Phase relations in the Bi$_2$O$_3$–SrO–CuO system at 800°C

R Horyń, I Filatow, J Ziaja and M Wolcyrz

Institute for Low Temperatures and Structure Research, Polish Academy of Sciences, 50-950 Wrocław, PO Box 937, Poland

Abstract. Phase relations in the Bi$_2$O$_3$–SrO–CuO system at 800°C are presented. Several binary and ternary phases existing within this system have been identified and characterised by x-ray powder diffraction and density and overall oxygen content determination. Among them, particular 'A' and 'B' phases (both of variable composition) represent potential interest from the point of view of superconductivity. Evidence of the actual stoichiometry of the 2201-type superconductor ($T_c = 9$–20 K) and of the most probable distribution of structural component atoms within its elementary unit subcell is given. A new interpretation of the general formula for the Bi-based superconducting cuprates has been proposed.

1. Introduction

Superconductivity at 9–20 K in ternary bismuth cuprates was first reported by Michel *et al* [1] for the Bi$_2$O$_3$–SrO–CuO system. Addition of calcium oxide to this system led Meada *et al* [2] to discover bulk superconductivity at 85 K and evidence of superconductivity at 110 K.

Since that time there have been plenty of publications concerning this problem, especially that of crystal structure of phases responsible for the effect observed [3–11]. As a result, it has been established that the transition at 85 K came from a Bi$_2$Sr$_2$CaCu$_2$O$_{8+x}$ phase (shortly denoted as 2212), while that at 110 K from Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+x}$ (2223).

According to Torardi *et al* [12], both the phases belong to the series described by the general formula Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{4+2n}$ with n denoting the consecutive Cu–O structure layers, and representing the cases of $n = 2$ and $n = 3$, respectively. In this respect, the phase superconducting at 9–20 K, found by Michel *et al* [1], would be the first member ($n = 1$) of this series. Thus, till now, the series is composed of three representatives with their critical temperatures (T_c) gradually increasing with n.

It is worth mentioning here that the crystal structures of these phases have been found to exhibit modulation [3, 4, 13–15]. Evidently, this makes recognition of their real structures very difficult. Quite recently this problem has been approached more seriously by Zandbergen *et al* [16]. Nevertheless, further evidence is necessary to improve our knowledge on the average structure of these phases.

As to the preparation conditions, it is known that while the 2201 and 2212 phases are more or less easily

preparable, considerable difficulties have been encountered in preparation of 2223. In spite of this, basic features of the 2223 phase, such as its chemical nature, local crystal structure and physical properties, have already been determined [17].

If the first member of the series, i.e. the 2201 phase, is considered, some important discrepancies still exist. These mainly refer to the chemical composition of this phase. Majority of up-to-date reports (see for instance [12, 13, 17, 18]) confirm the formula of 2201. However, the results on crystal structure of the 2201 phase, reported in [12], seem to be unsatisfactory (too large a temperature factor B for Bi atoms as compared with that for O$_1$). On the other hand, there are at least two papers, [1] and [19], which claim to know the formula of the 2202 phase.

The aim of this work was to determine the phase relations prevalent in the Bi$_2$O$_3$SrO–CuO system at 800°C, at least within its central part, and to explain the problem outlined above. The primary importance of this lies in that, for the other representatives of the series, the 2201 phase is considered to be a structural matrix.

2. Experiment

Samples, each of about 1 g of total weight, were prepared from Bi$_2$O$_3$, CuO and SrCO$_3$ components, all of 99.9% purity.

Appropriate mixtures of these reagents were pressed to pellets and sintered in open air at 800–870°C. Gold capsules served as sample holders. The sintering was considered to be finished after 3–4 cycles of 24 h long

exposures to the temperatures given above, with subsequent regrinding and pressing. The last cycle of heating was performed at 800 °C; afterwards the samples were quenched in air by placing the Au capsules on a thick copper plate.

The phase composition that settled in each sample was determined by means of x-ray powder diffraction. For this purpose, STOE and/or DRON-type diffractometers and Co K or Cu K radiation were applied. From the x-ray patterns, the phase relations prevalent at 800 °C in the Bi–Sr–Cu–O system were deduced. In this respect, only the samples free from the melting effect were considered.

All of the single- or almost single-phase samples were the subject of some deeper characterisation, given below.

(a) *Determination of the average valency of the copper component.* The procedure consisted in double iodometric titration, described in [20], with a slight modification, addition of ammonium rhodine before titration, to capture all Cu^{1+} ions created due to reaction with KI. The method was verified by full reduction (by hydrogen at 450 °C), in some test samples, of Bi–Cu–O and Sr–Cu–O types and has been found to be quick and, for our purposes, satisfactory.

(b) *Density measurement.* Densities were determined pycnometrically at $25° \pm 0.1$ °C, with the use of CCl_4 as the immersion medium. Fine powdered samples of about 1 g mass were subjected to outgassing (10^{-4} Torr) and next saturated with CCl_4 by its vapour condensation.

(c) *Resistivity against temperature characteristics.* Details on low temperature resistivity measurements of Bi–Sr–Cu– and other types of phases will be given in the following paper [21].

