Results and discussion

### 3.1. Resistivities of Bi-Sr-Cu-O samples versus temperature

For this purpose, samples of the A, B and  $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_{8+x}$  phases [1] were used. Additionally, several multiphase samples, coming from the very close neighbourhood of the B-phase region, were also measured. The results obtained are presented in figures 1 and 2.

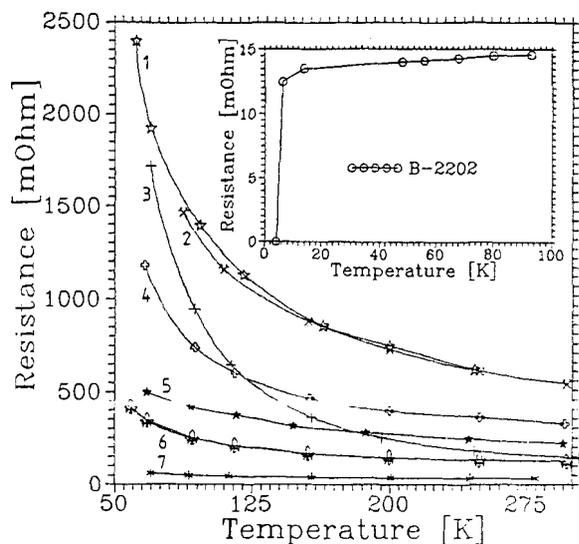
The following conclusions deserve mention:

(i) The metal-type to insulator-like behaviour of resistivity develops along the series: B phase.  $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_{8+x}$ , A phase (compare the resistivity ratio ( $R_T/R_{300}$ ) of appropriate samples, figure 2). This correlates well with the gradual multiplication of the basal plane cell parameters reported for these phases in [1].

(ii) Apart from the unquestioned effect of thermal treatment, as reported in [6], the occurrence of superconductivity in the B phase samples seems to also depend on chemical composition (see figure 1).

### 3.2. Preparation and resistivities of the 2201 structure type solid solutions of the B phase with calcium

Since the B phase field of existence in the  $\text{Bi}_2\text{O}_3\text{-SrO-CuO}$  system represents a triangle [1], its



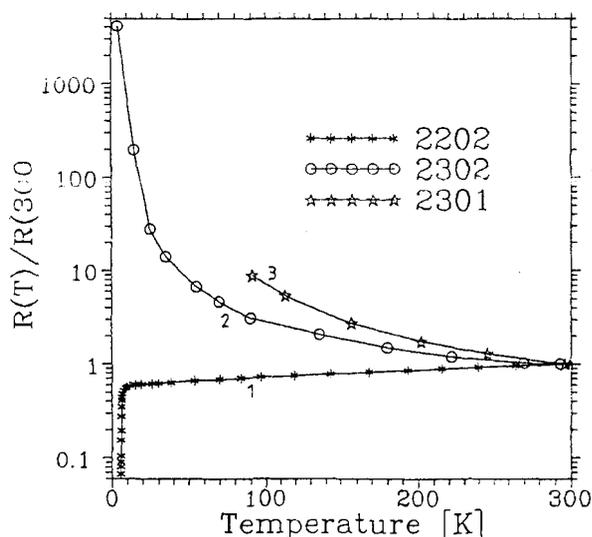
**Figure 1.** Temperature dependence of the resistivity of different samples, namely:

- 1,  $\text{Bi}_{0.45}\text{Sr}_{0.39}\text{Cu}_{0.16}\text{O}_{1+\delta}$  (A + B +  $\text{Bi}_4\text{Sr}_3\text{O}_9$ );
  - 2,  $\text{Bi}_4\text{Sr}_3\text{Cu}_3\text{O}_{12+x}$  (B); 3,  $\text{Bi}_4\text{Sr}_3\text{Cu}_2\text{O}_{11+x}$  (B);
  - 4,  $\text{Bi}_4\text{Sr}_5\text{Cu}_3\text{O}_{14+x}$  (A); 5,  $\text{Bi}_3\text{Sr}_4\text{Cu}_2\text{O}_{10+x}$  (A);
  - 6,  $\text{Bi}_2\text{Sr}_2\text{Cu}_1\text{O}_{6+x}$  (A); 7,  $\text{Bi}_{0.30}\text{Sr}_{0.45}\text{Cu}_{0.25}\text{O}_{1+\delta}$  (A +  $\text{Sr}_4\text{Cu}_7\text{O}_{12}$ ).
- Inset:  $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$  (B).

