TERNARY AND QUATERNARY OXIDES OF Bi, Sr AND Cu

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Abstract. Among the phases present in the products of thermal treatments of mixtures of analytical grade Bi₂O₃, Sr(OH)₂.8H₂O and CuO, a cubic perovskite, BiSr₃O₅.₅, with 1:1 order at the B-cations sublattice and a = 8.493(7) Å has been found. This oxide appears to substitute some Cu for Bi giving rise to materials with lower a values. After been grown from mixtures of the same reagents at Bi:Sr:Cu molar ratios (0.7-2.2):(1.0-2.2):1 using techniques of static and revolving crucibles, crystals of four phases have been studied by X-ray diffraction, electron microscopy and electron diffraction, namely the superconducting Raveau oxide, A; a second phase, A₁, very similar to A; and the oxides with Bi:Sr:Cu molar ratios 2:2:1, K; and 4:8:5, G. The conditions (composition, crystallization rate) which lead to A, A₁ or K are established. Each of these phases distinguishes from the two others by its oxygen content, which decreases in the order A > A₁ > K.

1. INTRODUCTION

Prior to the discovery of superconductivity in an oxide of Bi, Sr and Cu, several solid phases were known in the two-component regions of the ternary system Bi₂O₃-SrO-CuO. Nevertheless that discovery has created a new interest in ternary and quaternary copper oxides, of which the following phases are at present known.

Oxides of Bi and Cu. Although two compounds of stoichiometries Bi₄CuO₇ and Bi₂Cu₂O₅ have been mentioned²,³, the oxide best characterized⁴-⁷ is tetragonal CuBi₂O₄, with unit-cell parameters (Å) a = 8.510, c = 5.814. The crystal structure of CuBi₂O₄ has been simultaneously refined⁸,⁷ in the space groups S.G. P4/ncc (No. 130)⁸ and I₄ (No. 79)⁹, with Cu in a square planar coordination.

Oxides of Sr and Cu. Whereas the existence of two Sr and Cu (II) oxides, Sr₂CuO₃ and SrCuO₂, is well established, only the tetragonal oxide SrCu₂O₂ of Sr and Cu (I) is known¹⁰, with S.G. 14/amd (No. 141)¹¹, a = 5.48, c = 9.82, SrO₆ octahedra and Cu in linear two-coordination with oxygen. Sr₂CuO₃ is¹²,¹³orthorhombic, a = 12.684, b = 3.9064, c = 3.4957, S.G. Immm (No. 71), and includes SrO₆ polyhedra and planar CuO₄ squares; and CuSrO₂ is¹³,¹⁴also orthorhombic, a = 3.9136(2), b = 16.3313(8), c = 3.5730(2), S.G. Cmcm (No. 63). Besides a not too well characterized Sr cuprate (III) hydrate¹⁶, SrCu₂O₄.nH₂O, a new oxide of Sr and Cu containing some Cu (III) and formulated as Sr₁₄Cu₂₄O₄₁, has been recently reported¹⁷,¹⁸. The crystal structure of orthorhombic Sr₁₄Cu₂₄O₄₁ is incommensurate and can be described¹⁷ as the result of two interpenetrating structures: one with Sr-(Cu₂O₃ sheets)- Sr layers in an orthorhombic cell with dimensions (Å) of a = 11.459(2), b = 13.368(5), c = 3.931(1), and a second structure with layers of (CuO₂ chains) in a cell having the mentioned a and b values but with c = 2.749(1).

Oxides of Bi and Sr. The first phase described¹⁹,²⁰ in the system Bi₂O₃-SrO is a rhombohedral solid solution with the homogeneity range s = 14-26, being s the mol percent Sr/(Sr+Bi). This phase, S.G. R₃m (No. 166), has a rhombohedral primitive unit-cell with a = 9.6-9.8 Å and α = 23.8°-23.4°, or a threec primitive hexagonal cell with a = 3.97 Å, c = 28.1-28.6 Å. In this oxide, that can be formulated as
Bi$_{2-2x}$Sr$_x$O$_{3-2x}$ with x = 2s/(100+s), the metal lattice always seems to remain complete, whereas there is a variable number of vacant positions of the oxygen lattice.