3. Results and discussion

Phase relations found for the Bi_2O_3–SrO–CuO system, as valid at 800 °C for the partial pressure of oxygen in the air, are presented in figure 1. We feel it necessary to emphasise that this diagram is far from the real one. Several fragments of it need improvement, and the reasons for uncertainties will become obvious in the course of further discussion.

Now consider the ten binary phases of the system represented by the sides of the triangle (figure 1). Counting clockwise from the CuO corner, they are; $Sr_4Cu_7O_{12}$ [22], $SrCuO_2$ [23], Sr_2CuO_3 [24], X—a phase of rather large domain of existence with its compositional centre corresponding to the formula $Sr_7Bi_2O_{10}$, $Sr_3Bi_2O_6$, $SrBiO_{2.5}$ [25], $Sr_3Bi_4O_9$, $SrBi_2O_4$, Y—another wide ranging homogeneous phase with its midpoint composition reflected by the formula $SrBi_4O_7$, and, finally, $CuBi_2O_4$ [26].

Some of these phases have already been studied and described in literature, others have not. From the point of view of superconductivity, none of them is inter-
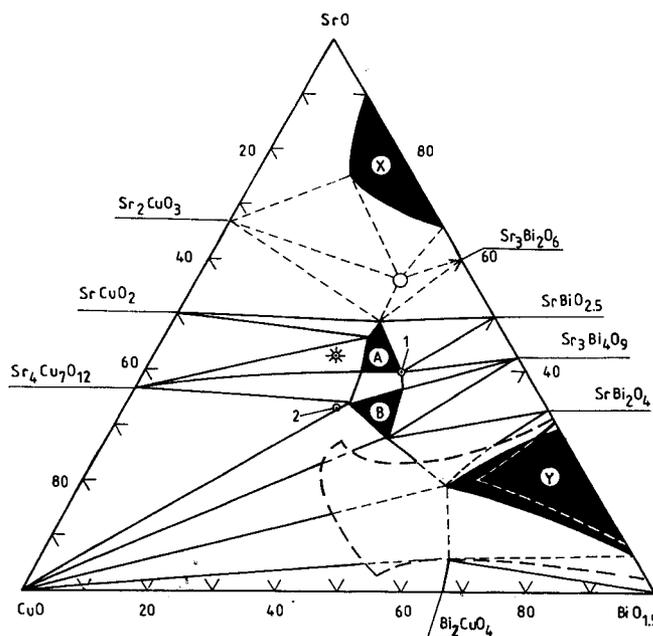
Figure 1. Phase diagram of Bi_2O_3–SrO–CuO system at 800 °C.

esting, which is why these phases have not been studied in detail in this work, beyond the x-ray powder diffraction patterns (see figures 2–6) helpful for identification purposes.

When considering melting effects, it should be pointed out that at 800 °C the presence of the liquid phase was noticed in several samples, all with a rather high concentration of Bi_2O_3. In figure 1 the liquid phase field has been tentatively marked with the broken line.

As far as real ternary phases are concerned, we can state that at 800 °C the Bi_2O_3–SrO–CuO system contains at least two such individuals, marked as A and B phases. Two other phases, marked on the diagram with a circle and with an asterisk, respectively, are still the subject of some doubt. This problem will be discussed further.

Figure 2. X-ray powder diffraction pattern of the $Sr_7Bi_2O_{10}$ (X phase) sample (Cu K_α radiation).

Figure 3. X-ray powder diffraction pattern of the $Sr_3Bi_2O_6$ sample (Co K_α radiation).
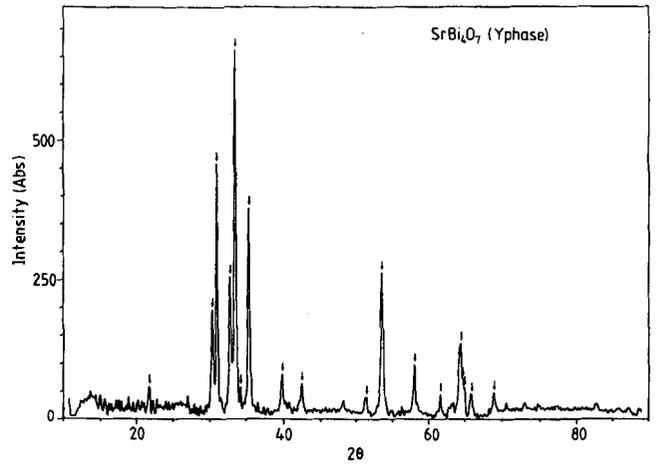
Figure 6. X-ray powder diffraction pattern of the $SrBi_4O_7$ (Y phase) sample (Co K_α radiation).

