Phase Equilibria and Crystal Chemistry in Portions of the System \( \text{SrO-CaO-Bi}_2\text{O}_3-\text{CuO} \), Part II—The System \( \text{SrO-Bi}_2\text{O}_3-\text{CuO} \)

1. Introduction

The discovery of high transition temperature (\( T_c \)) superconductivity in cuprates by Bednorz and Müller [1] and its confirmation by Takagi et al. [2] as being due to the phase \( \text{La}_2-x \text{Ba}_x \text{CuO}_4 \) led to a world-wide search for other compounds with higher \( T_c \). These researches first produced \( \text{La}_{2-x} \text{Sr}_x \text{CuO}_4 \) [3] and quickly led to the discovery of a mixed phase composition in the system \( \text{BaO-Y}_2\text{O}_3-\text{CuO} \) with a \( T_c \sim 90 \text{ K} \) [4], well above liquid nitrogen temperature (77 K). Identification of the superconducting phase as \( \text{Ba}_2\text{YCu}_3\text{O}_{6+z} \) [5] has resulted in hundreds of published reports on the properties of this phase. Our own phase equilibria studies of the system \( \text{BaO-Y}_2\text{O}_3-\text{CuO} \) [6,7] have shown that CO\(_2\) is an important constituent of bulk ceramics that are prepared in air.

Phases with still higher \( T_c \) were found in the systems \( \text{SrO-CaO-Bi}_2\text{O}_3-\text{CuO} \) and \( \text{BaO-CaO-Tl}_2\text{O}_3-\text{CuO} \) [8,9]. These phases belong mostly to a homologous series \( A_x\text{Ca}_{2-x}B_x\text{Cu}_3\text{O}_{6+4} \) (\( A = \text{Sr}, \text{Ba} \); \( B = \text{Bi}, \text{Tl} \)) although another series \( A_x\text{Ca}_{2-x}B\text{Cu}_3\text{O}_{6+3} \) (\( A = \text{Ba}, B = \text{Tl} \)) can also lead to superconducting phases [10]. Still other compounds have been discovered with high \( T_c \), i.e., \( \text{Pb}_2\text{Sr}_2\text{YCu}_3\text{O}_{6+4} \) [11], \( \text{Ba}_{2-x}\text{K}_x\text{BiO}_3 \) [12] (with no Cu ions) and \( \text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4 \) [13]. The \( \text{Tl}^{+3} \) containing phases with the largest values of \( n \), so far have the highest confirmed \( T_c \) up to \( \sim 125 \text{ K} \) [9]. However, the phases in the \( \text{Tl}^{+3} \) system are difficult to prepare as bulk single phase samples, and the relevant phase equilibria have not been determined, owing to the extreme volatility of Tl and...
the poisonous nature of Tl vapors. In the Bi\textsuperscript{3+} containing systems the phase with \( n = 2 \) and \( T_c \sim 80 \text{ K} \) is easily prepared. However, its exact single-phase region is not well known and a structure determination has not been completed because of very strong incommensurate diffraction that is apparently due to a modulation of the Bi positions. Higher \( n \) (and higher \( T_c \)) phases have not been prepared as single phase bulk specimens (without PbO). Thus, we undertook a comprehensive study of the phase equilibria and crystal chemistry of the entire four component system SrO-CaO-Bi\textsubscript{2}O\textsubscript{3}-CuO. It is hoped that a complete understanding of the crystal chemistry and thermodynamics of the many phases formed will lead to a better understanding of the processing parameters for the preparation of bulk ceramics with reproducible and useful properties.