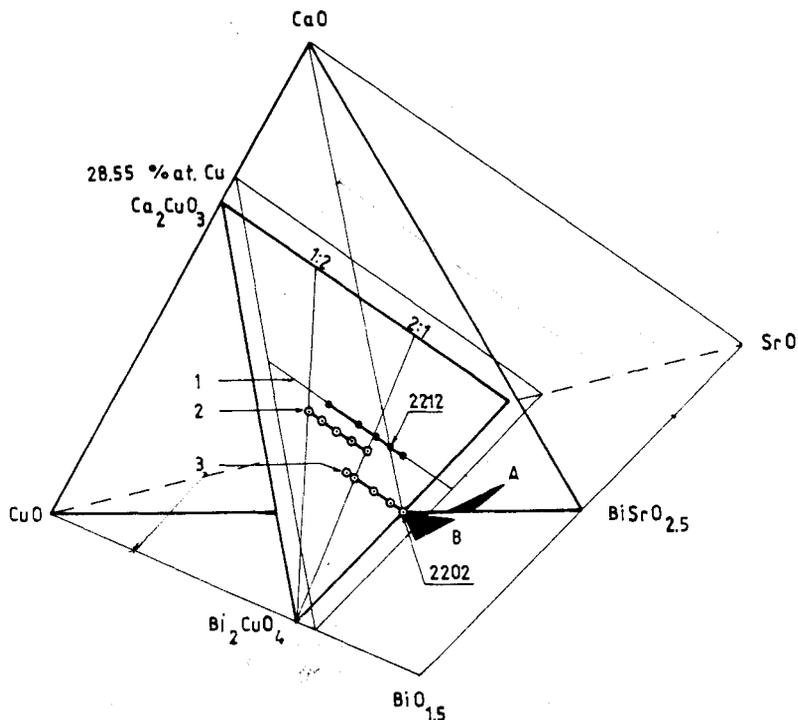
eventual extension to the quaternary system with calcium should have the shape of a trigonal prism. As for the direction in which the prism would penetrate the quaternary space (no matter how deep), the most probable seems to be that one which results from direct substitution of strontium with calcium in Sr-O type layers.

Following this idea we tried to reconstruct one of the three edges of the prism, namely that edge which would possibly originate from the composition point  $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_7$ , (precisely speaking, from a composition of very close stoichiometry, as the multiphase nature of the latter remains unquestionable at  $800^\circ\text{C}$  [1]).

As a result, a series of samples comprising the pseudoternary system  $\text{Sr}_2\text{CuO}_3\text{-Bi}_2\text{CuO}_4\text{-Ca}_2\text{CuO}_3$



**Figure 2.** Temperature dependence of the resistivity ratio for samples: 1,  $\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_{7+x}$  (B); 2,  $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_{8+x}$  [1]; 3,  $\text{Bi}_2\text{Sr}_3\text{Cu}_1\text{O}_{7+x}$  (A +  $\text{BiSrO}_{2.5}$ ).



**Figure 3.** Solid solutions of the 2201- and 2212-type structures; their position and extent in the quaternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$ . 1, series of  $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_3\text{Cu}_2\text{O}_{8+\delta}$  type reported in [9]; 2, series of  $\text{Bi}_8(\text{Sr}_{1-x}\text{Ca}_x)_8\text{Ca}_4\text{Cu}_{10}\text{O}_y$  type; 3, series of  $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Cu}_2\text{O}_y$  type.

(figure 3) and reflected by the general formula  $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Cu}_2\text{O}_y$ , were made. The lattice parameters, densities and the average valence of copper found for the series are presented in table 1 and in figure 4. Figure 5 shows the results of low-temperature resistivity measurements.