It is interesting to note that, except for the circle-marked phase, all the remaining ternary phases have been found to exhibit a comparatively low room-temperature electrical resistivity, the latter rising gradually from the B phase, through the asterisk-marked
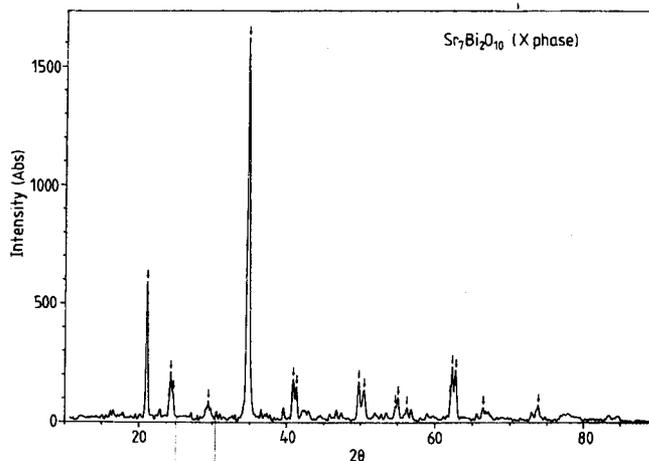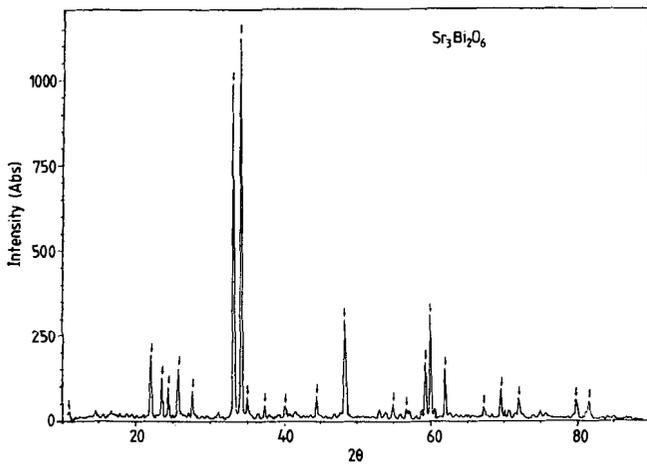

Figure 4. X-ray powder diffraction pattern of the $Sr_3Bi_4O_9$ sample (Co K_α radiation).
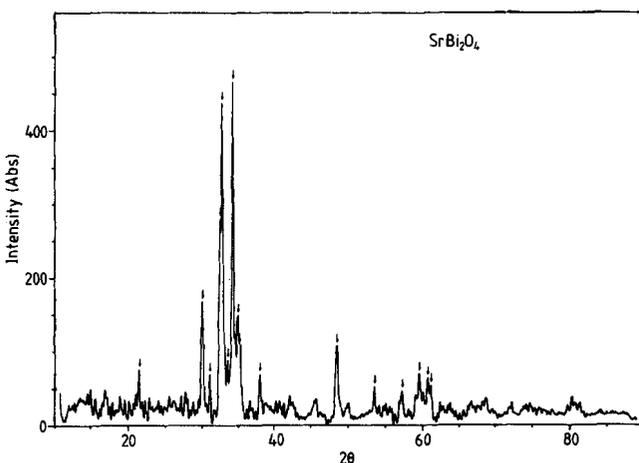
Figure 5. X-ray powder diffraction pattern of the $SrBi_2O_4$ sample (Co K_α radiation).

phase, to the A phase. This may indicate the importance of these phases as potential superconductors. Indeed, in the case of some samples containing the B phase, our preliminary tests have confirmed this expectation. The results are to be published in a separate work [21].

Considering the x-ray diffraction pattern of the B phase (figure 7) and the appropriate data gathered in table 1, it appears that our tetragonal B phase is nothing else but the famous Michel's 2202-type superconductor [1]. Admittedly, the 2202 composition (point number 2 in figure 1) does not lie within the field of existence of the B phase, but this may be the situation which only exists at 800 °C.

Once again remember that most authors ascribe the x-ray pattern given in figure 7 to a phase of the 2201 formula. As can be seen in figure 1, the 2201 composition (point number 1) has nothing to do with the B phase. It lies within the field of existence of our ortho-rhombic A phase, which, according to the x-ray diffraction pattern presented in figure 8, exhibits quite a different spectrum and evidently a more complex one. A comparison of the x-ray diffraction data presented in tables 1 and 2 for the B and A phase, respectively,

Figure 7. X-ray powder diffraction pattern of the $Bi_4Sr_3Cu_3O_{12.165}$ sample (Cu K_α radiation).

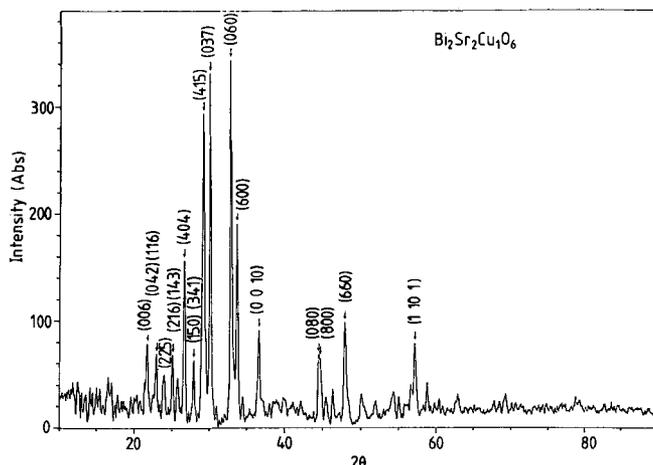**Figure 8.** X-ray powder diffraction pattern of the $Bi_2Sr_2Cu_1O_x$ sample (Cu K_α radiation).

reveals an interesting feature; a superstructure suggesting triplication of the A-phase basal plane parameters a and b as compared with those of the B phase, the c parameter remaining practically the same (24.5 Å) for both of them. Precisely speaking, the triplication is accompanied by notable orthorhombic distortion of the A-phase elementary unit cell. Both of the phases coexist along a fairly large compositional interval (see the two-phase field of coexistence in figure 1), and both occur stably up to their melting or decomposition points (around 900 °C for the A and 870 °C for the B phase).

