

# New aspects in the crystal chemistry of $(M_2Cu_2O_3)_m(CuO_2)_n$ -type ( $M = Ca, Sr, Y, Bi$ ) cuprates

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The structural regularities of  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type ( $M = Ca, Sr, Y, Bi$ ) cuprates with ladder-type planes have been considered. On the basis of the structural studies of the samples grown by floating-zone and flux methods, it was concluded that the phase  $(M_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$ , described as the  $m/n = 1/1$  member, with Cu-deficient Cu–O ribbons in the series  $(M_2Cu_2O_3)_m(CuO_2)_n$  can be treated as an individual structural type intermediate between  $SrCu_2O_3$  and incommensurate-type phases  $(M_2Cu_2O_3)_m(CuO_2)_n$  with  $m \neq n$ . The deficiency of the Cu sites in CuO ribbons is a particular crystal-chemistry feature of this structural type, in addition to the geometrical feature ( $m = n$ ). The structural type of the ‘Cu-deficient ladder’ can transform into the incommensurate-type phases  $(M_2Cu_2O_3)_m(CuO_2)_n$  ( $m/n = 5/7, 7/10, 9/13$  etc.) in the presence of free  $[CuO_4]^{6-}$  radicals in the melt. A realization of the  $(M_2Cu_2O_3)_m(CuO_2)_n$  phase with a particular  $m/n$  value is caused by the type of  $M$  cation. On the basis of recent data, the role of trivalent ions in the chemical composition of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds was also analyzed. The occurrence of the superconductivity in  $(Sr, Ca)CuO_2$  samples is discussed by analogy with cuprates of the infinite-layer structure.

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## 1. Introduction

Superconducting cuprates possess the  $CuO_2$  plane, which is assumed to play a principal role in high- $T_c$  superconductivity. Recently, particular attention has been paid to cuprates with the  $Cu_2O_3$  plane (Fig. 1), which has been predicted (Rice *et al.*, 1993) to manifest high- $T_c$  superconductivity. The superconductivity was indicated experimentally (Leonyuk *et al.*, 1996; Uehara *et al.*, 1996) in the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds (where  $M$  are divalent and trivalent cations), which contain the  $Cu_2O_3$ -type plane in one of two sublattices (Jensen *et al.*, 1993). However, a surprisingly large difference in the  $T_c$  values of various  $(M_2Cu_2O_3)_m(CuO_2)_n$  samples is noticed. On the one hand, the transition from the normal to the superconducting state was indicated at ambient pressure at 80–85 K (Leonyuk *et al.*, 1996) in the single crystals  $(M_2Cu_2O_3)_m(CuO_2)_n$  ( $M = Ca, Sr, Bi, Y$ ) with  $m/n$  values of 5/7 (Leonyuk, Babonas, Rybakov *et al.*, 1998; Szymczak *et al.*, 1999) and 1/1 (Leonyuk, Rybakov *et al.*, 1998). On the other hand, the samples  $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41.84}$  corresponding to the member  $m/n = 7/10$  of the series were superconducting at 3–4.5 GPa at 9–12 K (Uehara *et al.*, 1996). A superconductivity observed at 80 K in the related crystals of the  $SrCuO_2$ -type (Leonyuk, Babonas, Rybakov *et al.*, 1998) is considered as an anomaly so far. The difference in the experimental results

mentioned above requires a further study of the crystal-chemistry features of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type phases.

In the present paper, the results of our recent studies on the growth and structure of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds are summarized. The structures of various Sr/Ca cuprates will be characterized in §2. In §3, the model of the ‘Cu-deficient ladder’-type structure will be considered on the basis of the crystal-chemistry analysis of  $(M_2Cu_2O_3)_m(CuO_2)_n$  and related compounds. The commensurate-type version of the  $m/n = 1/1$  member in the series of  $(M_2Cu_2O_3)_m(CuO_2)_n$  compounds will be described. This model is used in §4 to develop the scheme of the phase formation for the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds grown by the floating-zone and flux methods. The structural features of the superconducting  $SrCuO_2$ -type crystals are discussed in §5. The provided crystal chemistry analysis of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds is summarized in §6.

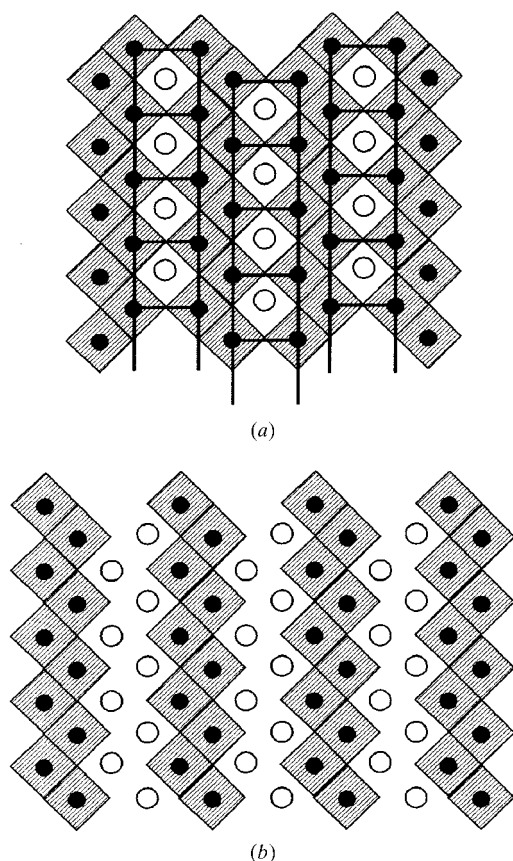
## 2. Ladder-type and related structures of Sr/Ca cuprates

By analogy with a widely studied class of silicates (Bokii, 1971), two groups of the Ca- and Sr-type structures can be distinguished in cuprates. On the one hand, in the Ca-type structures, the characteristic structural units are composed of

separate Cu—O squares and ordinary CuO<sub>2</sub> planes. On the other hand, the typical structural units in the Sr-type structures contain doubled Cu—O squares, dimers and ladder-type planes Cu<sub>2</sub>O<sub>3</sub> (Leonyuk, Babonas, Rybakov *et al.*, 1998). The structural type of cuprates containing both Ca and Sr depends on a relative concentration of cations Sr/Ca, (Sr, Ca)/Cu and on the growth conditions. The dependence of the structure on the Ca/Sr ratio is better revealed in the single crystals than in ceramic samples.

