Proceedings of the International Workshop "Oxide Materials for Electronic Engineering" (OMEE-2009), Lviv 2009

# The 5:7 Member of the Spin-Ladder Series in the Bi–Sr–Ca–Cu–O System

O. ZAREMBA<sup>a,\*</sup>, O. SHCHERBAN<sup>a</sup>, L. AKSELRUD<sup>a</sup>, R. GLADYSHEVSKII<sup>a</sup>, F. BANFI<sup>b</sup> AND E. GIANNINI<sup>b</sup>

<sup>a</sup>Department of Inorganic Chemistry, Ivan Franko National University of Lviv

Kyryla i Mefodiya St. 6, UA-79005 Lviv, Ukraine

<sup>b</sup>Department of Physics of Condensed Matter, University of Geneva

Quai Ernest-Ansermet 24, CH-1211 Geneva, Switzerland

The crystal structure of the  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  spin-ladder compound was determined from single-crystal X-ray diffraction data. The precursor powder was prepared from stoichiometric amounts of SrCO<sub>3</sub>, CaCO<sub>3</sub>, CuO, and Bi<sub>2</sub>O<sub>3</sub> by calcination at 820 °C for 20 h and pressed to form a rod used for the crystal growth. The travelling-solvent-floating-zone method was applied in an image furnace to grow large single crystals. The composite commensurate structure was solved and refined in space group F222, Pearson symbol oF224, a = 11.340(2), b = 12.829(2), c = 19.441(3) Å, Z = 4. The composite incommensurate structure of the  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  compound was solved and refined in the (3 + 1)-space group F222(00 $\gamma$ ), a = 11.340(2), b = 12.829(2),  $c_1 = 2.7773(4)$ ,  $c_2 = 3.8882(6)$  Å, q = 0.7143.

PACS numbers: 61.46.-w, 61.66.-f

### 1. Introduction

Many layered multicomponent cuprates belong to the well-known family of high-temperature superconductors (see for example [1]). There exists also another family of cuprates, the so-called spin-ladder compounds, which are described by the general formula  $[M_2Cu_2O_3]_m[CuO_2]_n$ , where M is generally Sr and/or Ca with m/n = 5/7, 7/10or 9/13 (see for example [2]). Their crystal structures are constructed by two different types of Cu–O layer. These layers are built of straight (ribbon-like) or zigzag (ladder-type) chains of  $CuO_4$  squares and are intergrown via layers of M cations. Alternatively their crystal structures can be described in four-dimensional space as composite structures, incommensurate along the direction [001], with two interpenetrating sublattices,  $M_2Cu_2O_3$ and  $CuO_2$  (see for example [3]). Superconductivity at high pressure  $(T_c = 12 \text{ K})$  has been observed for a member with m/n = 7/10 [4].

Kato et al. [5], Szymczak et al. [6], Shvanskaya et al. [7] grew single crystals of doped  $(Sr,Ca)_{10}Cu_{17}O_{29}$  and determined their crystal structures in three-dimensional space (space group F222). In the present work, the crystal structure of Bi-doped  $(Sr,Ca)_{10}Cu_{17}O_{29}$  spin-ladder compound, representative of the  $[M_2Cu_2O_3]_m[CuO_2]_n$ series with m = 5 and n = 7, is refined in three- and four-dimensional space and discussed.

#### 2. Experimental

The travelling-solvent-floating-zone (TSFZ) method was applied to grow large single crystals. The feed rods for the crystal growth were prepared using the solid-state method. Pure carbonates SrCO<sub>3</sub>, CaCO<sub>3</sub>, and oxides  $CuO, Bi_2O_3$  were mixed in stoichiometric amounts and ball-milled in an agate mortar with isopropanol, dried and calcined in air. Three calcination steps were carried out at increasing temperatures between 800 and 890 °C. with intermediate grinding every 12 h. Rods of cylindrical shape were pressed isostatically from powder and sintered in air at 890 °C for 12 h. Single crystal growth was performed in an image furnace with two 400 W halogen lamps as heat sources. Pre-melting was performed at 24 mm/h, in order to increase the density and homogeneity of the feed rod. TSFZ melting was performed at  $\approx 0.7$  mm/h, while counter-rotating both the feed and the seed rod at  $\approx 10$  rpm. Both the pre-melting and the crystal growth were performed under  $p(O_2) =$ 3 bar with oxygen flow rate of 0.5 l/h. High-quality up to 3 mm long crystals were obtained. The crystal structure of the  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  compound was determined from single-crystal X-ray diffraction data (STOE IPDS II diffractometer, Mo $K_{\alpha}$ radiation, graphite monochromator).