From figure 4 it can be seen that the solid solutions extend up to  $x = 0.5$ . The replacement of strontium in Sr-O type layers results in noticeable change (decrease) of the  $c$ -lattice parameter. Dimensions of the unit basal plane remain practically unchanged.

Within the composition given above, the samples are multiphased, as evidenced by the x-ray diffraction patterns. The secondary phases present in the series were the same as those found in the terminal one, i.e. in 2202 [1]. However, except for the terminal sample, all the remaining samples contained in addition a third phase with concentration gradually growing with

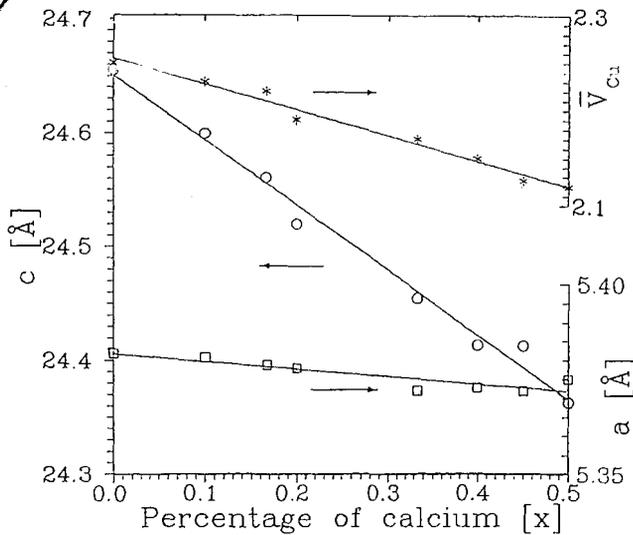
calcium content. From  $T_c$  (figure 5) one can easily deduce that this phase must be of the 2212-type structure.

The occurrence of this structure type in the series prepared is quite unexpected. Note that with increasing calcium content quantities of the accompanying CuO and  $\text{Cu}_7\text{Sr}_4\text{O}_{12}$  phases remain intact. Thus, these phases do not take part in creation of the 2212-type secondary phase. Besides, linear decrease of lattice parameters, observed within the series of 2201-type solid solutions, unequivocally reflects the introduction of calcium to the structure of the major phase. So, where do the additional quantities of CaO and CuO necessary for creation of the 2212-structure type phase come from?

To answer this question we must assume that the 2201-type solid solutions are constructed in some unusual way. We are convinced that they should be

**Table 1.** Lattice parameters, densities and average valence of copper in solid solutions of  $\text{Bi}_2(\text{Sr}_{1-x}\text{Ca}_x)_2\text{Cu}_2\text{O}_y$ .

Sample composition				Phase compositions and lattice constants of the 2201-type structure phase	Density (g cm <sup>-3</sup> )	Mean valence of copper (V)
Bi	(Sr + Ca)	Ca	Cu			
2	(2 + 0)	0	2	$\text{Bi}_{0.35}\text{Sr}_{0.34}\text{Cu}_{0.31}\text{O}_y$ (B-phase); $a = 5.382 \text{ \AA}$ , $c = 24.655 \text{ \AA}$ ; traces of CuO and $\text{Cu}_7\text{Sr}_4\text{O}_{12}$	6.90	2.25
6	(5 + 1)	0	6	Solid solutions of B-phase; $a = 5.379 \text{ \AA}$ , $c = 24.560 \text{ \AA}$ ; traces of CuO, $\text{Cu}_7\text{Sr}_4\text{O}_{12}$ and of 2212-type structure phase	6.94	2.22
3	(2 + 1)	0	3	Solid solutions of B-phase; $a = 5.372 \text{ \AA}$ , $c = 24.454 \text{ \AA}$ ; traces of CuO, $\text{Cu}_7\text{Sr}_4\text{O}_{12}$ and of 2212-type structure phase	7.11	2.17
2	(1 + 1)	0	2	Solid solutions of B-phase; $a = 5.375 \text{ \AA}$ , $c = 24.362 \text{ \AA}$ ; traces of CuO, $\text{Cu}_7\text{Sr}_4\text{O}_{12}$ and of 2212-type structure phase	7.276	2.10