In the light of the evidence presented above, the discrepancy concerning the chemical composition of the first representative of the series $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ seems to be satisfactorily solved on behalf of Michel's 2202. However, another problem arises, namely, should we treat the general formula describing the crystallochemical nature, of all the superconducting

bismuth cuprates found to date, as still obligatory? If so, how would one get a satisfactory matching between the crystal structure of its first representative ($n = 1$) and at least one composition from the field of existence of our B phase, to say nothing of its whole domain of existence? After all, crystal structure data available in [12] and by an error referred to as 2201 stoichiometry, look generally to be acceptable.

In our opinion, the answer to the first question is positive, provided that the exact interpretation of the formula cited above is taken. Note that since the very beginning the formula has been presented as reflecting only chemical compositions of the compounds: all the chemical elements involved (no matter what their position in crystal structure) have been gathered together and their contributions expressed with numbers. The above refers especially to oxygen of different structure layers, and, because of this, the formula is so misleading. As a result, we face an anomalous situation that, within

Table 1. X-ray powder diffraction data for $Bi_4Sr_3Cu_3O_{12.165}$ (B phase) (Cu K_α). Lattice parameters for the tetragonal subcell: $a = 5.392$, $c = 24.573$ Å (this work); $a = 5.385$, $c = 24.630$ Å [34].

N	H	K	L	sin²θ observed	sin²θ calculated	I/I₀
1	0	1	1	0.02093	0.02143	7.7
2	0	0	6	0.03476	0.03537	12.0
3	1	1	3	0.04945	0.04964	76.0
4	0	0	8	0.06271	0.06289	30.0
5	1	1	5	0.06588	0.06536	100.0
6	1	0	7	0.06960	0.06856	9.7
7	2	0	0	0.08140	0.08160	84.4
8	1	1	7	0.08846	0.08895	7.9
9	2	0	4	0.09770	0.09730	4.1
	0	0	10		0.09826	
10	1	0	9	0.10030	0.10000	7.1
11	2	1	0	0.10244	0.10201	6.3
12	2	0	8	0.14473	0.14449	18.6
13	1	1	11	0.15996	0.15970	7.8
14	2	2	0	0.16334	0.16320	17.7
15	1	1	13	0.20695	0.20686	7.2
16	3	1	3	0.21278	0.21280	7.2
17	2	2	8	0.22520	0.22607	6.0
18	3	1	5	0.22837	0.22895	10.4

Table 2. X-ray powder diffraction data for $Bi_3Sr_4Cu_2O_{10.5}$ (A phase) (Cu K_α). Lattice parameters for the orthorhombic subcell: $a = 15.840$, $b = 16.221$, $c = 24.454$ Å (this work); $a = 5.425$, $b = 23.254$, $c = 24.427$ Å [34].

N	H	K	L	sin²θ observed	sin²θ calculated	I/I₀
1	0	3	1	0.02139	0.02129	1.6
2	0	0	6	0.03592	0.03572	27.9
3	0	4	2	0.04009	0.04005 }	10.4
	1	1	6		0.04034 }	
4	2	2	5	0.04351	0.04328	13.1
5	2	1	6		0.04743 }	15.3
	1	4	3	0.04751	0.04737 }	
	1	3	5		0.04746 }	
6	4	0	4	0.05379	0.05371	45.4
7	1	5	0	0.05894	0.05873 }	13.7
	3	4	1		0.05835 }	
8	0	0	8	0.06324	0.06350 }	6.0
	1	4	5		0.06324 }	
9	4	1	5	0.06431	0.06489	86.3
10	0	3	7	0.06865	0.06891	100.0
11	1	5	4	0.07455	0.07461 }	6.0
	2	5	3		0.07476 }	
12	5	3	0	0.07915	0.07941	12.0
13	0	6	0		0.08117 }	57.9
	0	5	5	0.08138	0.08117 }	
	2	4	6		0.08125 }	
14	1	5	5		0.08354 }	12.0
	5	0	5	0.08354	0.08392 }	
	5	3	2		0.08338 }	
15	6	0	0	0.08533	0.08512 }	50.3
	0	6	2		0.08514 }	
16	0	4	8	0.09922	0.09957 }	26.8
	0	0	10		0.09921 }	
17	3	0	9	0.10147	0.10164 }	7.1
	4	0	8		0.10133 }	
18	0	0	12	0.14289	0.14287	8.2
19	0	8	0	0.14448	0.14431 }	18.6
	0	6	8		0.14467 }	
20	8	0	0	0.15061	0.15133	10.9
21	8	0	2	0.15506	0.15530	13.7
22	6	6	0	0.16628	0.16630	26.8
23	0	8	6	0.18082	0.18002 }	10.9
	0	6	10		0.18038 }	

the series, each representative (phase) would have fixed chemical composition, for instance: $Bi_2Sr_2CuO_6(2201)$ for $n = 1$, $Bi_2Sr_2CaCu_2O_8(2212)$ for $n = 2$ and so on. Reality is more complex, and there is some evidence in literature that, as for our B phase, all the remaining representatives of the series exhibit variable composition.