The summary of the formation of Ca/Sr cuprates is illustrated in Fig. 2, which is an extended version of the figure presented by Takano (1994). The scheme shows that cuprates with a ladder-type plane are represented by two structural types: (i) SrCu<sub>2</sub>O<sub>3</sub> (Sr<sub>n-1</sub>Cu<sub>n+1</sub>O<sub>2n</sub>, where n = 3, 5, 7, ...) (Hiroi *et al.*, 1991), a compound that is unstable at normal conditions; and (ii) (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(CuO<sub>2</sub>)<sub>n</sub>-type compounds, which are stable at normal conditions (Leonyuk, Babonas, Rybakov *et al.*, 1998). In addition to the Cu<sub>2</sub>O<sub>3</sub> planes, the (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(CuO<sub>2</sub>)<sub>n</sub>-type compounds possess another structural unit which is composed of relatively isolated Cu—O ribbons of the Cu—O squares sharing edges.

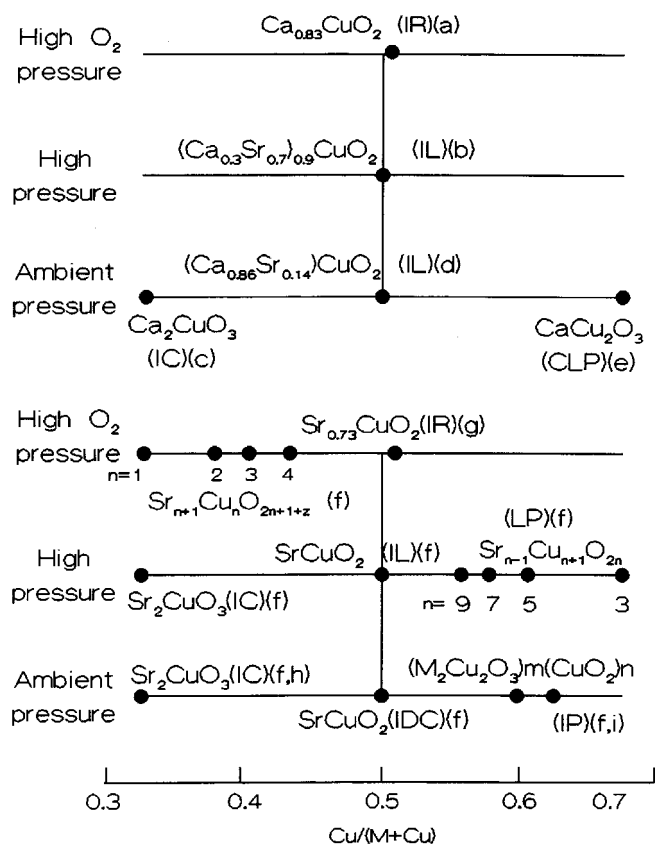
The structure of (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(CuO<sub>2</sub>)<sub>n</sub> compounds can be efficiently analyzed (Leonyuk *et al.*, 1999) in the fragment



**Figure 1**  
The projection of the structures for (a) SrCu<sub>2</sub>O<sub>3</sub> in the (ab) plane and (b) SrCuO<sub>2</sub> in the (bc) plane. Full and empty circles are Cu and Sr atoms, respectively, the O atoms are located at the corners of the Cu—O squares. The Sr atoms as well as the neighboring Cu—O double chains in SrCuO<sub>2</sub> are located above and below the plane of the figure.

approximation. From this point of view, the (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>m</sub>-(CuO<sub>2</sub>)<sub>n</sub>-type compound is considered as a polysome AB in the polysomatic series with end members MCu<sub>2</sub>O<sub>3</sub> (A) and M<sub>1-x</sub>CuO<sub>2</sub> (B). The structures of polysomes are represented by the combination of mA and nB slabs characteristic of two end members A and B.

A formation of various ladder-type and related structures follows from the phase diagram of the SrO—CuO system (Slobodin *et al.*, 1990). Three compounds, SrCu<sub>2</sub>O<sub>3</sub>, Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> and Sr<sub>3</sub>Cu<sub>5</sub>O<sub>8</sub>, having very similar powder diffraction patterns were fixed at close growth conditions. The compound Sr<sub>3</sub>Cu<sub>5</sub>O<sub>8</sub> of orthorhombic symmetry (a = 3.956, b = 13.399, c = 11.464 Å) crystallized at 1253 K. A structural transition for Sr<sub>3</sub>Cu<sub>5</sub>O<sub>8</sub> was noticed at 1233 K. The Sr<sub>3</sub>Cu<sub>5</sub>O<sub>8</sub> compound was concluded to be the most stable. The SrCu<sub>2</sub>O<sub>3</sub> compound is stable only at high pressures. The incommensurate-type phase Sr<sub>14</sub>Cu<sub>24</sub>O<sub>41</sub> is probably not a primary compound, *i.e.* there is no melt that would be in equilibrium



**Figure 2**  
The identified phases of complex Ca (upper part) and Sr (lower part) cuprates obtained at various growth conditions for different cation composition Cu/(M+Cu), where M = Ca, Sr. The particular Cu-containing structural units are isolated Cu—O ribbons (IR), infinite layers (IL), isolated Cu—O chains (IC) and isolated double chains (IDC), ladder planes Cu<sub>2</sub>O<sub>3</sub> (LP), corrugated ladder planes (CLP), and a combination of ladder planes and the planes of the Cu—O ribbons in incommensurate phases (IP) (M<sub>2</sub>Cu<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(CuO<sub>2</sub>)<sub>n</sub>. The corresponding structures were analyzed by (a) Meijer *et al.* (1998); (b) Azuma *et al.* (1992); (c) Teske & Müller-Buschbaum (1970); (d) Siegrist, Zahurak *et al.* (1988); (e) Teske & Müller-Buschbaum (1969a); (f) Takano (1994); (g) Karpinski *et al.* (1997); (h) Teske & Müller-Buschbaum (1969b); (i) Jensen *et al.* (1993) and Leonyuk, Rybakov *et al.* (1998).