The effect of small SrO additions on the polymorphism of Bi$_2$O$_3$ was studied some years later by high temperature X-ray diffraction, and the tentative partial phase diagram in the temperature range 500-900 °C was proposed$^{21}$. This diagram includes the above mentioned rhombohedral phase of variable composition and a solid solution of cubic symmetry. The system Bi$_2$O$_3$-SrO has been studied some years ago$^{22}$, in the temperature range 620 to 1000 °C by thermal and high-temperature X-ray diffraction analyses. Table I includes the composition, approximate stability regions, crystal system, and unit-cell parameters of the different phases that were found, comprising five solid solutions and three oxides of constant composition, two of which

Table I. Approximate stability regions, symmetry, and unit-cell parameters for oxides of compositions Bi$_{2-2x}$Sr$_x$O$_{3-2x}$, according to reference $^{22}$.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>x</th>
<th>T °/C</th>
<th>Symmetry</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi$_2$O$_3$</td>
<td>0.01-0.12</td>
<td>730-820</td>
<td>C</td>
<td>5.67</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>0.20-0.40</td>
<td>700-900</td>
<td>R</td>
<td>4.0</td>
<td>-</td>
<td>28.7</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>0.18-0.43</td>
<td>620-700</td>
<td>R</td>
<td>3.97</td>
<td>-</td>
<td>28.2</td>
</tr>
<tr>
<td>Bi$_2$SrO$_4$</td>
<td>0.50</td>
<td>620-800</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Y</td>
<td>0.58-0.64</td>
<td>820-940</td>
<td>T</td>
<td>13.239(2)$^b$</td>
<td>4.257(1)$^b$</td>
<td>-</td>
</tr>
<tr>
<td>Y'</td>
<td>0.58-0.62</td>
<td>900-930</td>
<td>C</td>
<td>4.41(2)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$O$_5$</td>
<td>0.67</td>
<td>650-950</td>
<td>O</td>
<td>14.293(2)</td>
<td>7.651(2)</td>
<td>6.172(1)</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$O$_6$</td>
<td>0.75</td>
<td>810-980</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

C: cubic T: tetragonal R: rhombohedral O: orthorhombic M: monoclinic

$^a$ excluding four metastable solid solution obtained by annealing $\alpha_1$ in different conditions

$^b$ for x = 0.615: see ref. 23.

$^c$ for T = 950 °C

have been characterized more recently: Bi$_2$SrO$_4$ is$^{26}$ monoclinic, S.G. C2/m (No. 12), with a = 19.2882(16), b = 4.3520(4), c = 6.1015(5), $\beta$ = 94.839(7)$^o$; and Bi$_2$Sr$_2$O$_5$ is$^{25}$ orthorhombic, S.G. Pmam (No. 51) with the crystallographic constants a = 6.1713(6), b = 14.3074(15), c = 3.8262(4), closely related to those shown in Table I. Some months ago a new oxide of molar ratio Bi:Sr = 1:3 (x = 0.857) has been described$^{26}$ as crystallizing in the orthorhombic system with a = 17.147, b = 16.758, c = 16.998 Å.

Oxides of Bi, Sr and Cu. The first superconducting material in the system Bi-Sr-Cu-O was described by the group of Raveau$^1$ and formulated as Bi$_2$Sr$_2$Cu$_2$O$_7+x$, with an orthorhombic unit-cell of parameters (Å) a = 5.32, b = 26.6, c = 48.8 and a superconducting transition at 7 K, which was soon confirmed$^{27}$. In a preliminary publication$^{28}$ our group reported that mixtures of Bi$_2$O$_3$, SrCO$_3$ and CuO in the molar ratios Bi: Sr: Cu = 2:2:2 lead to the oxide Bi$_2$Sr$_2$CuO$_6+x$, here designed as 221, mixed with small amounts of CuO; and that all the reflexions of the X-ray diffraction patterns of the 221 oxide can be indexed in an orthorhombic unit-cell of parameters (Å) a = 5.390(2), b = 26.973(8), c = 24.69(4). Subsequent diffraction studies (X-ray, electron, neutron) confirmed the composition 221 and propounded the substructures included in Table II.

The actual structure of 221 is a long-period modulated superstructure with different modes that can be observed by electron diffraction and high-resolution electron microscopy. The presence of superstructures was soon established$^{27}$ and corroborated later by various authors$^{32,35,37,26}$. Superstructures of the following types
have been described\textsuperscript{35}: base-centered monoclinic with parameters (Å) \(a = 5.4, b = 27, c = 26.9, \alpha = 66.3^\circ\); monoclinic with \(a = 5.1, b = 27, c = 12.6, \alpha = 77.6^\circ\); and base-centered orthorhombic with \(a = 5.4, b = 22.6, c = 24.6\).