Contrary to that presented above and the commonly accepted interpretation of the formula, our proposition is to consider it as a code, according to which the series is constructed, not composed. In agreement with the present knowledge concerning crystal structure of the phases under discussion, we identify the formula as that able only to reflect the number and sequence of layers of Me–O type, existing within the elementary unit cell (precisely, within a half of it) of each particular representative of the series. Thus, it says that, depending on n, crystal structure develops along the series in the way that there is a constant number of Bi–O and Sr–O type layers equal to 2 and a variable number of layers of Ca $(n - 1)$ and of Cu–O type (n). Considering the atomic capacity of each particular layer as well as real distribution of atoms within the layers the formula says nothing. It is highly probable that the layers are not composed of atoms of a particular component only, i.e. Bi, Sr or Ca. Of course these elements are the main occupants of the layers, but deficient or mixed occupation remains unquestioned. A comparatively large domain of existence of the B phase found here proves this. Generally speaking, the literature is full of reports—till now seemingly inconsistent with the formula and mutually discrepant—which, when interpreted in terms given above, become quite sensible. For instance, according to Tarascon et al [10], the chemical composition of the 85 K phase (2212) corresponds to (2, 1.5, 1.5, 2), while according to [27], its most probable formula is (2, 1.7, 0.8, 2). Similarly, considering the (2223) representative of the series, one can find (2, 1.4, 1.2, 3) in [27] and (2234) in [28]. Evidently, all this is because the series is composed of real phases, i.e. chemical individuals of variable composition and not point-fixed compounds. The general formula reflects only layered characters of structure of these phases and nothing more.

In order to answer our second question, intentionally we are going to try the 2202 composition, though we realise that for this purpose any other sample but a single B phase would be much more convenient.

According to the diagram (figure 1), the 2202 sample should contain some negligible quantities of CuO and $Cu_7Sr_4O_{12}$. Indeed, the x-ray diagram (figure 9) proves this. Note that, due to $Cu_7Sr_4O_{12}$, the diffraction line (200) is slightly enhanced when compared with the same line of pure B phase. As for the chemical composition of the B phase in the 2202 sample, we can assume that it corresponds to 0.35 $BiO_{1.5}$, 0.34 SrO and 0.31 $CuO_{1.125}$. Concentration of oxygen in CuO is higher than one which would result from the average valency of copper found (see table 4).

Now, we assume that the density of our 2202 sample $(6.90\,g\,cm^{-3})$ corresponds to pure B phase of the com-

Figure 9. X-ray powder diffraction pattern of the $Bi_2Sr_2Cu_2O_{7.24}$ sample (Cu K_α radiation).

position given above. With this simplification we can determine the total number of molecules (z) of MeO_{1+x} type, existing within the elementary unit cell of the dimensions given in table 3.

$$d_{exp} = 6.90 < d$$

$$= z \frac{Bi_{0.35}Sr_{0.34}Cu_{0.31}O_{1.21375}}{6.02 \times 5.382 \times 5.382 \times 24.655} 10 \quad (g\,cm^{-3}). \quad (1)$$

The resulting value, $z = 20.88$, permits, in turn, to find the number of atoms in each of the structural compo-

Table 3. X-ray powder diffraction data for B-phase terminal composition in a $Bi_2Sr_2Cu_2O_{7.24}$ sample (Cu K_α). Lattice parameters: $a = 5.382$, $c = 24.655$ Å (tetragonal subcell) (this work); $a = 5.32$, $b = 26.6$, $c = 48.8$ Å (orthorhombic subcell) [1]; $a = 3.8097(4)$, $c = 24.607(3)$ Å (tetragonal subcell) [18].

N	H	K	L	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	I/I_0
1	0	1	1	0.02149	0.02149	8.5
2	0	0	6	0.03518	0.03519	14.3
3	1	1	1	0.04185	0.04201	3.3
4	1	1	3	0.04980	0.04983	80.9
5	0	0	8	0.06260	0.06257	25.3
6	1	1	5	0.06550	0.06545	100.0
7	1	0	7	0.06814	0.06831	13.9
8	2	0	0	0.08210	0.08207	87.5
9	2	0	2	0.08590	0.08598	4.1
10	1	1	7	0.08892	0.08894	3.4
11	0	0	10	0.09800	0.09764	4.5
	2	0	4		0.09755	
12	1	0	9	0.09922	0.09951	8.3
13	2	1	0	0.10208	0.10244	6.8
14	2	0	6	0.11740	0.11726	3.4
15	2	0	8	0.14470	0.14464	16.2
16	1	1	11	0.15922	0.15933	9.1
17	2	2	0	0.16410	0.16413	24.0
18	2	2	6	0.19927	0.19973	4.2
19	1	1	13	0.20708	0.20592	5.3
20	3	1	3	0.21400	0.21397	8.6
21	2	2	8	0.22706	0.22632	6.7
22	3	1	5	0.22970	0.22924	13.8
23	0	0	16	0.24987	0.25028	4.6
24	3	1	11	0.32330	0.32346	4.2
25	4	0	0	0.32830	0.32827	3.8

nents within the volume fixed above, namely: Bi 7.35, Sr 7.14, Cu 6.51, (21 atoms of metallic elements); and O, 25.488 with the probable upper limit equal to 25.5 or 26 atoms for the theoretical density $d_x = 6.94\,\mathrm{g\,cm^{-3}}$.