**Table 1**

The characteristics (average cation radius  $r_M$ , formal Cu valence  $V_{Cu}$ , lattice parameters and  $T_c$  values) of the phases indicated in the investigated group of  $(M_2Cu_2O_3)_m(CuO_2)_n$  crystals.

Sample N	$r_M$ (Å)	$V_{Cu}$	Chemical composition	$a$ (Å)	$b$ (Å)	$c$ (Å)	$T_c$ (K)†
<i>m/n = 1/1, Fmmm</i>							
1031	1.28	2.94	$(Sr_{0.49}Ca_{0.48}Bi_{0.03})_2Cu_{3.38}O_{5.98}$	11.360 (4)	12.906 (6)	3.9067 (8)	87 [6]
1292	1.38	1.87	$(Y_{0.12}Pr_{0.29}Sr_{0.56}Ba_{0.03})_2Cu_{3.82}O_{6.00}$	11.331 (4)	12.972 (4)	3.9672 (8)	NSC [6]
1369	1.28	1.64	$(Ca_{0.96}Sr_{0.99}Bi_{0.05})(Cu_{4.53}Al_{0.17})O_6$	11.393 (5)	13.042 (5)	3.9137 (9)	NSC
<i>m/n = 5/7, F222</i>							
1317	1.26	2.48	$(Sr_{3.5}Y_{0.1}Ca_{5.9}Al_{0.1}Bi_{0.3}Pb_{0.1})(Cu_{15.1})O_{29}$	11.319 (2)	12.763 (2)	19.49 (1)	80 [2]
800	1.27	2.31	$(Ca_{4.86}Sr_{4.42}Bi_{0.05})Cu_{17}O_{29}$	11.349 (7)	12.896 (5)	19.49 (3)	84 [5]
1098	1.28	2.39	$(Ca_{5.84}Sr_{4.02}Bi_{0.14})Cu_{15.84}O_{29}$	11.346 (1)	12.809 (3)	19.52 (1)	82 [5]
1380	1.26	2.30	$(Ca_{5.03}Sr_{3.48}Bi_{0.31})Cu_{16}O_{29}$	5/7			80
1298	1.29	2.29	$(Sr_{6.1}Y_{0.4}Ca_{3.3}Bi_{0.1}Pb_{0.1})Cu_{16.4}O_{29}$	11.346 (3)	12.996 (3)	19.586 (9)	NSC [2]
1366	1.28	2.24	$(Sr_{5.35}Ca_{3.7}Bi_{0.3}Y_{0.21}Al_{0.1})Cu_{17}O_{29}$	5/7			NSC
1382	1.24	2.39	$(Ca_{5.4}Sr_{2.43}Bi_{0.46})(Cu_{16.57}Al_{0.43})O_{29}$	5/7			NSC
<i>m/n = 7/10, Cmma</i>							
1285	1.20	2.04	$(Y_{1.3}Nd_{3.7}Sr_{2.5}Ca_{6.5})(Cu_{23.2}Ca_{0.4}Sr_{0.4})O_{41}$	11.294 (6)	12.515 (2)	27.544 (8)	NSC [21]
<i>m/n = 9/13</i>							
1284	1.26	2.01	$(Y_{2.2}Nd_{5.5}Sr_{9.7}Ba_{0.6})Cu_{31}O_{53}$	11.2962 (14)	12.8850 (9)	3.9686 (3)	NSC [21]
				11.2936 (6)	12.8815 (10)	2.7213 (2)	
1289	1.27	2.04	$(Y_{2.2}Pr_{5.2}Sr_{10.0}Ba_{0.6})Cu_{30.7}O_{53}$	11.3183 (8)	12.967 (2)	3.9616 (6)	NSC [21]
				11.3176 (1)	12.970 (2)	2.7348 (6)	
1286	1.26	2.15	$(Y_{1.3}Sm_{3.2}Sr_{3.7}Ca_{9.8})Cu_{30.5}O_{53}$	11.312 (2)	12.946 (2)	3.9510 (6)	NSC [21]
						2.7353 (6)	

† NSC denotes nonsuperconducting crystals.

with this compound. This assumption was confirmed by the data presented by Vallino *et al.* (1989): only one sublattice parameter  $c1 \approx 3.9$  Å was indicated instead of  $c = 27$  Å typical for  $Sr_{14}Cu_{24}O_{41}$ . Siegrist, Schneemeyer *et al.* (1988) also studied the single crystals with the lattice parameter  $c \approx 3.9$  Å and the superstructure leading to a sevenfold increase of the  $c$  axis.

### 3. Structural type $(M_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$

It is reasonable to assume that in the group of  $(M_2Cu_2O_3)_m(CuO_2)_n$  compounds the parameters  $m$  and  $n$  define an individual modification of the incommensurate-type phase. The most investigated phases are  $m/n = 7/10$  (Siegrist, Schneemeyer *et al.*, 1988) and  $m/n = 5/7$  (Jensen *et al.*, 1993). The phase  $m/n = 9/13$  was also indicated (Leonyuk, Babonas, Maltsev, Shvanskaya & Dapkus, 1998) in which the  $M$  sites were occupied by large rare-earth elements and Ba. In what follows below, we shall discuss the arguments why the structure with  $m/n = 1/1$ , in which only the parameter  $c \approx 3.9$  Å characteristic of the ladder-type plane is indicated, can be considered as an individual modification. The model for the formation of various  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type phases will also be considered.