A prerequisite to understanding the phase equilibria of the four-component system is adequate definition of the phase relations in the bounding binary and ternary systems. The ternary system SrO-CaO-CuO was the first to be investigated and the results were published separately \[14\]. The solubilities of CaO in the solid solutions that are based on SrO:CuO phases were determined, and a ternary phase Ca\textsubscript{1-x}Sr\textsubscript{x}CuO\textsubscript{2} \((x = 0.14-0.16)\) was discovered. The structure of this ternary phase was refined by Siegrist et al. \[15\]. The present paper discusses the experimental determination of the phase relations and crystal chemistry of the ternary system SrO-Bi\textsubscript{2}O\textsubscript{3}-CuO as well as its boundary binary systems. A portion of the binary SrO-CuO system was previously published \[16\], and the structure of the compound "Sr\textsubscript{4}Cu\textsubscript{3}O\textsubscript{11}" was determined \[17\]. Because of the relative importance of the phase Sr\textsubscript{2}Bi\textsubscript{2}CuO\textsubscript{6}, a separate paper was prepared concerning the composition, unit cell dimensions and symmetry of this phase \[18\]. The experimental details, phase relations and crystal chemistry of the binary CaO-Bi\textsubscript{2}O\textsubscript{3} and the two remaining ternary systems CaO-Bi\textsubscript{2}O\textsubscript{3}-CuO and SrO-CaO-Bi\textsubscript{2}O\textsubscript{3} are reported in separate publications \[19,20\].

In the following discussion of phase equilibria and crystal chemistry, the oxides under consideration will always be given in the order of decreasing ionic radius, largest first, e.g., SrO>Bi\textsubscript{2}O\textsubscript{3}>CuO. The notation \( \frac{1}{2} \text{Bi}_2\text{O}_3 \) is used so as to keep the metal ratios the same as the oxide ratios. The standard cement/ceramic notation is used for short hand with \( S=\text{SrO}, B=\frac{1}{2}\text{Bi}_2\text{O}_3 \) and \( C=\text{CuO} \). Thus compositions may be listed simply by numerical ratio, e.g., the formula Sr\textsubscript{2}Bi\textsubscript{2}CuO\textsubscript{6} can be written as S\textsubscript{2}B\textsubscript{2}C or simply 2:2:1.

### 2. Experimental Procedures

In general, about 3.5 g specimens of various compositions in binary and ternary combinations were prepared from SrCO\textsubscript{3}, Bi\textsubscript{2}O\textsubscript{3}, and CuO. Neutron activation analyses of the starting materials indicated that the following impurities (in \( \mu \text{g/g} \)) were present: in CuO—3.9Cr, 2.8Ba, 28Fe, 410Zn, 0.09Co, 1.9Ag, 0.03Eu, 14Sb; in Bi\textsubscript{2}O\textsubscript{3}—2.1Cr, 0.002Sc, 26Fe, 21Zn, 0.6Co, 0.5Ag, 0.0008Eu, 0.2Sb; in SrCO\textsubscript{3}—320Ba, 0.001Sc, 6.3Fe, 3.7Zn, 0.1Co, 0.002Eu. The constituent chemicals were weighed on an analytical balance to the nearest 0.0001 g and mixed either dry or with acetone in an agate mortar and pestle. The weighed specimen was pressed into a loose pellet in a stainless steel die and fired on an MgO single crystal plate, or on Au foil, or on a small sacrificial pellet of its own composition. The pellets were then calcined several times at various temperatures from \( \sim 600 \text{ °C} \) to \( 850 \text{ °C} \), with grinding and repelletizing between each heat treatment. Duration of each heat treatment was generally about 16-20 h. For the final examination a small portion of the calcined specimen was refired at the desired temperature (1-8 times), generally overnight, either as a small pellet or in a small 3 mm diameter Au tube, either sealed or unsealed. Too many heat treatments in the Au tube generally resulted in noticeable loss of Cu to the Au vessel.

When phase relations involving partial melting were investigated, specimens were contained in 3 mm diameter Au, Pt or Ag/Pd tubes and heated in a vertical quench furnace. This furnace was heated by six MoSi\textsubscript{2} hairpin heating elements with vertical 4-in diameter ZrO\textsubscript{2} and 1-in diameter Al\textsubscript{2}O\textsubscript{3} tubes acting as insulators. The temperature was measured separately from the controller at a point within approximately 1 cm of the specimen by a Pt/90Pt10Rh thermocouple, calibrated against the melting points of NaCl (800.5 °C) and Au (1063 °C). After the appropriate heat treatment the specimen was quenched by dropping it into a Ni crucible, which was cooled by He flowing through a copper tube immersed in liquid N\textsubscript{2}.