A comparison of the elementary unit cell content given above, with that resulting from the 4-molecular content of the 2201 matrix proposed in [12], reveals one extra atom of a metallic element (probably Cu) and 1.5 or two extra atoms of oxygen. The problem is how to find a place for these atoms. Our proposition concerning the total distribution of atoms within the crystal structure of the 2201 matrix is as follows.

$$[Bi_{7.35}Cu^{3+}_{0.65}][Sr_{7.14}Cu^{2+}_{0.86}][Cu^{2+}_{4.00}Cu^{3+}_{1.00}][O_{25.5}]$$
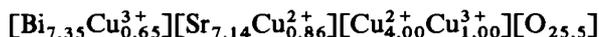
This scheme says that, except for the Cu–O layers, all the remaining structure layers are composed of a mixture of atoms of at least two components. Moreover, within the Cu–O layers, an extra occupancy occurs, evidently for the extra atom of a metallic element mentioned above.

Considering the total content of Cu^{3+} (1.68 atoms/cell) that arises from the average valency of copper, as well as the requirements of particular structure layers for appropriate amounts of Bi and Sr substituents, there is no other way but to assume that the extra occupancy is subject to Cu^{3+}. It may also be Cu^{1+}, as $(Cu^{3+} + 2O^{2-}) = (Cu^{1+} + O_2^{2-})$ [29]. This, in turn, involves the necessity to treat the Cu–O layers as containing separate sets of atomic positions for these ions. Indeed, each Cu–O layer contains two such positions (4f in space group Cccm of non-conventional setting $(0, 0, 0)$ $(0, \frac{1}{2}, \frac{1}{2})+)$, which are empty in the crystal structure of the 2201 matrix [12], and which can be used to locate the Cu^{3+} ions with the occupancy factor $\frac{1}{4}$.

The x-ray diffraction pattern calculated for the model given above is presented in figure 10. As can be seen, the result of fitting looks satisfactory, and although it reflects a simplified variant (with 24 oxygen
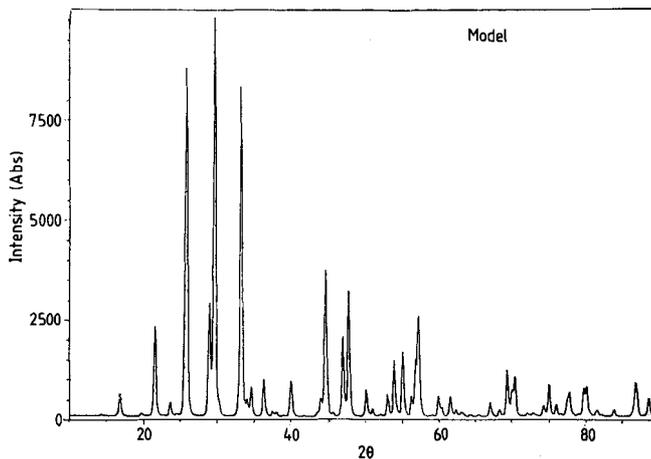
Figure 10. X-ray diffraction pattern calculated for the model of the 2201 overall composition and atomic distribution in 2202 sample.

atoms only), we are convinced that it can serve as a proper basis for further adjustment, for instance with neutron diffraction.

In order to verify the scheme of distribution presented above, several other samples of the B phase have been tested in the same manner. Results of the testing are summarised in table 4. An excellent agreement of the experimental and calculated values obtained is really meaningful, especially if the total number of molecules (z) is considered. Note that none of the B phase samples tested herein has exhibited this parameter to be less than 21 or close to 20, which would mean a 4 × 5 atomic (2201) content of the structure subcell as suggested in [12]. Thus, the extra occupancy of the Cu–O layers within the 2201 structural type is undoubtedly real and seems to be valid for all domains of existence of the B phase. It is strange that despite incomplete occupation of the 4f extra positions available in Cu–O

Table 4. Lattice parameters, results of density and chemical analysis of some samples of B-phase and proposed distribution of atoms within the appropriate elementary cell ($z = 21$). *, the multiphase sample composed of $Bi_{0.35}Sr_{0.34}Cu_{0.31}O_{1.21375}$ terminal B phase and some traces of CuO and $Cu_7Sr_4O_{12}$. $\bar{V}_{Cu} = [(+3)N_{Cu^{3+}} + (+2)N_{Cu^{2+}}]/N_{Cu}$