In three-dimensional space the reflections in the diffraction patterns shown in Fig. 1 obey the conditions of space groups F222, Fmm2 and Fmmm: h+k, h+l, and k+l=2n. Least-squares full-matrix refinements based on F were carried out using the Xtal 3.7.2 system [8]. The

<sup>\*</sup> corresponding author; e-mail: oksanaromaniv@yahoo.com

positions of the cations were obtained by direct methods and the positions of oxygen atoms were taken from difference Fourier maps. All the atom sites were refined in anisotropic approximation. The occupation of the mixed cation sites was constrained to give full occupation with the amount of Bi fixed according to the composition determined by energy distribution of X-ray (EDX). The microprobe analysis of the single crystal was carried out using an electron microscope LEO 438VP equipped with a Tracor Northern System, which made it possible to determine the content of metals. Experimental details of the structural refinement are listed in Table I. A structure refinement in four-dimensional space was carried out using the WinCSD-2000 program [9]. The occupation of the mixed cation site was refined as Sr/Ca ratio.



Fig. 1. X-ray diffraction patterns taken with an imaging plate of a single crystal of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ .

The bulk materials were prepared from oxides and carbonates by solid-state reaction in air and characterized by powder X-ray diffraction.

#### 3. Results and discussion

Attempts to partly substitute Bi for the alkaline-earth cation in the  $(Sr,Ca)_{14}Cu_{24}O_{41}$  compound (the representative of the  $[M_2Cu_2O_3]_m[CuO_2]_n$  homologous series with m = 7 and n = 10) resulted in the formation of another member of the same structure series,  $(Bi,Sr,Ca)_{10}Cu_{17}O_{29}$  (m = 5 and n = 7). The composite commensurate structure was solved and refined in space group F222, Pearson symbol oF224, a = 11.340(2), b = 12.829(2), c = 19.441(3) Å, Z = 4. The metal content was determined by microprobe analysis of the single crystal (Fig. 2, Table II). Figure 3 shows the stacking of layers in the structure of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ . The structure is built as intergrowth of three different types of atomic layer along the *b*-axis, like the structure of the  $(Sr_{0.57}Ca_{0.43})_{14}Cu_{24}O_{41}$  compound [10, 11]. The first type of layer, of composition  $CuO_2$ , is constructed

TABLE I Experimental details of the structure refinement for  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ .

(=-0.02.0-0.39 0.00.39)10 0 011 0 29	
space group	F222
a [Å]	11.340(2)
b [Å]	12.829(2)
c [Å]	19.441(3)
V [Å <sup>3</sup> ]	2828.2(8)
Z	4
F(000)	4078
$D_x \ [\mathrm{g \ cm^{-3}}]$	5.157
$\mu [\mathrm{mm}^{-1}]$	23.314
crystal size [mm]	$0.178\times0.166\times0.208$
radiation, wavelength [Å]	Mo $K_{\alpha},0.71073$
$\theta$ range [°]	2.62 - 31.84
range of $h, k, l$	$-16 \div 14; -19 \div 19; -28 \div 28$
absorption correction	analytical
$R_{\mathrm{int}}(F)$	0.1101
$R_{\sigma}(F)$	0.0817
number of measured reflections	16530
number of independent reflections	1347
number of reflections with $F > 2\sigma(F)$	975
number of refined parameters	137
R	$0.082(0.056^a)$
wR	$0.025(0.023^a)$
S (goodness of fit)	$1.63(1.83^a)$
$\Delta \rho_{\rm max} \ [{\rm e} \ {\rm \AA}^{-3}]$	2.37
$\Delta \rho_{\rm min}$ [e Å <sup>-3</sup> ]	-2.25
extinction parameter	0.026(3)

<sup>a</sup> on reflections with  $F > 2\sigma(F)$ .

by CuO<sub>4</sub> squares linked by edges, resulting in the formation of infinite straight chains along the *c*-axis (Fig. 4). In the other type of Cu–O layer, which has composition Cu<sub>2</sub>O<sub>3</sub> (Fig. 5), CuO<sub>4</sub> squares share edges and corners to form infinite zigzag chains. The third type of layer, which separates CuO<sub>2</sub> and Cu<sub>2</sub>O<sub>3</sub> layers, contains only Bi, Sr and Ca atoms (Fig. 6). In the structure studied here the CuO<sub>2</sub> layers are situated at y = 1/4 and the Cu<sub>2</sub>O<sub>3</sub> layers at y = 0 of space group F222.