### Table II. Crystal structures proposed for the superconducting oxide of approximate composition Bi\(_2\)Sr\(_2\)CuO\(_6+\_x\)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>S.G.</th>
<th>(a/\AA)</th>
<th>(b/\AA)</th>
<th>(c/\AA)</th>
<th>(\alpha)</th>
<th>(Z)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>-</td>
<td>5.381(1)</td>
<td>-</td>
<td>24.65(1)</td>
<td>-</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>T</td>
<td>14/\textit{mm}</td>
<td>3.8097(4)</td>
<td>-</td>
<td>24.607(3)</td>
<td>-</td>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>O</td>
<td>\textit{Amaa}</td>
<td>5.392</td>
<td>5.394</td>
<td>24.537(1)</td>
<td>-</td>
<td>4</td>
<td>31</td>
</tr>
<tr>
<td>O</td>
<td>-</td>
<td>10.8</td>
<td>53</td>
<td>24</td>
<td>-</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td>T</td>
<td>14/\textit{mm}</td>
<td>3.801(3)</td>
<td>-</td>
<td>24.61(9)</td>
<td>-</td>
<td>2</td>
<td>33</td>
</tr>
<tr>
<td>O</td>
<td>\textit{Amaa}</td>
<td>5.362(3)</td>
<td>5.374(1)</td>
<td>24.622(6)</td>
<td>-</td>
<td>3</td>
<td>34</td>
</tr>
<tr>
<td>T</td>
<td>-</td>
<td>5.4</td>
<td>-</td>
<td>24.6</td>
<td>-</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>\textit{C2}</td>
<td>26.856</td>
<td>5.380</td>
<td>26.908</td>
<td>113.5</td>
<td>4</td>
<td>36</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>5.4</td>
<td>26</td>
<td>28</td>
<td>116</td>
<td>37</td>
<td></td>
</tr>
</tbody>
</table>

\(T\): tetragonal \quad \textit{O}: orthorhombic \quad \textit{M}: monoclinic

Preliminary studies of the authors showed that some other phases appear for compositions Bi, 1.5-2.2; Sr, 1.8-2.2; Cu, 1; and that slight variations in the initial concentration of Bi and Sr favor the appearance of these phases. On the other hand, we observed that the nominal composition 2:2:1 is metastable and changes when heated for a long time. These observations are related to the results of some recent studies\textsuperscript{26,38-40}. One of them\textsuperscript{26} concludes that three phases coexist at the ideal 221 composition: a superconducting material with the approximate composition Bi\(_2.125\)Sr\(_{1.875}\)Cu\(_{1.031}\)O\(_{6}\), and two oxides, Bi\(_{1.7}\)Sr\(_{1.5}\)Cu\(_{7}\)O\(_y\) and Sr\(_{3}\)Cu\(_{5}\)O\(_y\), the first of which with parameters \(a = 5.425, b = 23.254, c = 24.427\) Å. The second study\textsuperscript{38} points out that nominal 221 is actually a solid solution tolerating a range of Sr deficiency, i.e., Bi\(_{2-x}\)Sr\(_{2-x}\)CuO\(_6\) (\(x = 0.1-0.5\)); that superconducting behaviour is observed for \(x = 0.1-0.25\), the solid solution undergoing a metal-to-insulator transition for higher \(x\) values; and that the stable phase at the 221 composition is a semiconductor designed as the collapsed 221 phase. The results of the third study\textsuperscript{39} confirm the existence of one oxide with Bi:Sr:Cu ratios of 2:2:1, and a solid-solution phase with \((2.2-x):(1.8+x):1\) ratios, for \(x = 0-0.08\). Only this second phase is a superconductor at 9 K and \(x = 0.08\). The 2:2:1 compound\textsuperscript{39}, the collapsed\textsuperscript{38} 221 phase, and the oxide formulated\textsuperscript{26} as Bi\(_{1.7}\)Sr\(_{1.5}\)Cu\(_{7}\)O\(_y\) show the same X-ray diffraction pattern, that was indexed\textsuperscript{39} with \(a = 23.73(1), b = 13.242(6), c = 4.081(1)\) Å. By a combination of electron diffraction and single crystal and powder X-ray diffraction, the phase of composition 221 has been more recently found\textsuperscript{40} to have a commensurate lattice with monoclinic symmetry, S.G. \(C2/m\) or \(C\), \(a = 24.473(2), b = 5.4223(5), c = 21.959(2)\) Å and \(\beta = 105.40(1)^\circ\). In short, it appears that the superconducting oxide thought at the beginning as having the composition 221, is a solid solution with a range of Sr deficiency; and that stoichiometric 221 is not a superconductor. Hence, the structural data shown in Table II correspond to the Sr-deficient solid solution, and stoichiometric 221 is monoclinic, with the X-ray diffraction data\textsuperscript{39} indicated. These two phases will be labelled here as A and K respectively.