Chemical composition			Lattice parameters (Å)	Densities (g cm⁻³) obs./calc.	$\bar{V}_{Cu}$ obs./calc.	Distribution of the atoms through the layers
Bi	Sr	Cu				
2	2	2*	$a = 5.382$	6.90/6.938	2.25/2.253	$[B_{7.35}Cu^{3+}_{0.65}]$
						$[Sr_{7.14}Cu^{2+}_{0.86}]$
			$c = 24.655$			$[Cu^{2+}_{4.0}Cu^{3+}_{1.0}]$
4	3	3	$a = 5.392$	7.22/7.246	2.11/2.095	$[Bi_{8.0}]$
						$[Sr_{6.3}Cu^{2+}_{1.7}]$
			$c = 24.573$			$[Cu^{2+}_4(Bi_{0.4}Cu^{3+}_{0.6})]$
3.7	3.3	3	$a = 5.378$	7.15/7.09	2.21/2.195	$[Bi_{7.77}Cu^{3+}_{0.23}]$
						$[Sr_{6.93}Cu^{2+}_{1.07}]$
			$c = 24.620$			$[Cu^{2+}_4Cu^{3+}_1]$
4.2	3.3	2.5	$a = 5.384$	7.29/7.437	2.16/2.190	$[Bi_8]$
						$[Sr_{6.93}Bi_{0.82}Cu^{2+}_{0.2}]$
			$c = 24.594$			$[Cu^{2+}_4Cu^{3+}_1]$

type layers, the B phase does not exhibit a maximum ($z = 24$) content of the subcell, i.e. 3×8 atoms on each of the layers, the latter resulting from full activation of the extra positions mentioned above.

It is worth noticing here that, except for the 4f positions, the 2201-structure matrix contains two sets of additional positions situated between each Bi–O double layer. They are 4d and 4c in the $Cccm$ space group of non-conventional setting and can easily accept four molecules of Me–O type (for instance Cu–O). To our knowledge (see for instance [30]) in real samples they may play an important role. Further evidence on this problem will be given in an accompanying paper [31].

Based on the preliminary results concerning the B phase, two conclusions can be drawn.

(i) Evident variation of the $\bar{V}_{Cu}$ against sample composition and against temperature (as illustrated in figure 11) may be explained by random distribution of atoms within the Me–O type structural layers which, being specific for each particular composition, may additionally vary somewhat against temperature.

(ii) Chemical composition, which would correspond in 2201 structural type to atomic occupation of the Me–O type layers free of any substitution, should be 8805. A simple extension of this scheme to the remaining two representatives of the series gives the following stoichiometries: 88410 for the $n = 2$ representative and 88815 for $n = 3$.

From the phase diagram (figure 1) it follows that, free of any substitution, atomic arrangement does not occur in the B phase. In this respect, the phase can be considered as typically off-stoichiometric, and similar to plenty of superconducting phases of A15 type. Appropriate tests on the remaining phases of the series are in progress.

Another interesting problem, which we were faced with during the work, refers to the state of oxidation of copper in various phases found within the Bi–Sr–Cu–O system. It is necessary to admit that a higher than $(2+)$ state of oxidation of copper has been found and not only in the case of the B phase. Two other phases, namely $Cu_7Sr_4O_{12}$ and the phase marked on the phase diagram with an asterisk, were shown to contain some amounts of Cu^{3+}. This may indicate that, under the experimental conditions applied, phase relations found here reflect only roughly those prevalent in a strict Cu^{2+}-oxide ternary system with bismuth and strontium. Precisely, they should be related to the more complex case containing two copper oxides.

Indeed, taking into account the three possible states of oxidation of copper, three inseparable ternary subsystems; Me'_2O_3–MeO–Cu_2O, Me'_2O_3–MeO–CuO and Me'_2O_3–MeO–$"Cu_2O_3"$ should be considered for proper identification of phase relations prevalent within the main compositional tetrahedron of the Me'–Me–$Cu^{(1-3)+}$–O type. This problem has already been discussed in [32].

The asterisk-marked phase of the 2302 stoichiometry seems to represent the case of a very stable interme-
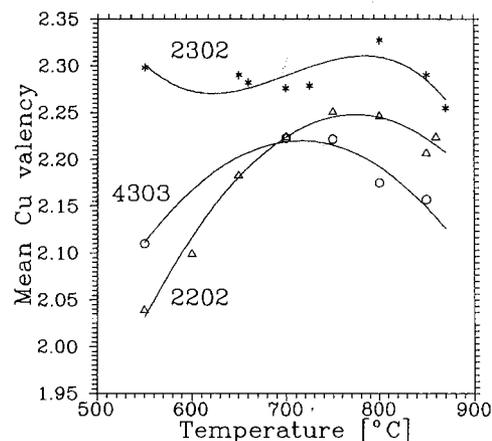

Figure 11. Mean Cu valency against temperature for $Bi_2Sr_2Cu_2O_x$, $Bi_4Sr_3Cu_3O_x$ and $Bi_2Sr_3Cu_2O_x$ samples.

diate compound existing in between the appropriate ternary systems of Cu^{2+} and Cu^{3+} mentioned above. Up to 850 °C, samples of the 2302 composition show coexistence of two phases, i.e. $Cu_7Sr_4O_{12}$ and the A phase. Above 850 °C a new structure is created (see figure 12 and table 5). Its characteristic feature is that, once brought into existence, it does not disappear on heating below 850 °C. At 800 °C the phase remains as stable as at the temperature of its creation. So, it cannot be considered as existing only within some temperature interval above 850 °C. Also, it is not a case of a metastable phase. Based on the tests on average valency of copper in the 2302 phase (see figure 11), we decided to exclude its existence in the Bi_2O_3–SrO–CuO ternary system. Note that, contrary to the B phase (samples 2202 and 4303 in figure 11), the only temperature at which the average valency of copper in the 2302 phase would reach the value $2+$, happens to exceed the temperature interval of stability of this phase.