Fig. 2. Typical dispersive X-ray spectrum of a single crystal grown from a sample of composition  $(Bi_{0.7}Sr_{5.7}Ca_{7.6})Cu_{24}O_z$ .



Fig. 3. Stacking of layers in the structure of  $[M_2Cu_2O_3]_5[CuO_2]_7$ ; the displacement ellipsoids of the metal atom sites are shown at the 99% probability level.



Fig. 4. Infinite straight chains of  $CuO_4$  squares ( $CuO_2$  layer at y = 1/4).

The final atomic coordinates and equivalent parameters displacement for the structure of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  are presented in Table III. The ratios of Sr and Ca atoms are almost the same in the three mixed cation positions. Seven atom positions are occupied by Cu atoms and ten positions by O Selected interatomic distances are listed in atoms. Table IV. The atoms in the Cu–O layers are tightly bonded, and the usual interatomic distances  $d_{\rm Cu-O}$  in related structures range from 1.92 to 1.94 Å [1]. In the structure of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  the distances from each Cu atom to four O atoms are near the usual values, except for the sites Cu(4) and Cu(5), which are both linked to O(7). The coordination numbers of the mixed cation sites (Bi/Sr/Ca) range from 6 to 7 and the coordination polyhedra may be derived from a tetragonal prism or antiprism by removing one or two vertices from one basal plane.

Superconductivity in spin-ladder compounds appears upon applying high pressure [4]. The aim of our investigations was to create a pressure effect by substitu-



Fig. 5. Infinite zigzag chains of  $CuO_4$  squares ( $Cu_2O_3$  layer at y = 0).



Fig. 6. Rows of Bi, Sr and Ca atoms.

TABLE II

Results of the microprobe analysis of a single crystal grown from the sample of composition  $(Bi_{0.7}Sr_{5.7}Ca_{7.6})Cu_{24}O_z$ .

Element (line)	Intensity	[wt%]	[at.%]
$\operatorname{Bi}(M)$	2982	2.19(15)	0.66(5)
$\operatorname{Sr}(L)$	32588	21.55(26)	15.45(19)
$\operatorname{Ca}(K)$	40496	14.68(15)	23.01(23)
$\mathrm{Cu}(K)$	80732	61.59(46)	60.88(45)

tion in the cation sublattice. In comparison with the Bi-free phase  $(Sr_{0.57}Ca_{0.43})_{14}Cu_{24}O_{41}$  (a = 11.377(1), b = 12.983(1),  $c = 27.395(2) = 10 \times 2.7395(2)$  Å [10]), the cell parameters a and b of the Bi-containing phase  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  are smaller, whereas the c-parameter is larger ( $c = 19.441(3) = 7 \times 2.7773(4)$  Å). This means that incorporation of Bi leads to a reduction of the interlayer spacing by 1.2%, thus favoring charge transfer for superconductivity; the chains of CuO<sub>4</sub> squares are extended and narrowed by 1.4 and 0.3%, respectively.

The composite incommensurate structure of the  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$  compound was solved and refined from single-crystal diffraction data in the (3 + 1)-space group  $F222(00\gamma)$ : a = 11.340(2), b = 12.829(2),  $c_1 = 2.7773(4)$ ,  $c_2 = 3.8882(6)$  Å, q = 0.7143, R = 0.031 (all reflections), R = 0.029 (main reflections), R = 0.032 (satellite reflections) (Table V). The Cu<sub>2</sub>O<sub>3</sub> layers contain Cu(1), O(2) and O(3) atoms, whereas the CuO<sub>2</sub> layers contain Cu(2) and O(1) atoms. The interatomic distances indicate covalent type of bonding between copper and oxygen atoms (Table VI).

The modulation of the structure is presented in Fig. 7 as the change of the interatomic distances along the fourth coordinate  $x_4$ . In the case of the M–O distances significant modulation is observed for the M–O(2) distances only with the maximum value (2.709 Å) at  $x_4 = 0.45$  and the minimum value (2.358 Å) at  $x_4 = 0.95$ . The curve of the dependence for Cu(1)–O(2) distances exhibits a maximum (1.984 Å) at  $x_4 = 0.80$  and a minimum (1.909 Å) at  $x_4 = 0.23$ , whereas for the Cu(2)–O(1) distances the maximum (1.921 Å) occurs at  $x_4 = 0.65$  and the minimum (1.868 Å) at  $x_4 = 0.15$ .