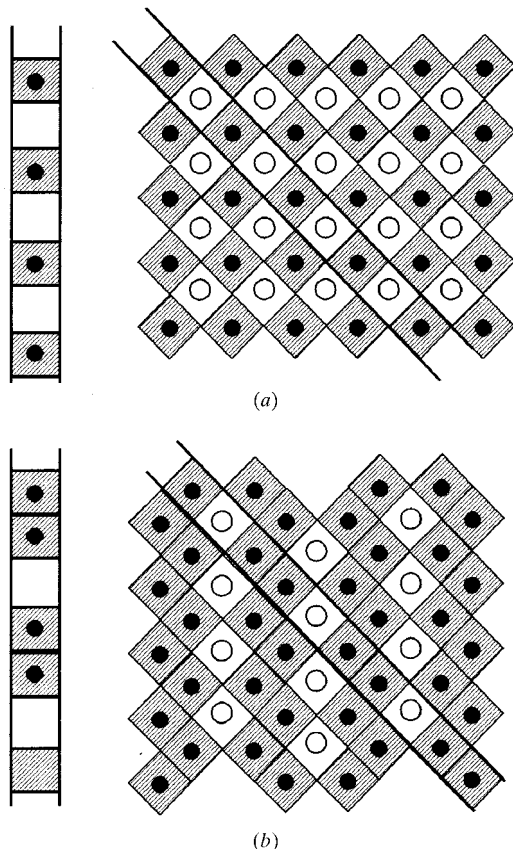
In the recent studies of  $(M_2Cu_2O_3)_m(CuO_2)_n$  compounds, the phase  $m/n = 1/1$  (Table 1) was indicated, which was similar to that for  $(Sr, Y)Cu_{1.71}O_3$  (space group  $Fmmm$ ,  $a = 11.329$ ,  $b = 12.965$ ,  $c = 3.936$  Å) observed by Siegrist, Schneemeyer *et al.* (1988). The single-crystal structural refinement was carried out for two samples and the detailed data were presented by Leonyuk, Rybakov *et al.* (1998). The set of reflections in the

XRD pattern for a superconducting single crystal was described with a high accuracy ( $R = 3.4\%$ ) by the model of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type phase in a commensurate version ( $m = n = 1$ ) [space group  $Fmmm$ ,  $a = 11.360$  (4),  $b = 12.906$  (6),  $c = 3.9067$  (8) Å] with a disordered plane of the Cu—O ribbons. It should be noted that the sample under consideration could also be described in the ‘incommensurate version’. In the detailed studies of the diffraction pattern for this sample (Schwer, 1998), the following parameters of two sublattices (1, 2) have been determined:  $a1 = 11.359$  (1),  $b1 = 12.913$  (2),  $c1 = 3.9057$  (4) Å and  $a2 = 11.364$  (1),  $b2 = 12.910$  (1),  $c2 = 2.7522$  (4) Å. In the model of the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type structure, the commensurate approximation was obtained for  $m/n = 31/44 = 0.704$  with the average value  $c = 121.08$  Å. A simpler commensurate version corresponded to the value  $m/n = 12/17 = 0.705$ . In both cases, the  $m/n$  values were close to that ( $7/10 = 0.7$ ) for the most frequently met  $(M_2Cu_2O_3)_7(CuO_2)_{10}$ -type compound. However, the reflections from the sublattice with the Cu—O ribbons were weaker by an order of magnitude as compared to those from the sublattice with the ladder plane, presumably due to a deficiency of the Cu—O ribbons. As a result of the difference in the intensity of the reflections assigned to two sublattices, the  $c1$  value can be selected as a basic parameter for the whole structure considered in the commensurate approximation for  $m/n = 1/1$ . Therefore, the characterization of the structure by  $m/n = 1/1$  illustrates rather that the fragment containing the ladder plane is better developed than another fragment. The main feature of such a structure is the deficiency of the Cu—O ribbons close to 1/3 (occupancy 0.52–0.68). Similar values of the Cu-site occupation in various

samples (Leonyuk, Rybakov *et al.*, 1998; Siegrist, Schneemeyer *et al.*, 1988) can hardly be accidental and can be considered as a typical feature of this phase.

The phase  $\text{Sr}_3\text{Cu}_5\text{O}_8$  is close to  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  with  $m/n = 1/1$  by the lattice parameters (Table 1) and diffraction pattern (Table 2). The chemical formula  $\text{Sr}_3\text{Cu}_5\text{O}_8$  indicates the phase to be Cu deficient as compared to incommensurate phases  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  with  $m/n = 5/7$  or  $m/n = 7/10$ . The ratio  $M/\text{Cu}$  in  $\text{Sr}_3\text{Cu}_5\text{O}_8$  is 0.6, while it is 0.70 and 0.71 in  $M_{10}\text{Cu}_{17}\text{O}_{29}$  and  $M_{14}\text{Cu}_{24}\text{O}_{41}$ , respectively, and 0.50 in  $\text{SrCu}_2\text{O}_3$ . Therefore, it is reasonable to assume that the phase with parameter  $c = c1 \sim 3.9 \text{ \AA}$  is intermediate between  $\text{SrCu}_2\text{O}_3$  and  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ . The following model can be proposed to explain the mechanism for the formation of this phase.

Let us assume that the ordinary  $\text{CuO}_2$  plane in the infinite-layer structure  $\text{CaCuO}_2$  and the ladder-type plane  $\text{Cu}_2\text{O}_3$  in  $\text{SrCu}_2\text{O}_3$  are decomposed into the isolated Cu—O ribbons of the Cu—O squares sharing edges (Fig. 3). The Cu sites in the Cu—O ribbons will be occupied by 1/2 and 2/3 for cuprate-forming cations Ca and Sr, respectively, owing to the difference in cation radii. It should be noted that the phase  $\text{SrCu}_2\text{O}_3$  is obtained only at high pressure (Hiroi *et al.*, 1991) (Fig. 2). The instability of the  $\text{SrCu}_2\text{O}_3$  phase at ambient pressure may be due to the shape of the Sr polyhedron, which is a  $c$ -elongated tetragonal prism fixed by the Cu—O squares. When Sr



**Figure 3**  
The separation of (a) ordinary  $\text{CuO}_2$  and (b) ladder  $\text{Cu}_2\text{O}_3$  planes into isolated Cu—O ribbons.

**Table 2**

Comparison of XRPD patterns (interplane distances  $d_{hkl}$  normalized intensities  $II_{\text{max}}$  and  $hkl$  values) for sample N1 characterized in Fig. 4(a),  $\text{Sr}_3\text{Cu}_5\text{O}_8$  [ $F$  symmetry,  $a = 11464$ ,  $b = 13339$ ,  $c = 3956 \text{ \AA}$  (Slobodin *et al.*, 1990)] and sample N1369 [main 'Cu-deficient ladder' phase, space group  $Fmmm$ ,  $a = 11393$  (5),  $b = 13042$  (5),  $c = 39137$  (9)  $\text{\AA}$ ].