A phase marked on the diagram with a circle exhibits a similar feature and therefore seems to belong to the same category of phenomena, but till now we have had insufficient evidence to prove it.
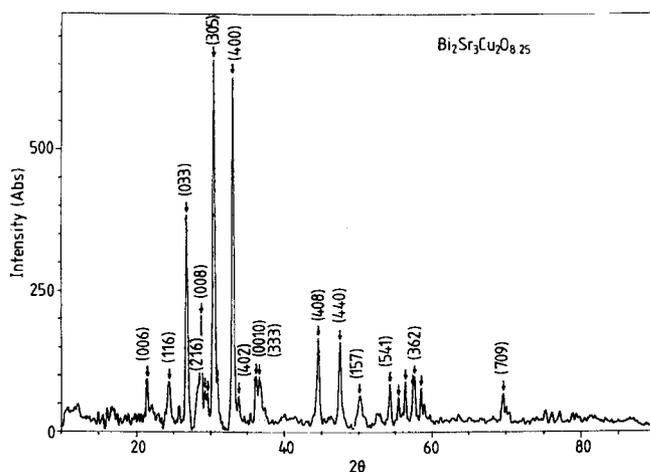

Figure 12. X-ray diffraction pattern of the $Bi_2Sr_3Cu_4O$ sample (Cu K_α radiation).

Table 5. X-ray powder diffraction data for $Bi_2Sr_3Cu_2O_{8.37}$ (Cu K_α). Lattice parameters for the orthorhombic subcell: $a = 10.833$ Å, $b = 10.807$ Å, $c = 24.694$ Å (this work); $a = 4.888$ Å, $b = 5.396$ Å, $c = 24.804$ Å [34].

N	H	K	L	$\sin^2\theta$ observed	$\sin^2\theta$ calculated	I/I_0
1	0	0	6	0.03476	0.03503	12.0
2	1	1	6	0.04499	0.04516	11.7
3	0	3	3	0.05379	0.05448	57.6
4	3	1	3	0.05931	0.05934	10.0
5	2	1	6	0.06025	0.06033	12.0
6	0	0	8	0.06188	0.06227	30.8
7	3	2	0	0.06554	0.06582	9.8
8	0	2	7	0.06804	0.06800	22.8
9	3	0	5	0.06941	0.06983	100.0
	0	3	5		0.07005	
10	4	0	0	0.08116	0.08089	95.4
11	4	0	2	0.08495	0.08479	8.6
12	0	0	10	0.09692	0.09730	12.5
13	3	3	3	0.09905	0.09998	12.5
14	3	2	6	0.10069	0.10085	7.6
15	4	0	8	0.14391	0.14317	23.5
16	4	4	0	0.16217	0.16218	22.6
17	1	5	7	0.17964	0.17974	8.8
18	5	4	1	0.20838	0.20866	11.3
19	4	5	3	0.21673	0.21666	7.4
20	4	5	4	0.22347	0.22347	11.0
21	0	6	7	0.23086	0.23057	8.6
22	3	6	2	0.23252	0.23229	11.7
23	0	2	15	0.23937	0.23925	8.8
24	7	0	9	0.32652	0.32655	7.4

To summarise, we would like to point out that the asterisk-marked phase 2302 exhibits a prominent crystallographic similarity to the two phases A and B, already discussed. It looks as if the basic tetragonal subcell, characteristic of the B phase, undergoes a gradual development consisting in duplication (the case of the 2302 phase) and triplication (the case of A phase) of its basal plane edges, accompanied by a gradual orthorhombic distortion of the original matrix. The c parameter (of about 24.6 Å) remains unchanged throughout the series.

A tentative explanation of the reason for such a phenomenon seems to lie in a high ability of the 2201 structural type to form various types of superstructures according to chemical composition. Some of them may occur as the result of an ordering of occupation of the appropriate atomic positions along the basal plane lattice parameters a and b. This becomes true with the absence of calcium (the A and 2302 phases). Some other phases (the 2212 and the 2223-type structures) exist just because of the presence of some additional quantities of calcium, and, as found by experiment, in this case the process of ordering evolves along the c axis of the matrix structure.

Just before submission of this work to print, we received preprints of the papers by Chakoumakos *et al* [33] and Ikeda *et al* [34] treating the same subject. We are glad that our results satisfactorily clarify all the problems marked in [33] as being doubtful or just improperly interpreted. Of them, the impossibility of

preparation of a pure 2201 structural type phase in samples of 2201 stoichiometry, the Sr deficient character of this structure type and the problem of so-called 'collapsed 2201 phase' seem to be most pronounced. Of the papers cited above, the results of Ikeda *et al* are, in general, very close to those presented herein. Some discrepancies can be noticed, but they refer to very complex and still discussable phase relations found within the system.

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