At least five additional oxides with various Bi:Sr:Cu molar ratios have been described. Two of them, 2:7:2 and 4:9:1, are apparently stabilized by the presence of Li\(_2\)CO\(_3\), but do not form without it\textsuperscript{39}. Table III includes X-ray diffraction data for these oxides. The cubic oxide which appeared with some impurities from nominal molar ratios 2:4:1 showed\textsuperscript{52} the reflexions of a perovskite with 1:1 order at the B-cation sublattice. The authors found later that for Bi: Sr ratios 1:2 and 1:3 a very similar perovskite is formed without copper. This result led them to explore the Sr-rich region of the phase diagram Bi\(_2\)O\(_3\)-SrO. On the other hand, the authors...
Table III. Unit-cell constants for oxides with various Bi:Sr:Cu ratios

<table>
<thead>
<tr>
<th>Bi:Sr:Cu</th>
<th>Symmetry</th>
<th>a/Å</th>
<th>b/Å</th>
<th>c/Å</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 3 2</td>
<td>0</td>
<td>4.888</td>
<td>5.596</td>
<td>24.804</td>
<td>26</td>
</tr>
<tr>
<td>4 8 5</td>
<td>0</td>
<td>5.389</td>
<td>24.050</td>
<td>34.035</td>
<td>26</td>
</tr>
<tr>
<td>4 8 5</td>
<td>0</td>
<td>5.373(2)</td>
<td>23.966(4)</td>
<td>33.907(6)</td>
<td>41</td>
</tr>
<tr>
<td>2 4 1</td>
<td>C</td>
<td>8.480(1)</td>
<td>-</td>
<td>-</td>
<td>42</td>
</tr>
<tr>
<td>2 7 2</td>
<td>0</td>
<td>8.769(2)</td>
<td>8.360(2)</td>
<td>7.983(3)</td>
<td>39</td>
</tr>
<tr>
<td>4 9 1</td>
<td>T</td>
<td>11.694(3)</td>
<td>-</td>
<td>9.466(4)</td>
<td>39</td>
</tr>
</tbody>
</table>

C: cubic  O: orthorhombic  T: tetragonal

found that not too long treatments of mixtures with nominal composition 221 at 780-790 °C gave A and small amounts of Bi2Sr2O5; that K was obtained with loss of mass after long treatments at 900 °C; and that K, when exposed to the air, becomes A1, a phase whose X-ray diffraction pattern looks very similar to that of A. These results led them to grow crystals of A, K and A1 in different conditions. The preliminary results of these experiments are included in this paper.

2. EXPERIMENTAL

Six polycrystalline samples of the compositions indicated in Table IV were prepared by solid-state reactions from mixtures of analytical grade Bi2O3 and SrCO3, which were ground and successively heated in air at 800, 900 and 950 °C in alumina crucibles. After each thermal treatment, which lasted five hours, the samples were weighed, reground and characterized by X-ray diffraction using a SIEMENS Kristalloflex D500.