N1		$\text{Sr}_3\text{Cu}_5\text{O}_8$		N1369		$hkl$
$d_{hkl}$ ( $\text{\AA}$ )	$II_{\text{max}}$ (%)	$d_{hkl}$ ( $\text{\AA}$ )	$II_{\text{max}}$ (%)	$d_{hkl}$ ( $\text{\AA}$ )	$II_{\text{max}}$ (%)	
3.5947	1	3.60	5	6.5954	3	020
3.3499	29	3.35	15	3.2533	30	111
2.8925	100	2.89	100	2.8239	100	102
2.8704	8	2.87	63			240
2.6890	10	2.69	50	2.6631	10	131
2.6369	7	2.64	8	2.6059	5	311
2.3393	1	2.34	5			420
2.1781	11	2.18	39	2.1412	8	331
1.9707	1	1.978	14			440
1.9125	6	1.911	11	1.8936	1	002
1.8913	1	1.897	8	1.8217	2	600
		1.870	4			022
1.8388	8	1.837	13	1.8183	2	202
1.8127	3	1.812	19	1.7913	3	620
1.6752	22	1.676	20			531
1.6329	1	1.632	15			080
1.5940	2	1.593	8			242
		1.517	10			551
						371

cuprate is grown at ambient pressure, the characteristic Sr polyhedron is the anti-cube, which can be formed by the  $45^\circ$  rotation of two neighboring ladder planes. However, each second Cu—O ribbon should be removed from the 'rotated' plane as Sr cannot be located above the Cu atoms. As a result, the structural unit of two ladder-like planes  $(M\text{Cu}_2\text{O}_3)(M\text{Cu}_2\text{O}_3) = (M_2\text{Cu}_2\text{O}_3)(\text{Cu}_2\text{O}_3)$  transforms into the building unit  $(M_2\text{Cu}_2\text{O}_3)(\text{CuO}_3)$  (Leonyuk, Rybakov *et al.*, 1998). A high formal Cu valence (3+) in the plane of the Cu-deficient  $\text{CuO}$  ribbons is an important parameter for a characterization of such a Cu-deficient ladder structure. From the viewpoint of crystallography (Veblen, 1991), the process of the phase formation described above can be considered as a particular version of chemical twinning.

We have also grown the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type crystals with  $c = c2 \sim 2.75 \text{ \AA}$ . It is reasonable to assume that these crystals represent the second version of the  $m/n = 1/1$ -type structure, in which the second fragment containing the Cu—O ribbons is better developed. This structure can be considered as originating from the  $M_{1-x}\text{CuO}_2$ -type structure, which as a separate compound is stable only at high pressures. In this case, the formation of the structural fragments can be represented as the following process:  $(M_{1-x}\text{CuO}_2)(M_{1-x}\text{CuO}_2) \rightarrow (M_{2-x}\text{CuO}_2)(\text{CuO}_2)$ . Cations are assigned to the first term on the right-hand side with a characteristic deficiency of the  $M$  sites. The second term is assumed to be transformed into the ladder-type plane to develop the overall structure of the  $m/n = 1/1$  type and further to the structure of the  $m \neq n$  type:  $(M_{2-x}\text{CuO}_2)(\text{CuO}_2) \rightarrow (M_{2-x}\text{CuO}_2)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma}) \rightarrow (M_{2-x}\text{CuO}_2)(\text{Cu}_2\text{O}_3) \rightarrow (M_{2-x}\text{CuO}_2)_n(\text{Cu}_2\text{O}_3)_m$ . It should be noted that in this case the formation of the  $M$ -deficient phases is expected as it was noticed in the  $m/n = 5/7$ -type compounds. The complexes, which are necessary for the development of

**Table 3**

The temperature–concentration conditions (load composition, maximum heating temperature  $T_{\max}$ , the time  $t_{\max}$  at  $T_{\max}$ , cooling rate  $\nu$ , decanting temperature  $T_{\text{dec}}$ ) for the phase formation in the system Bi–Sr–Ca–Cu–O.

Load composition †	$T_{\max}$ (K)	$t_{\max}$ (h)	$\nu$ (K h <sup>-1</sup> )	$T_{\text{dec}}$ (K)	Crystal grown ‡
4–3–3–4	1253	–	4	1123	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ SC (N1317)
3.2–3–3–4 +0.8 Cd	1253	–	4	1123	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ SC (N1098, N1380)
4–3.2–2.8–4	1253	–	4	1123	$(M_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$ SC (N1031)
2–2–2–4	1253	–	4	1123	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ SC (N800)
4–2–4–4	1313	–	4	1158	$\text{Ca}_2\text{CuO}_3$ (N1377)
3.36–3–3–4 +0.64 Pb	1313	–	2	1153	$\text{Ca}_2\text{CuO}_3$ (N1381)
3.60–4–2.96–6 +0.40 Pb +0.04 Y	1321	–	2	1160	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ NSC (N1366)
3.60–4–2.96–6 +0.40 Pb +0.04 In	1320	–	2	1160	$(M_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$ NSC (N1369)
3.2–3–3–4 +0.8 Cd	1179	10	0.8	1129	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ (N1396)
3–3–3–6 +1.0 Cd	1180	10	0.8	1137	$(M_2\text{Cu}_2\text{O}_3)_5(\text{CuO}_2)_7$ (N1403)
3–3–3–6 +1.0 Cd	1194	10	1.5	1151	$a = 3.41, b = 5.12, c = 16.42 \text{ \AA}, \alpha = 98.64, \beta = 95.90, \gamma = 90.00^\circ$ (N1405)
3–3–3–6 +1.0 Cd	1196	10	0.2	1171	$a = 2.75, b = 13.38, c = 13.05 \text{ \AA}$ (N1409)

† The sequence of the numbers denotes the relative amount of Bi<sub>2</sub>O<sub>3</sub>–SrO–CaO–CuO, respectively. ‡ SC denotes superconducting crystal.

the process described above, are present in the melt: the complete Cu–O ribbons are the fragments of CuO and the isolated CuO squares are the fragments of Bi<sub>2</sub>CuO<sub>4</sub> resulting from the interaction between CuO and Bi<sub>2</sub>O<sub>3</sub>. The conclusion that the Cu- and M-deficient phases can be possibly formed is of great importance: according to our preliminary data, only such deficient phases manifest the superconductivity at normal pressures.