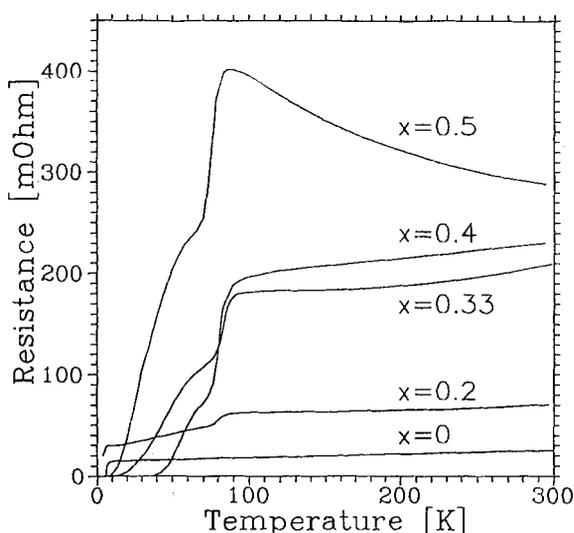


**Figure 4.** The lattice parameters and the average valence of copper versus percentage of calcium ( $x$ ) for the series of 2201-type structures.

overabundant (overcrowded), i.e. characteristic of an increasing content of atoms ( $Z$ ) per elementary unit subcell versus calcium introduction. With this assumption some quantities of the 2212-type structure can occur by means of an inner process of ordering, in spite of the presence of well defined separate components necessary for its construction.

It is quite obvious that solid solutions thus constructed should be characteristic of much higher densities than those classical ones which would result from simple substitution of strontium with an element such as calcium which is more than two times lighter. What is more, the average valence of copper in such overcrowded solid solutions should exhibit a visible variation instead of remaining on a constant level characteristic of the terminal sample.

The results presented in table 1, strongly support the point of view given above. The analytical confirmation



**Figure 5.** Low-temperature resistance dependence for the series of 2201-type structures.

of this phenomenon will be presented the following paper [7].

As for the sample resistivities, we can state that introduction of calcium to the Sr-O layers results in the development of semiconducting behaviour of the compound (figure 5). Again, because of the multiphase character of these samples it is difficult to distinguish *a priori* which structure matrix (the 24 Å or the 30 Å one) possesses this property. We assume it is both.

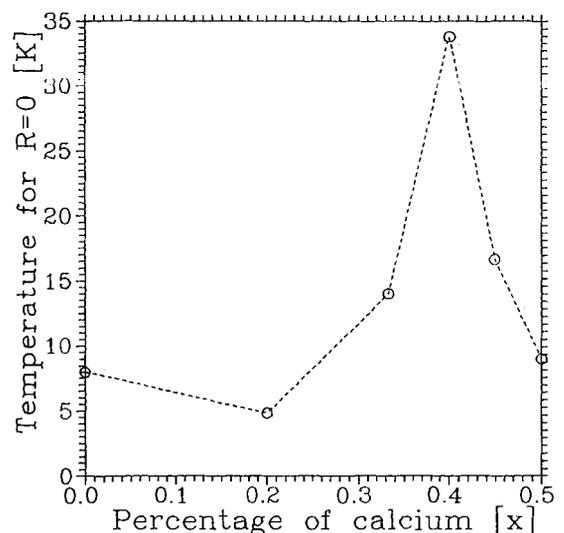
Quite an unusual situation occurs, however, if we analyse the critical temperatures at which the samples exhibit zero resistance. It seems that within the series of solid solutions of the 2201-type structures there is a certain concentration of calcium ( $x \approx 0.4$  or %Ca = 0.1333, see figure 6) for which the transition temperature reaches the maximum value of about 40 K, i.e. twice as high as that found by Michel *et al* [8]. Thus a possibility of an enhancement of  $T_c$  in Ca-doped samples of the 2201-structure type reported in [9] seems to be proved.