Table IV. Phases identified in six polycrystalline samples of compositions Bi2-2xSr0.3xO3-2x

<table>
<thead>
<tr>
<th>No.</th>
<th>Bi : Sr</th>
<th>x</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0</td>
<td>0.75</td>
<td>J-E(s)</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>0.77</td>
<td>J-E</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>0.78</td>
<td>E+J</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>0.80</td>
<td>E+J(s)</td>
</tr>
<tr>
<td>5</td>
<td>1.1</td>
<td>0.85</td>
<td>E+J(t)</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
<td>0.86</td>
<td>E</td>
</tr>
</tbody>
</table>

J Bi2Sr3O6  E BiSr3O5.5  s small amounts  t traces

The crystals were grown from mixtures of 99.9 % Bi2O3, Sr(OH)2.8H2O and CuO at the molar ratios and conditions shown in Table V. Dense-alumina crucibles were used. Revolving crucibles (60 r.p.m.) with the direction of rotation changing every 10 seconds in a furnace QUASTAR 89 were employed for sample nos. 9-12. Except indicated otherwise (sample nos. 1, 9-11) the samples were preheated at 850 °C for 12 hours, quenched, ground, and led to the temperature T (°C), maintained at this temperature for t hours as a melt, cooled to 750 °C at 2°C h⁻¹, and quenched. A portion of the crystals as grown was pulverized and characterized by X-ray diffraction. The d-spacings and relative intensities were measured as indicated elsewhere. The morphological study of the crystals was performed using a JEOL scanning microscope JSM 35-C. For high resolution electron microscopy and electron diffraction, a microscope JEOL JEM-2000 FX was employed. The resistivity measurements were made using a standard four-probe method.

3. RESULTS AND DISCUSSION

Table IV includes the phases identified in six polycrystalline samples of compositions Bi2-2xSr0.3xO3-2x (0.75 < x < 0.86): Bi2Sr3O6 and BiSr3O5.5. The oxide with Bi: Sr = 2:3 molar ratio shows the following d spacings (Å) with the relative intensities in parentheses: 4.68(10); 4.38(8); 4.23(7); 4.01(10); 3.75(6); 3.14(90); 3.04(100); 2.18(50); 1.81(20); and 1.79(30). The oxygen content for BiSr3O5.5 has been adjusted assuming Bi (V), because the mass changes were followed by weighing before and after each operation and showed that almost all the whole Bi (III) oxidized in the course of the thermal treatments. The X-ray powder diffraction pattern for BiSr3O5.5 shows
Table V. Phases identified in crystals grown from mixtures of various Bi:Sr:Cu molar ratios

<table>
<thead>
<tr>
<th>No.</th>
<th>Bi: Sr: Cu</th>
<th>T/°C</th>
<th>t/h</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.0 2.0 1</td>
<td>890a</td>
<td>6</td>
<td>A+AI(s)</td>
</tr>
<tr>
<td>2</td>
<td>2.0 2.0 1</td>
<td>930</td>
<td>6</td>
<td>A</td>
</tr>
<tr>
<td>3</td>
<td>2.2 1.8 1</td>
<td>930</td>
<td>6</td>
<td>A1+A(t)</td>
</tr>
<tr>
<td>4</td>
<td>1.8 2.0 1</td>
<td>1000</td>
<td>6</td>
<td>K</td>
</tr>
<tr>
<td>5</td>
<td>1.5 2.0 1</td>
<td>1000</td>
<td>6</td>
<td>K</td>
</tr>
<tr>
<td>6</td>
<td>1.8 2.2 1</td>
<td>930</td>
<td>6</td>
<td>K+G(s)</td>
</tr>
<tr>
<td>7</td>
<td>1.0 1.5 1</td>
<td>1000</td>
<td>6</td>
<td>A1+G</td>
</tr>
<tr>
<td>8</td>
<td>0.7 1.0 1</td>
<td>1000</td>
<td>6</td>
<td>G</td>
</tr>
<tr>
<td>9*</td>
<td>2.0 2.0 1</td>
<td>940b,c</td>
<td>1</td>
<td>K</td>
</tr>
<tr>
<td>10*</td>
<td>2.0 2.0 1</td>
<td>940d,c</td>
<td>1</td>
<td>K</td>
</tr>
<tr>
<td>11*</td>
<td>2.0 2.0 1</td>
<td>940c</td>
<td>1</td>
<td>A1</td>
</tr>
<tr>
<td>12*</td>
<td>2.0 2.0 1</td>
<td>940</td>
<td>1</td>
<td>A1+K+A1</td>
</tr>
</tbody>
</table>

*revolving crucible  
^a cooled to R.T.  
_b crystallized at 15 °Ch^-1  
_c no pretreatment at 850°C  
_d crystallized at 5 °Ch^-1  
(s) small amounts  
(t) traces  
A, Raveau phase;  
A1, new phase;  
K, 221 oxide;  
G, Bi4Sr8Cu5O19