As noted above, the structure of the  $(M_2\text{Cu}_2\text{O}_3)(\text{CuO}_3)$ -type compound with a better developed fragment containing the ladder plane and characterized by the 1/3 deficiency of the Cu sites in the Cu–O ribbons can be called the ‘Cu-deficient ladder-type structure’. It is composed of two subsequent Cu–O planes: the ladder ( $\text{Cu}_2\text{O}_3$ ) and deficient-ladder ( $\text{CuO}_3$ ) type planes. The latter plane, which has been originated from the ladder plane, consists of the isolated CuO ribbons with deficient Cu sites. The vacant Cu sites in such a ‘deficient-ladder’ plane can be filled if the melt is enriched by free Cu–O building units, *i.e.*  $[\text{CuO}_4]^{6-}$  radicals. With increasing Cu concentration, the ‘deficient-ladder’ plane transforms according to the following sequence:  $(\text{CuO}_3) \rightarrow (\text{Cu}_{1+\delta}\text{O}_{3-\gamma}) \rightarrow (\text{Cu}_{1+\delta}\text{O}_{2+\gamma}) \rightarrow (\text{CuO}_2)$ . As a result, the incommensurate-type  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  compounds can be formed with the  $m/n$  values depending on the type of M cations. The formal Cu valence in  $(M_2\text{Cu}_2\text{O}_3)(\text{CuO}_3)$  is higher than 2+ for divalent and trivalent cations M, indicating the possibility of hole doping (Carter *et al.*, 1996; Osafune *et al.*, 1997).

The model discussed above shows that the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type compounds with  $m/n = 1/1$ , in which one fragment is more developed than another, are less homogeneous regarding the chemical composition, as compared to the other members ( $m \neq n$ ) of this series. With respect to the occupation of the Cu sites, the structural type of the Cu-deficient ladder can be considered as intermediate between  $M\text{Cu}_2\text{O}_3$  and  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type phases with  $m/n = 5/7, 7/10, 9/13$ . According to the structural data, the Cu deficiency is still noticed in the phase  $m/n = 5/7$  and disappears in the phases with higher  $m/n$  values.

It is reasonable to emphasize a variety of the incommensurate-type structures. In addition to well known  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type phases with  $m/n = 5/7, 7/10$ , the Cu-deficient ladder-type compound  $(M_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$  of two possible modifications should be taken into account. The physical properties of various samples can be caused by the formation of different phases or modifications.

#### 4. Role of the growth conditions in the formation of $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ compounds

The formation of complex cuprates like  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  depends strongly on the growth conditions. The role of the initial load composition on the phase formation and the specific features of the various growth methods will be discussed. The difference between the samples grown from the melt and by a floating-zone method is emphasized.

As noted above, various phases were indicated in the investigations of the system SrO–CuO (Slobodin *et al.*, 1990). When Bi oxide is added into the initial load, the phase diagram becomes more complicated (Slobodin *et al.*, 1991). However, the co-crystallization of Sr cuprates with Bi cuprate of the Bi-2201-type occurs below 1133 K. The Bi-2212-type phase is absent in the primary phases of the Bi<sub>2</sub>O<sub>3</sub>–SrO–CuO system (Nakamura *et al.*, 1991) and can be formed below 1073 K as a result of a decomposition of the Bi-2201-type phase taking into account the other components of the melt. On the other hand, the presence of Bi<sub>2</sub>O<sub>3</sub> favors the crystal growth owing to an increase of the melt mobility and mass transfer. The addition of solvent results in a significant decrease of the melting temperature of the initial load to 1253–1243 K. As a result, in the primary crystallization process, the SrCuO<sub>2</sub>-phase is not formed and the quality of the samples with a ladder-type structure should be improved.

When rare-earth (RE) oxides are added to the melt composed of Sr, Cu and Bi oxides, the crystallization temperature of the Bi-2212-type phase increases (Leonyuk *et al.*, 1995). However, the co-crystallization of the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type phases with Bi-2212 and SrCuO<sub>2</sub>

can be avoided using the decanting technique. On the other hand, the RE-doped  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds can be obtained using the load containing RE oxides.

The presence of oxygen pressure in the floating-zone method results in an increase of the melt mobility. In addition, the decomposition  $4CuO \rightarrow 2Cu_2O + O_2$  starting at 1273 K is suppressed. However, the use of the oxygen pressure during the growth from the melt with flux is not efficient because of a relatively low temperature and high melt mobility.

Recently, we have obtained a series of incommensurate  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type and 'deficient-ladder'  $(Sr_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$ -type crystals (Tables 1, 2) using the melt of the composition close to  $4BiO_{1.5}-3SrO-3CaO-4CuO$  (Table 3). The alumina crucibles with a reversed temperature gradient were heated up to 1373 K. The melt was decanted at 1173 K. The single crystals of the  $(M_2Cu_2O_3)_m(CuO_2)_n$  phase were easily separated from the crust composed of isometric transparent  $(Ca, Sr)Al_2O_5$  crystals. The structural characteristics (Tables 1 and 3) were obtained by a single-crystal structure determination.

It should be noted that the XRPD patterns are very similar for all the members of the  $(M_2Cu_2O_3)_m(CuO_2)_n$  series. Therefore, in order to distinguish the  $(M_2Cu_2O_3)_m(CuO_2)_n$ -type compounds with different  $m/n$  values, a Rietveld analysis of the XRPD pattern or a single-crystal determination in the commensurate approximation should be performed.