### 3.3. Preparation and resistivities of the 2212-type structure solid solutions

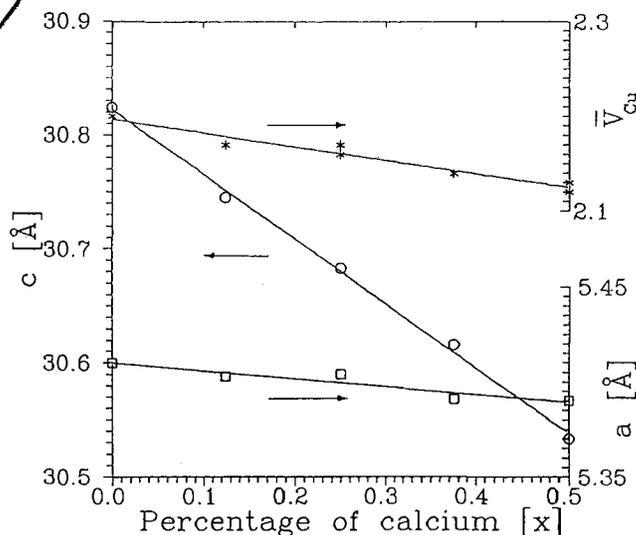
As suggested in [1] we had started the exploration of the domain of existence of the 2212-type phase with the composition 4425. This stoichiometry seemed to fulfil the case of pure occupancy of the Me-O type structure layers.

Based on this sample, a series of solid solutions of the general formula  $\text{Bi}_8(\text{Sr}_{1-x}\text{Ca}_x)_8\text{Ca}_4\text{Cu}_{10}\text{O}_y$  has been made (see figure 3). For a comparison, the series of solid solutions of the  $\text{BiSr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$  type and of the same structure, reported in [10], have been marked on figure 3, to illustrate the multidimensional shape of the domain homogeneity of the 2212-type structure.

Lattice parameters, densities and the average valence of copper found for our series are presented in



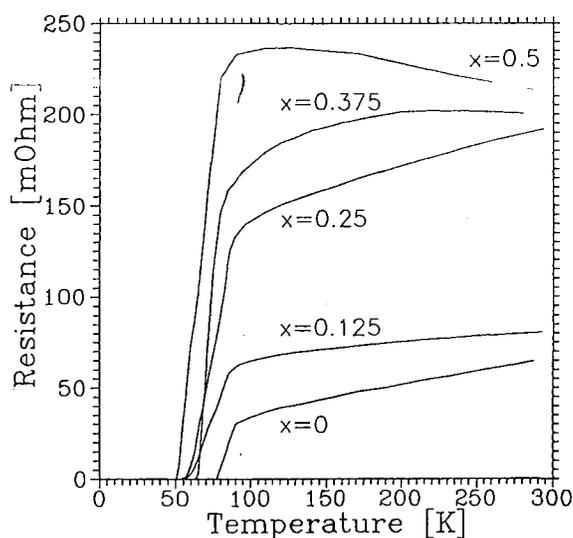
**Figure 6.** Temperature for zero resistance versus percentage of calcium ( $x$ ) for the series of 2201-type structures.



**Figure 7.** The lattice parameters and the average valence of copper versus percentage of calcium ( $x$ ) for the series of 2212-type structures.

figure 7. and table 2. Figure 8 shows the results of low-temperature resistivity measurements.

Similar to the case of the 2201-type structure solid solutions, introduction of calcium to the 2212-type



**Figure 8.** Low-temperature resistance dependence for the series of 2212-type structures.

crystal structure results in a decrease of its lattice constant  $c$  with the dimensions of the basal plane constants practically unchanged. The series extends up to  $x = 0.5$  and in this respect it behaves in exactly the same manner as that reported in [10] for a somewhat shifted series of  $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$  type compounds.

Considering the average valence of copper within the series (figure 7), the reasonable explanation of its behaviour will be the subject of a separate paper [7].

Contrary to the series of solid solutions of the 2201-structure type, the 2212 type exhibits a negative effect of calcium addition on  $T_c$  (figure 8). As can be seen, with the substitution parameter ( $x$ ) increasing the sample  $T_c$  values decrease and the semiconducting character of the samples clearly develops.