All the experiments on crystal growth led to abundant masses of crystals in which the phases included in Table V (A, A1, K and G) were identified. Three of these, A, K and G, are relatively well known: A, that was present in sample nos. 1, 2 and 12, is the Raveau phase with the unit-cell parameters included in Table II; K is monoclinic 40 221, which appears as major product after crystallising sample nos. 4, 5, 6, 9 and 10; and G (samples 6-8) is orthorhombic 26, 41 Bi4Sr8Cu5O19. Crystals of A1, a new phase closely related to A, are obtained from sample nos 3, 7, and 11. The relation between the X-ray diffraction patterns of both phases is shown in Fig. 1. The morphologies of A and A1 can only be distinguished by the way of their faces being developed. Crystals of A have planar faces, ordinarily well developed, some of them with edges up to 5 mm long, but forming irregular triangles as Fig. 2 shows. The A1 phase shows a similar morphology and strong tendencies to be delaminated and to grow by steps. Consequently, voluminous crystals of A1 cannot easily be grown. When static crucibles are employed, nominal mixtures with Bi:Sr ratio larger than 1 (sample no. 3) lead to A1 as the major product, whereas stoichiometric 221 gives phase A (sample nos. 1 and 2). The

Fig. 1. Comparison of X-ray diffraction patterns of A1 and A.
presence of traces of A1 in sample no. 1 can be related with the removal of some oxygen during the 15 days required for lowering from 750 °C to room temperature.

Crystals of phase K are obtained using static crucibles from nominal mixtures with Bi: Sr ratios smaller than 1 (sample nos. 4, 5). For still smaller Bi: Sr ratios, the oxide Bi₄Sr₃Cu₅O₁₉ is progressively stabilized (sample nos. 6-8). Crystals of the K oxide show an elongated development and form needle-shaped or fibrous masses including many crystals (Fig. 3).

The results obtained in the experiments with rotating crucibles (sample nos. 9-12) also suggest that the oxygen content increases in the order K < A1 < A. The rapid crystallization of sample nos. 9 and 10 leads to crystals of K, which is the phase with the smaller oxygen content. For a slower crystallization (sample no. 11), crystals of A1 result. In the case of pretreated sample no. 12, with smaller oxygen content, the three phases appear at different heights of the crucible: A, at the bottom; A1, at the top; and K between A and A1. This suggests that A has incorporated all the oxygen of the melt at the expense of K, and that the external portion of K has oxidized in contact with air.

Although K crystals obtained in static crucibles (sample nos. 4, 5) are grown from mixtures with Bi: Sr ratios smaller than 1, and polycrystalline K is prepared from stoichiometric 221 after long thermal treatments at 900 °C in which some Bi can be lost, K crystals are grown in rotating crucibles at high crystallization rates from stoichiometric 221 mixtures (sample nos. 9-10). This suggests that this composition, 221, is also included in the stability region of the K phase.

In the selected-area diffraction pattern from a crystal of A1 (sample no. 3), satellites along the b axis were observed. Although the (001) planes of A1 ordinarily present a large number of deformations, modulations of 2.7 nm can be seen in Fig. 4, that represents the high-resolution (HR) lattice image taken with the incidence [001]. The wavy aspect of the (001) planes can also be observed. The high-resolution lattice image of Fig. 5, taken with the incidence [100] from another crystal of A1.

Fig. 2. Optical photomicrograph of the A phase.

Fig. 3. SEM micrograph showing needle-like crystals of K up to 10 mm long.
(sample no. 3), contains modulations of 1.2 nm along the c axis. And Fig. 6, with the high-resolution lattice image of a different A₁ specimen (sample no. 1) taken with the incidence [100], displays modulations of 11 and 9.5 nm along b and c axes respectively, the last of which comparable to those of $4 \times 2.4 = 9.6$ nm observed in the A phase by depth profile Auger analysis45. In short, modulations along b and c axes observed in the A phase are also evident for A₁.

Figs. 7 and 8 show the selected-area diffraction pattern taken with the incidence [010] from a crystal of the K phase (sample no. 4) and the high-resolution lattice image of the same crystal showing modulations of 2.4 nm along the c axis.
Fig. 7. Selected-area diffraction pattern from a crystal of the K phase.

Fig. 8. HR lattice image of phase K taken with the incidence [010].

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