45

Site	Wyckoff position	x	y	2	$U_{\rm eq}$ [Å <sup>2</sup> ]
$M(1)^a$	8f	0	0.1310(3)	0	0.013(1)
$M(2)^b$	16k	-0.0028(3)	0.1307(2)	0.1985(1)	0.015(1)
$M(3)^c$	16k	0.0036(2)	0.1296(2)	0.3995(1)	0.0117(9)
Cu(1)	8e	0.3337(3)	0	0	0.010(1)
Cu(2)	16k	0.3352(2)	0.0037(3)	0.2002(1)	0.0133(9)
Cu(3)	16k	0.3332(2)	-0.0034(2)	0.3999(1)	0.0120(8)
Cu(4)	4c	1/4	1/4	1/4	0.019(2)
Cu(5)	8h	1/4	1/4	0.3934(3)	0.019(1)
Cu(6)	8h	1/4	1/4	0.5363(2)	0.024(2)
Cu(7)	8h	1/4	1/4	0.6761(2)	0.021(2)
O(1)	8e	0.166(1)	0	0	0.03(1)
O(2)	16k	0.168(1)	0.001(1)	0.1995(7)	0.013(4)
O(3)	16k	0.1670(9)	-0.008(1)	0.3998(8)	0.013(5)
O(4)	4b	1/2	0	0	0.006(9)
O(5)	$8 \mathrm{g}$	1/2	0	0.198(1)	0.05(1)
O(6)	$8 \mathrm{g}$	1/2	0	0.402(1)	0.011(6)
O(7)	16k	0.146(1)	0.236(1)	0.3309(8)	0.030(8)
O(8)	16k	0.133(1)	0.240(2)	0.4649(9)	0.021(6)
O(9)	16k	0.1307(9)	0.2683(9)	0.609(1)	0.020(6)
O(10)	8j	0.142(2)	1/4	3/4	0.03(1)

Atomic coordinates and equivalent displacement parameters for  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ .

 ${}^{a}M(1) = 0.02Bi + 0.39(2)Sr + 0.59(2)Ca; {}^{b}M(2) = 0.02Bi + 0.47(2)Sr + 0.51(2)Ca; {}^{c}M(3) = 0.02Bi + 0.37(1)Sr + 0.61(1)Ca.$ 

# TABLE V

 $Atomic \ coordinates \ and \ displacement \ parameters \ for \ composite \ structure \ of \ (Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}.$ 

Site	Wyckoff position	$x_0$	$y_0$	$z_0$	$B_{ m eq}$ [Å <sup>2</sup> ]
Cu(1)	8e	0.16581(6)	0	0	0.80(1)
O(2)	8e	0.3324(4)	0	0	0.42(3)
O(3)	4a	0	0	0	1.18(3)
$\mathrm{M}^{a}$	8f	0	0.36985(6)	0	1.10(1)
Cu(2)	4c	1/4	1/4	1/4	1.31(1)
O(1)	8j	0.6364(4)	1/4	1/4	1.60(3)
$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
0.42(1)	1.50(1)	0.48(1)	0	0	-0.23(1)
0.46(1)	0.15(1)	0.66(2)	0	0	-0.20(2)
0.42(1)	1.94(1)	1.18(4)	0	0	0
0.97(1)	1.11(1)	1.23(1)	0	0.07(1)	0
0.59(1)	1.68(1)	1.65(2)	0	0	0
0.86(1)	2.88(1)	1.04(7)	0	0	-0.99(3)

<sup>*a*</sup> M = 0.449(3)Sr + 0.551(3)Ca.

The experimentally determined modulation vector  $(q = c_1/c_2)$  coincides with the theoretically calculated value for 5:7 members of the  $[M_2Cu_2O_3]_m[CuO_2]_n$  series (q = m/n = 0.7143).

A refinement on powder diffraction data of the crystal structure of the spin-ladder compound in the corresponding bulk sample ((3 + 1)-space group  $F222(00\gamma)$ , a = 11.349(1), b = 12.825(1),  $c_1 = 2.755(1)$ ,  $c_2 =$ 