In order to approach equilibrium phase boundaries by different synthesis routes, many specimens were prepared from pre-made compounds or two-phase mixtures as well as from end
members. These were weighed, mixed and ground in the same way as for the previously described specimens. Also, some specimens were: 1) annealed at some temperature \(T_1\) and analyzed by x-ray powder diffraction; 2) annealed at a higher or lower temperature \(T_2\) where a different assemblage of phases was observed; and 3) returned to \(T_1\) to demonstrate reversal of the reaction(s) between \(T_1\) and \(T_2\). All experimental details are given in tables la and lb. Phase identification was made by x-ray powder diffraction using a high angle diffractometer with the specimen packed into a 5 or 10 mil deep cavity in a glass slide. The diffractometer, equipped with a theta compensating slit and a graphite diffracted beam monochromator, was run at \(1^°/2\theta/\text{min}\) with CuKa radiation at 40 KV and 30 MA. The radiation was detected by a scintillation counter and solid state amplifier and recorded on a chart with \(1^°/2\theta=1\) in. For purposes of illustration and publication, the diffraction patterns of selected specimens were collected on a computer-controlled, step scanning goniometer and the results plotted in the form presented.

Equilibrium in this system has proven to be so difficult to obtain that a few specimens were prepared by utilizing an organic precursor route to obtain more intimate mixtures at low temperatures. It is relatively simple to make mixtures of SrO (with or without CaO) and CuO by utilizing acetate solutions or acrylic acid, but Bi\(\text{O}_3\) is not soluble in these solutions. The carbonates of all three (or four) oxides were therefore dissolved in lactic acid and dried by slow heating in a container with a large surface-to-volume ratio. This procedure yields an essentially single phase amorphous precursor for all compositions that contain less than about 66.7 mole percent Bi\(\text{O}_3\). At higher bismuth contents, pure Bi metal was formed by carbothermic reduction under even the lowest temperature drying procedures in air.

3. Experimental Results and Discussion

Most of the experiments performed on the binary and ternary mixtures of Sr\(\text{O}:\text{Bi}\(\text{O}_2\):\text{CuO}\) are reported in table 1a. Additional experiments specifically designed in an attempt to obtain crystals large enough for x-ray single crystal study are detailed in table 1b. Crystallographic data for various phases are reported in table 2.

3.1 The System Bi\(\text{O}_2\)-CuO

A phase diagram for this system was already published [21], and was redrawn as figure 6392 in Phase Diagrams for Ceramists (PDPC) [22]. It apparently contains only one compound, Bi\(\text{O}_2\)Cu\(\text{O}_4\) (Bi\(\text{C}\)), which is tetragonal, space group P4/ncc, \(a=8.510\), \(c=5.814\) Å [23]. The x-ray powder diffraction data for Bi\(\text{O}_2\)Cu\(\text{O}_4\) were also reported in [23]. The very limited number of experiments performed during the course of this work, as shown in table 1, confirms that this is the only compound formed in the system. No attempt was made to investigate the melting relations of this system because it does not have any great effect on the phase equilibria of the ternary system with Sr\(\text{O}\).