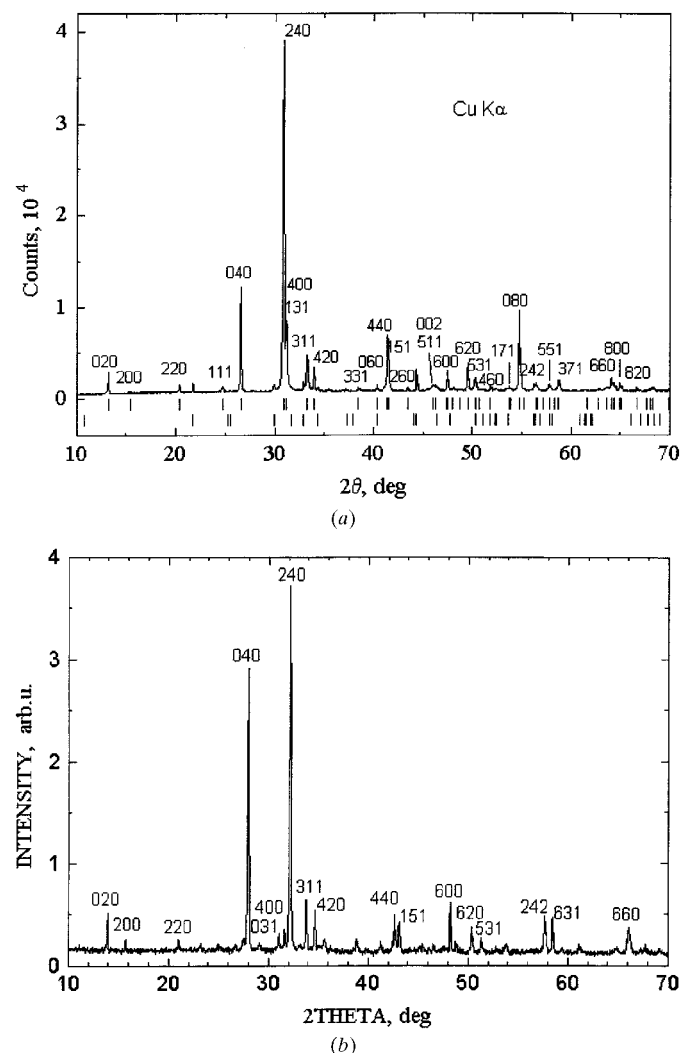
Fig. 4(a) presents the Rietveld analysis of the XRPD data for the sample (Vetkin *et al.*, 1998) grown by the floating-zone method at the oxygen pressure of 2 atm with copper oxide added directly into the initial crystallization zone. The sample was grown from the ceramic rod of the chemical composition corresponding to the stoichiometry of  $Sr_{14}Cu_{24}O_{41}$ . It was obtained that the sample represented the mixture of two phases,  $(Sr_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$  (space group  $Fmmm$ ,  $a = 11.473$ ,  $b = 13.406$ ,  $c = 3.944$  Å) and  $SrCuO_2$  (space group  $Cmcm$ ,  $a = 3.571$ ,  $b = 16.329$ ,  $c = 3.912$  Å). The XRPD pattern for the main phase was close to that for  $Sr_3Cu_5O_8$  (Slobodin *et al.*, 1990) (Table 2) and it was very similar to that obtained for the  $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41+\delta}$  sample (Isobe *et al.*, 1998) grown using a hot isostatic press apparatus at high pressure (1.96 GPa) and ascribed to the group of  $(M_2Cu_2O_3)_7(CuO_2)_{10}$ -type compounds.

Fig. 4(b) presents the XRPD data for the sample obtained by the floating-zone method using the load of the composition corresponding to  $(Ca, Y, Sr)_{14}Cu_{24}O_{41}$ . In this case, the amount of impurity phases was low and their reflections were too weak to determine their lattice parameters. The main phase of the symmetry  $Fmmm$  with lattice parameters  $a = 11.320$ ,  $b = 12.761$ ,  $c = 3.903$  Å corresponded to the structural type  $[(Ca, Sr, Y)_2Cu_2O_3](Cu_{1+\delta}O_{2+\gamma})$ . The quality of the sample was higher compared to the sample described above owing to the influence of yttrium, which caused an increase of the crystallization temperature. As yttrium atoms did not enter  $SrCuO_2$ , the 'Cu-deficient-ladder' phase was dominant during the crystallization process.

On the basis of the experimental data available, it is reasonable to propose the following scheme for the crystal-

lization of the phases by the floating-zone and flux methods. In the process of growth by the floating-zone method from the load  $14SrO + 24CuO$  (64 mol% CuO), the phase  $SrCuO_2$  is primarily formed. When the growth occurs at a high pressure, a two-leg ladder  $SrCu_2O_3$  can be obtained but only partially because of a lower copper content in the melt. At lower temperatures, the compound  $SrCuO_2$  can react with a residual melt leading to the formation of the phase  $(Sr_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$  or  $\beta$ - $Sr_3Cu_5O_8$ , which transforms partially to  $\alpha$ - $Sr_3Cu_5O_8$ .

At an early stage of the crystal growth by a flux method from a Bi-containing melt of the composition  $2Bi_2O_3 + 3SrO + 3CaO + 4CuO$ , copper and bismuth oxides react primarily forming  $Bi_2CuO_4$  with isolated Cu—O squares (Leonyuk, Babonas, Pushcharovskii & Maltsev, 1998). As a result, the Cu—O ribbons originating from CuO are broken and the



**Figure 4**  
The XRPD patterns for the samples grown by the floating-zone method from the melt of composition corresponding to (a)  $Sr_{14}Cu_{24}O_{41}$  (sample N1) and (b)  $(Ca, Y, Sr)_{14}Cu_{24}O_{41}$  (sample N2). Two sets of reflections shown in (a) correspond to  $(Sr_2Cu_2O_3)(Cu_{1+\delta}O_{2+\gamma})$  (space group  $Fmmm$ ,  $a = 11.473$ ,  $b = 13.406$ ,  $c = 3.944$  Å) and  $SrCuO_2$  (space group  $Cmcm$ ,  $a = 3.571$ ,  $b = 16.329$ ,  $c = 3.912$  Å), respectively.

viscosity of the melt lowers. The next two stages are similar to those for the floating-zone method resulting in the formation of  $\text{SrCu}_2\text{O}_3$  and  $(\text{Sr}_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$ . However, owing to the presence of the isolated  $\text{CuO}_4$  complexes in the melt, the filling of the Cu-deficient Cu—O ribbons is favored leading to the formation of the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type compound with a particular  $m/n$  value dependent on the  $M$  type.

In the presented scheme, it is assumed that the growth of incommensurate-type phases is the result of the complex formation in the melt at the second stage. A low growth rate and the presence of solvent, which breaks the Cu—O ribbons in CuO into separate complexes, favor this process. This scheme was confirmed by a successful crystallization of the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$ -type compounds in the system RE—Ba, Sr—Cu—O in the presence of solvent  $\text{BaCuO}_2$  (Table 3), which is the second cuprate containing the isolated Cu—O structural units (Leonyuk, Babonas, Pushcharovskii & Maltsev, 1998).