## TABLE IV

Atoms	d [Å]	Atoms	d [Å]
M(1)-2O(8)	2.47(1)	Cu(1)–O(1)	1.86(3)
$-2\mathrm{O}(6)$	2.55(2)	-O(4)	1.89(1)
$-2\mathrm{O}(1)$	2.55(2)	-2O(3)	1.95(2)
M(2)-O(10)	2.38(1)	Cu(2)-O(5)	1.88(1)
$-\mathrm{O}(7)$	2.39(1)	-O(2)	1.90(2)
$-\mathrm{O}(2)$	2.45(1)	-O(2)	1.95(2)
$-\mathrm{O}(6)$	2.57(2)	-O(5)	1.96(2)
$-\mathrm{O}(2)$	2.60(1)	Cu(3)– $O(6)$	1.89(1)
$-\mathrm{O}(5)$	2.61(2)	-O(3)	1.90(1)
-O(9)	2.63(1)	-O(2)	1.93(2)
M(3) - O(8)	2.37(1)	-O(1)	1.95(1)
$-\mathrm{O}(9)$	2.39(1)	Cu(4)-4O(7)	2.07(1)
$-\mathrm{O}(3)$	2.45(1)	Cu(5)-2O(7)	1.67(1)
$-\mathrm{O}(7)$	2.48(1)	-2O(8)	1.99(1)
$-\mathrm{O}(5)$	2.53(2)	Cu(6)-2O(8)	1.88(1)
$-\mathrm{O}(4)$	2.57(1)	$-2\mathrm{O}(9)$	1.93(1)
$-\mathrm{O}(3)$	2.59(1)	Cu(7)-2O(10)	1.89(1)
		-2O(9)	1.92(1)

=

Selected interatomic distances in the structure of	$(Bi_{0.02}Sr_0$	$_{.39}Ca_{0.59}$	$)_{10}Cu_{17}O_{29}.$
--	------------------	-------------------	------------------------



Fig. 7. Interatomic distances in the composite structure of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ .

3.9050(5) Å, q = 0.7055) showed the presence of the 7:10 member of  $[M_2Cu_2O_3]_m[CuO_2]_n$  series. Consequently, the structure of the spin-ladder compound observed in the single crystal corresponds to a metastable modification of  $[M_2Cu_2O_3]_m[CuO_2]_n$  with m/n = 5/7, whereas

TABLE VI Selected interatomic distances in the composite structure

Selected interatomic distances in the composite structure of  $(Bi_{0.02}Sr_{0.39}Ca_{0.59})_{10}Cu_{17}O_{29}$ .

Atoms	d [Å]
Cu(1)– $O(3)$	1.8803(7)
$-\mathrm{O}(2)$	1.889(4)
$-2\mathrm{O}(2)$	1.9442(1)
Cu(2)– $4O(1)$	1.894(3)
M-O(1)	2.185(3)
$-\mathrm{O}(1)$	2.221(3)
$-2\mathrm{O}(2)$	2.530(3)
$-2\mathrm{O}(3)$	2.5626(5)

the ceramics contain the stable modification with m/n = 7/10.

# References

- R. Gladyshevskii, Ph. Galez, in: Handbook of Superconductivity, Eds. Ch. Poole, Jr., Academic Press, San Diego 2000, Ch. 8, p. 267.
- [2] L. Shvanskaya, L. Leonyuk, G.-J. Babonas, A. Reza, R. Szymczak, V. Rybakov, V. Maltsev, in: Advances in Structure Analysis, Eds. R. Kuzel, J. Hasek, Czech and Slovak Crystallographic Association, Prague 2001, p. 277; V. Maltsev, L. Leonyuk, G.-J. Babonas, D. Pushcharovskii, ibid., p. 269.

- [3] A.F. Jensen, F.K. Larsen, B.B. Iversen, V. Petříček, T. Schultz, Y. Gao, Acta Crystallogr. B 53, 113 (1997).
- [4] M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori, K. Kinoshita, J. Phys. Soc. Jpn. 65, 2764 (1996).
- [5] K. Kato, E. Takayama-Muromachi, K. Kosuda, Y. Uchida, Acta Crystallogr. C 44, 1881 (1988).
- [6] R. Szymczak, H. Szymczak, M. Baran, E. Mosiniewicz-Szablewska, L. Leonyuk, G.-J. Babonas, V. Maltsev, L. Shvanskaya, *Physica C* **311**, 187 (1999).
- [7] L. Shvanskaya, L. Leonyuk, E. Sokolova, V. Maltsev, Z. Kristallogr. 215, 368 (2000).

- [8] Xtal3.7 System, Eds. S.R. Hall, D.J. du Boulay, R. Olthof-Hazekamp, University of Western Australia, 2000.
- [9] L.G. Akselrud, P.Y. Zavalii, Yu.N. Grin, V.K. Pecharsky, B. Baumgartner, E. Wolfel, *Mater. Sci. Forum.* 133-136, 335 (1993).
- [10] O. Romaniv, L.G. Akselrud, V.M. Davydov, R.E. Gladyshevskii, Ukr. Khim. Zh. 72, 67 (2006) (in Ukrainian).
- [11] E.M. McCarron, M.A. Subramanian, J.C. Calabrese, R.L. Harlow, *Mater. Res. Bull.* 23, 1355 (1988).