3.2 The System Sr\(\text{O}\)-CuO

Phase equilibria in the high CuO portion of the system were shown in [16], where the new compound "Sr\(\text{O}_4\)Cu\(\text{O}_4\)" (Sr\(\text{C}\)) was proven to exist along with the previously reported SrCu\(\text{O}_2\) [24] and Sr\(\text{O}_3\)Cu\(\text{O}_3\) [25]. Refined unit cell dimensions and standard x-ray powder diffraction data for the last two phases were recently reported: SrCu\(\text{O}_2\) (SC) [26] is orthorhombic (Cmcm) with \(a=3.5730(2)\), \(b=16.3313(8)\), \(c=3.9136(2)\) Å; Sr\(\text{O}_3\)Cu\(\text{O}_3\) (JCPDS 34-283) is also orthorhombic (Immm) \(a=3.4957\), \(b=12.684\), \(c=3.9064\) Å. The unit cell dimensions of Sr\(\text{O}_4\)Cu\(\text{O}_4\) (Sr\(\text{C}\)) [16,17] indicate that it is face centered orthorhombic with \(a=11.483(1)\), \(b=13.399(1)\) and \(c=3.9356(3)\) Å; there are also some superstructure peaks in the pattern which may possibly be indexed on an incommensurate cell that has a c-axis which is about 7 times that of the subcell. The partially indexed x-ray powder diffraction data is given in table 3 and the pattern is illustrated in figure 1.

Determinations of the melting relations in the high-SrO portion of the system were complicated by charge-capsule reactions (table 1). Specimens of Sr\(\text{O}_3\)Cu\(\text{O}_2\) and Sr\(\text{O}_3\)Cu\(\text{O}_3\) (SC and Sr\(\text{C}\)) were calcined to single phase and then small portions reheated in 3-mm diameter unsealed Pt tubes; Au capsules could not be used because the melting points of interest were higher than that of Au (1063 °C). Even though these experiments had a maximum duration of no more than 10 min at high-temperature, some CuO always alloyed with the Pt even at
### Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO

| Spec. no. | Composition, mole percent | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction |
|-----------|---------------------------|-----------------------------------|--------------------|------------------------------|
|           | SrO | Bi$_2$O$_3$ | CuO | Initial | Final |             |                               |
| 75.0      | 75  | 12.5        | 12.5 | 700     | 750   | SrCO$_3$+SrB+"7:2:2"              |
|           |     |             |      | 750     |       | SrB+SrCO$_3$+SrC+"7:2:2"         |
|           |     |             |      | 800     | 850   | SrB+SrC(+SrO7)                    |
|           |     |             |      |         | 900   | SrB+SrC(+SrO7)                    |
| 65        | 10  | 25          |      | 700     | 750   | SrCO$_3$+CuO+"7:2:2"+Sr$_3$Cu$_2$+SrB$_{2w}$ |
|           |     |             |      | 750     |       | "7:2:2"+SrC+SrB+CuO$_{2w}$       |
|           |     |             |      | 800     | 850   | SrC+SrB+"7:2:2"                   |
|           |     |             |      | 900     |       | SrC+SC+Sr$_3$B$_{2w}$+"7:2:2"$_{2w}$ |
| 64.29     | 28.57 | 7.14        |      | 700     | 750   | SrB+Sr$_3$B$_2$+"7:2:2"           |
| SrCO$_3$:Bi$_2$O$_3$:CuO$_2$ | 800×3 | 800×5 |     |         |       | SrB+Sr$_3$B$_2$+"7:2:2"           |
| #1        | 63.63 | 18.18       | 18.18 | 700     | 750   | "7:2:2"+SrB+Sr$_3$B$_2$+SrC+SC+CuO |
|           |     |             |      | 800     | 850   | "7:2:2"+SrB+Sr$_3$B$_2$+SC+SrC   |
|           |     |             |      | 800×3   |       | "7:2:2"+SrB+Sr$_3$B$_2$+SC+SrC   |
|           |     |             |      | 800×6   |       | "7:2:2"+SrB+Sr$_3$B$_2$+SC+SrC   |
|           |     |             |      | 850     |       | "7:2:2"+SrB+Sr$_3$B$_2$+SC+SrC   |
| #2        | S$_2$C:S$_3$B$_2$ | 2:1 | 875×1 |       |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
|           |     |             |      | 875×2   |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
|           |     |             |      | 875×4   |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
| #3        | S$_2$C:S$_3$B$_2$ | 2:1 | 800×3 |       |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
|           |     |             |      | 800×5   |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
|           |     |             |      | 900×3   |       | S$_2$B$_2$+S$_2$C+X(30.25°)      |
| #1        | 63.33 | 5.00        | 31.67 | 750     |       | S$_2$C+SC+SrB$_3$+X$_{er}$       |
| 1/2Bi$_2$O$_3$:S$_2$C | 1.00:6.33 | 750 |       | 900     |       | S$_2$C+SC+SrB$_3$+X$_{er}$       |
|           |     |             |      | 850     | 950   | S$_2$C+SC+SrB$_3$+X$_{er}$       |
| #2        | 1/2Bi$_2$O$_3$:S$_2$C | 1.00:6.33 | 875×5 |       |       | S$_2$C+SC+SrB$_3$+X               |
| #1        | 60   | 10          | 30   | 750     |       | S$_2$C+SC+SrB$_3$+X$_{er}$       |
| 1/2Bi$_2$O$_3$:S$_2$C | 1.3 | 750 |       | 900     |       | S$_2$C+SC+SrB$_3$+X$_{er}$       |
|           |     |             |      | 850     | 950   | S$_2$C+SC+SrB$_3$+X$_{er}$       |
| #2        | 1/2Bi$_2$O$_3$:S$_2$C | 1.3 | 875×5 |       |       | S$_2$C+SC+SrB$_3$+X               |
| #1        | 60   | 20          | 20   | 700     |       | S$_2$C+SC+SrB$_3$+X$_{er}$       |
|           |     |             |      | 750     | 800   | S$_2$C+SC+SrB$_3$+X$_{er}$       |
|           |     |             |      | 850     | 850   | S$_2$C+SC+unk(l1')+"7:2:2"       |
|           |     |             |      | 900     |       | SC+SrC+unk(l1')+"7:2:2"          |
|           |     |             |      | 900×3   |       | S$_2$B$_2$+SC+SrC                |
### Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition, mole percent | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction |
|-----------|---------------------------|-----------------------------------|--------------------|-----------------------------|
|           | SrO | Bi$_2$O$_3$ | CuO | Initial | Final |                         |                                |
| #2        |     |            |     |         |       | "7:2:2" + S$_3$B$_2$ + SC + S$_2$C + S$_3$B + CuO |
|           | 700 | 750        |     |         |       | "7:2:2" + S$_3$B$_2$ + SC + S$_2$C + S$_3$B |
|           | 800 | 800×3      |     | 800×6   |       | "7:2:2" + S$_3$B$_2$ + SC + S$_2$C + S$_3$B |
|           | 850 |           |     |         |       | S$_3$B$_2$ + S$_2$C + SC + "7:2:2" |
| #3        |     |            |     |         |       |                                |
|           | S$_3$C$_2$B$_2$ | 2:1   |     | 700     | 850   |                                |
|           | 875 | 875×5      |     | 875×2   |       |                                |
|           | 900 | S$_3$B$_2$ + SC + 8:4:5 |