#### 4. General conclusions

Results of this work, as well as those presented in [1], allow us to undertake the explanation of the most characteristic features of the structure types under discussion, namely variations in chemical composition, a comparatively low sensitivity of  $T_c$  to external pressure of oxygen, a much higher sensitivity of these parameters to the mutual contribution of the metallic structure components, and also to the temperature and time of thermal treatment applied.

It is highly misleading to identify the general formula  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  as a direct description of the chemical composition of some Bi-based cuprates, each of fixed (with  $n$ ) stoichiometry.

A proper meaning of the formula corresponds to a code, according to which the compounds under discussion are constructed but not composed. Thus, dependent on  $n$  (number of consecutive Cu-O layers), the crystal structure of each particular member of the series is built of two layers of Bi-O and Sr-O type, of  $n - 1$  layers of Ca-O and  $n$  layers of Cu-O type (all this in half an elementary unit cell).

Occupation of the separate structure layers with atoms is unfixed and may vary. So, the layers may be

**Table 2.** Lattice parameters, densities and average valence of copper in solid solutions of  $\text{Bi}_8(\text{Sr}_{1-x}\text{Ca}_x)_8\text{Ca}_4\text{Cu}_{10}\text{O}_y$ .

Sample composition				Phase compositions and lattice constants of the 2201-type structure phase	Density ( $\text{g cm}^{-3}$ )	Mean valence of copper ( $V$ )
Bi	(Sr + Ca)	Ca	Cu			
4	(4 + 0)	2	5	Single-phase; $a = 5.410 \text{ \AA}$ , $c = 30.824 \text{ \AA}$	6.57	2.20
8	(7 + 1)	4	10	Single-phase; $a = 5.403 \text{ \AA}$ , $c = 30.745 \text{ \AA}$	6.26	2.17
4	(3 + 1)	2	5	Single-phase; $a = 5.404 \text{ \AA}$ , $c = 30.683 \text{ \AA}$	6.52	2.17
8	(5 + 3)	4	10	Single-phase; $a = 5.391 \text{ \AA}$ , $c = 30.616 \text{ \AA}$	6.13	2.14
4	(2 + 2)	2	5	Single-phase; $a = 5.390 \text{ \AA}$ , $c = 30.533 \text{ \AA}$	6.32	2.13

deficient, randomly filled with atoms of at least two structure components or, as it is suggested in [1], for the Cu-O layers of the B phase, somewhat 'overcrowded'. This permits each representative of the series to exist within some definite range of concentration (domain of homogeneity). As an example we again refer to [10], where for the  $n = 2$  member of the series, solid solutions of  $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_y$  are reported, or to plenty of seemingly misleading and mutually exclusive results [3, 4, 5] concerning chemical composition of the phases.

The most stable structure type in the series is that characteristic of its first member, namely the 2201-type. Its domain of existence originates in the ternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CuO}$  and at  $800^\circ\text{C}$  it covers a comparatively large concentration range.

The 2201-structure type exhibits a great ability and tendency to form various types of superstructures versus chemical composition. One of them, consisting of multiplication of the basal plane elementary cell edges (with a  $c$ -parameter of about  $24.6 \text{ \AA}$  remaining constant), is realised within the ternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CuO}$ . The star-marked phase (2302) and the A phase (see figure 1 in [1]) both represent the case mentioned above, namely probable duplication and triplication of the 2201 parent structure basal plane parameter ( $a$ ).

It is highly probable that the type of superstructure found in the  $\text{Bi}_2\text{O}_3\text{-SrO-CuO}$  system as the A phase and the 2302 phase may be destroyed by addition of calcium. Thus, the 2201-type structure may enter the quaternary system  $\text{Bi}_2\text{O}_3\text{-SrO-CaO-CuO}$  as a large, three-dimensionally spaced phase.

Another type of superstructure, to which the 2201-type matrix has appeared to be sensitive, is that which results from the presence of some additional quantities of calcium and copper oxides. As soon as the concentration of these structure compounds exceeds the ability of the structure matrix to dissolve them within the Me-O type layers available, a set of separate layers of Ca-O and Cu-O type is created. This leads to the well known superstructures of the 2212- and 2223-type (the 80 K and 110 K superconductors), which are characteristic of  $n$ -dependent gradual increase of the matrix cell parameter ( $c$ ).