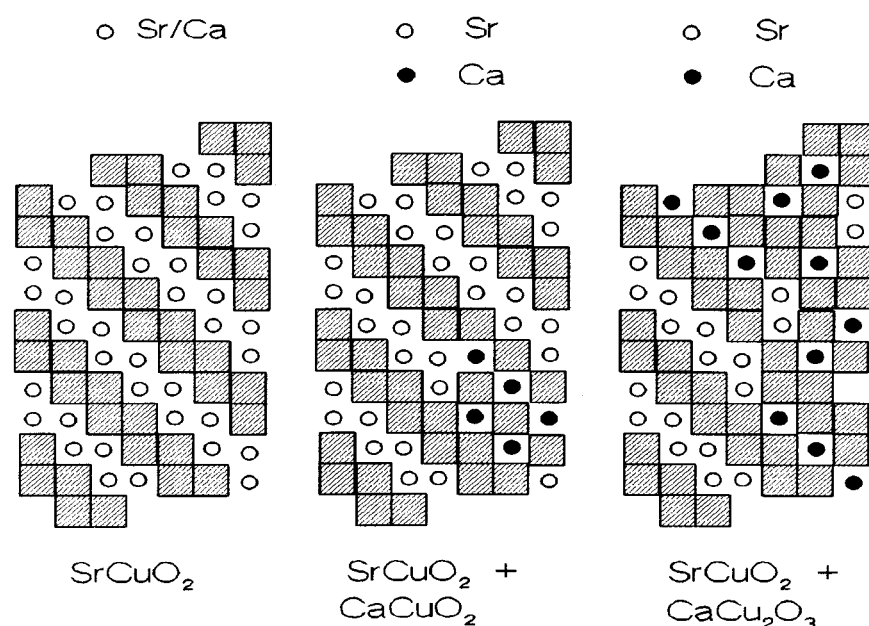
### 5. Particular features of the $\text{SrCuO}_2$ structural type

Recent studies (Leonyuk, Babonas, Rybakov *et al.*, 1998) have shown that some (Sr, Ca) $\text{CuO}_2$  crystals of the structural type  $\text{SrCuO}_2$  were superconducting at 80 K. However, this feature was not characteristic of all the samples from the same batch. Detailed investigations have shown that the local deviation of cation composition did not exceed 1% at the average value  $\text{Sr}/\text{Ca} = 0.53/0.47$  in nonsuperconducting samples. In contrast, in the superconducting (Sr, Ca) $\text{CuO}_2$  crystals of the  $\text{SrCuO}_2$ -type structure, the cation composition varied in a wider range of 5% at a Ca amount exceeding that of Sr. A possible interpretation of this experimental observation can be

proposed on the basis of the structural model for Ca(Sr) cuprates described above and the similarity between the structures of Ca and Sr cuprates.

An analogous alternate stacking of the Cu—O planes and the layers of cations composes the structure of  $\text{SrCu}_2\text{O}_3$  and  $\text{CaCuO}_2$  (Leonyuk, Babonas, Rybakov *et al.*, 1998). However, the Cu-containing units are different in Sr and Ca cuprates because of the difference in cation radii. In  $\text{SrCu}_2\text{O}_3$  and  $\text{CaCuO}_2$ , the characteristic units are the ladder-type plane (Cu—O squares sharing corners and edges) and the ordinary plane (Cu—O squares sharing corners), respectively. As a rule, these two cuprates are non-superconducting. However, in  $(\text{Sr}_{1-x}\text{Ca}_x)_{1-y}\text{CuO}_2$  with the infinite-layer-type structure, the superconductivity at 110 K was observed (Azuma *et al.*, 1992). The structural analysis (Adachi *et al.*, 1993; Shaked *et al.*, 1995) and high-resolution electron microscopy (Hiroi *et al.*, 1993) have shown that the  $(\text{Sr}_{1-x}\text{Ca}_x)_{1-y}\text{CuO}_2$  samples were multiphased and contained small superconducting fractions of another structural type. It is reasonable to assume that the inclusions were formed due to a local ordered arrangement of Sr and Ca.

A similar phenomenon is highly probable in the superconducting samples (Sr, Ca) $\text{CuO}_2$ . In the (Sr, Ca) $\text{CuO}_2$  compound with average  $\text{SrCuO}_2$ -type structure, the inclusions can be formed in the regions with predominant local Ca amount with the structural type typical for Ca cuprates (Fig. 5). As in the case of the (Sr, Ca) cuprate with an infinite layer structure (Azuma *et al.*, 1992), the local ordering of the Ca and Sr atoms may be responsible for the occurrence of new structural phases. Additional studies should be performed in order to estimate the role of the interphase boundaries at the intergrowth of cuprates of various structures.



**Figure 5**

The scheme of the defect formation in the ladder plane of the (Sr, Ca) $\text{CuO}_2$ -type structure owing to the local ordering of cations.

### 6. Conclusions

Detailed analysis of the regularities in the structure of ladder-type crystals grown by floating-zone and flux methods has shown that:

(i) the phase  $(M_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$  described earlier (Leonyuk, Rybakov *et al.* (1998) as the member  $m/n = 1/1$  in the series  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  can be considered as an individual ‘Cu-deficient ladder-type’ structure intermediate between  $\text{SrCu}_2\text{O}_3$  and incommensurate phases  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  ( $m \neq n$ );

(ii) in the absence of solvent, the compound of ‘Cu-deficient ladder-type’ structure  $(M_2\text{Cu}_2\text{O}_3)(\text{Cu}_{1+\delta}\text{O}_{2+\gamma})$  is preferably formed, even from the load corresponding to the chemical composition of the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  ( $m \neq n$ )-type compounds;

(iii) the formation of the  $(M_2\text{Cu}_2\text{O}_3)_m(\text{CuO}_2)_n$  ( $m/n = 5/7, 7/10, 9/13, \dots$ ) phases

occurs owing to the presence of free radicals  $[\text{CuO}_4]^{6-}$  in the melt;

(iv) several modifications of the incommensurate-type phases with different physical properties can be formed depending on the chemical composition and the growth conditions;

(v) the local ordering of cations in the  $(\text{Sr}, \text{Ca})\text{CuO}_2$  samples can be predicted leading to the formation of areas typical of Sr and Ca cuprates. The cation ordering is assumed to be similar to the superconducting phases of the infinite-layer-type structure.

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