Similarly to the 2201-structure type, the 2212-type and probably the 2223-type representatives can also exist within some range of concentrations as the appropriate solid solutions. As shown in section 3.3, this has already been confirmed with reference to the 2212-structure type.

Considering superconducting properties of the structure types under discussion, it is easy to predict that their sensitivity to some variation of the structure's overall oxygen index should be much weaker than that observed in the case of the 123-type family of superconducting phases. This is closely connected with the number of extra oxygen atoms (believed to be bounded within the Bi-O layers), accepted by crystal structures of each particular structure type due to the presence of some of  $\text{Cu}^{3+}$  ions. Provided the prediction given in [1]

is correct, the upper limit of these extra oxygen atoms should correspond to 0.75 atom per one structural layer of the Cu-O type. So, through all the series and for the ideal case of distribution, the number of these atoms per elementary unit cell should be as follows:

$$\begin{aligned} n = 1 & \quad \text{Bi}_8\text{Sr}_8(\text{Cu}_4^{2+}\text{Cu}_1^{3+})\text{O}_{24+1.5} \\ n = 2 & \quad \text{Bi}_8\text{Sr}_8\text{Ca}_4(\text{Cu}_8^{2+}\text{Cu}_2^{3+})\text{O}_{32+3.0} \\ n = 3 & \quad \text{Bi}_8\text{Sr}_8\text{Ca}_8(\text{Cu}_{12}^{2+}\text{Cu}_3^{3+})\text{O}_{40+4.5} \end{aligned}$$

Relatively weak dependence becomes evident if we compare the appropriate ratio (extra oxygen over the overall structure oxygen index), with that existing in the 123-type structure equal to  $1/7$ .

Contrary to the 123-type phases, superconducting properties of the Bi-based ones (probably also of those based on thallium) should exhibit much higher sensitivity to:

(i) *Mutual proportions of the metallic structure components.* This is clearly seen in figures 5 and 8 in which, with increasing calcium concentration, the original metallic character of the  $R(T)$  curves undergoes a continuous transformation to that typical for semiconductors. We hope that similar or even more drastic changes will occur if the domains of homogeneity of these phases are penetrated along different substitution-type directions.

(ii) *Thermal treatment.* Here we have in mind both the temperature and the time of the treatment. There are numerous papers emphasising this problem, i.e. the unusual behaviour of the Bi-based cuprates with respect to thermal treatment applied (see for example Poter *et al* [6]). Let us take two-step or three-step  $R(T)$  transition curves (see figure 5) suggesting a multiphase constitution of tested samples. It is highly probable that because of the temperature- and time-dependent character of the process in which the 2201-type matrix transforms to any of the two superstructures discussed above, both the time and the temperature of annealing applied by us (in the case of the 2201-type series 48 hours and  $800^\circ\text{C}$ ) might be sufficiently long and high, respectively, to activate creation of some quantities of the 2212-type phase. On the other hand, in the case of the 2212-type series of solid solutions, the same parameters ( $850^\circ\text{C}$ -24 hours and  $800^\circ\text{C}$ -24 hours) would be insufficient for full transformation of the 2201 matrix to its higher-ordered form.

The explanation given above is fully acceptable if we consider that, as for any diffusion-type order-disorder kind of phase transition, that one to which the 2201-type structure is highly sensitive is also weakly reversible (usually a much higher temperature has to be applied to reverse it), and because of this it proceeds within some temperature ranges with a time- and temperature-dependent speed.

(iii) *Random atom distribution.* Random distribution of atoms within the structure layers in these phases, which may occur due to mutual exchange of atoms between particular layers, results in a practically infinite

number of states with different physical properties. It is also quite reasonable to expect that any sample of a given structure type and of fixed composition, if subjected to a heat treatment at different temperatures, will exhibit quite different behaviour. The results of Poter *et al* [6] and quite recent reports of Tanaka *et al* [11] and Matsumoto *et al* [12] may serve as an excellent example for the above. For the same reason, the duration of heat treatment (even if performed at constant temperature) will cause some serious changes in physical properties of the sample, very often irreproducible. All this is in agreement with the results of experiment.

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