|           | 900 × 3 | S$_3$B$_2$ + SC + 8:4:5 |
| #1        | 55  | 35         | 10  | 875(Ag/Pd$^+$) | S$_3$B$_2$ + 2:2:1 + X |
|           | 900 | S$_3$B$_2$ + 2:2:1 + X |
| #1        | 55  | 20         | 25  | 875     | SC + S$_3$B$_2$ + 8:4:5 |
|           | 900 | SC + S$_3$B$_2$ + 8:4:5 |
|           | 875 | SC + S$_3$B$_2$ + 8:4:5 |
| #2        | 50  | 40         | 10  | 850     | S$_3$B$_2$ + 2:2:1 |
|           | 875 | S$_3$B$_2$ + 2:2:1 |
| #1        | 50  | 35         | 15  | 875     | S$_3$B$_2$ + 2:2:1 + 8:4:5 + SC$_{2u}$ |
|           | 900 | S$_3$B$_2$ + 2:2:1 + 8:4:5 + SC$_{2u}$ |
|           | 900 × 3 | S$_3$B$_2$ + 2:2:1 + 8:4:5 + SC$_{2u}$ |
| #2        | S$_3$B$_2$SC | 1.1667:1.0000 | 650 | 750 | 800 | 875 | 2:2:1 + S$_3$B$_2$ + SC |
|           |     |            |     |     |     |     | 2:2:1 + S$_3$B$_2$ + SC |
#1        | 50  | 25         | 25  | 700     | 750×2 | Sr$_2$CO$_3$ + CuO + S$_3$B$_2$ + Sr$_4$C$_{24}$ + "7:2:2" |
|           |     |            |     |         |       | * + SC$_{2u}$ + S$_3$C$_{24u}$ |
|           |     |            |     |         |       | * + 8:4:5 + SC$_{2u}$ + S$_3$C$_{24u}$ |
|           |     |            |     |         |       | * + 8:4:5 + SC$_{2u}$ + S$_3$C$_{24u}$ |
|           |     |            |     |         |       | 8:4:5 + * + SC$_{2u}$ |
|           |     |            |     |         |       | 8:4:5 + S$_3$B$_2$ + SC |
|           |     |            |     |         |       | 8:4:5 + S$_3$B$_2$ + SC |
|           |     |            |     |         |       | 8:4:5 + S$_3$B$_2$ + SC |
|           |     |            |     |         |       | 8:4:5 + S$_3$B$_2$ + SC |
Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition, mole percent* | Temperature of heat treatment; °C | Visual results of x-ray diffraction* |
|-----------|---------------------------|----------------------------------|-----------------------------------|
|           | SrO Bi$_2$O$_3$ CuO      | Initial Final                     |                                   |
| #2        | SC:S$_2$B$_2$ 1.0:0.5    | 880×1 880×5 900×3                 | SC+2:2:1+S$_2$B$_2$              |
|           |                           |                                  | 8:4:5+2:2:1+S$_2$B$_2$+SC        |
|           |                           |                                  | 8:4:5+S$_2$B$_2$+SC              |
| #3        |                           | 650 750 800                       | S$_2$B$_2$+SC+2:2:1               |
|           |                           | 875 900(Au')                     | SC+2:2:1+S$_2$B$_2$+8:4:5        |
|           |                           | 900×3(Au')                      | SC+8:4:5+S$_2$B$_2$              |
|           |                           | 900×6(Au')                      | SC+8:4:5+S$_2$B$_2$              |
|           |                           | 925(Au')                        | SC+8:4:5+S$_2$B$_2$              |
|           |                           | 950(Au')                        | part.melt                        |
|           |                           | 900(Au')                        | SC+S$_2$B$_2$+8:4:5              |
|           |                           | 875(Au')                        | SC+S$_2$B$_2$+8:4:5              |
| #1        | SC:S$_2$B$_2$ 18.5:1.0   | 750 850                          | SrCO$_3$+CuO+"7:2:2"+SC$_{tr}$   |
|           |                           |                                  | CuO+SC+"7:2:2"+S$_2$O$_3$       |
|           |                           |                                  | SC+S$_2$B$_2$+2:2:1+S$_4$C       |
|           |                           |                                  | SC+S$_2$B$_2$+2:2:1              |
|           |                           |                                  | SC+S$_2$B$_2$+2:2:1+8:4:5        |
|           |                           |                                  | SC+$S_2B_2+8:4:5$                |
| #2        | SC:S$_2$B$_2$ 18.5:1.0   | 875×5                            | SC+8:4:5+X                       |
| #1        | SC:S$_2$B$_2$ 18.5:1.0   | 750 850                          | SC+2:2:1+8:4:5                  |
|           |                           |                                  | SC+Rav+S$_2$B$_{tr}$            |
| #2        | SC:S$_2$B$_2$ 8.5:1.0    | 875×5                            | SC+8:4:5+3:2:2                  |
| #1        | SC:S$_2$B$_2$ 8.5:1.0    | 700 750×2                        | SrCO$_3$+CuO+Rav+unk(4.40°)     |
|           |                           |                                  | SrCO$_3$+CuO+Rav+unk(4.40°)     |
|           |                           |                                  | +unk(4.80°)                      |
|           |                           |                                  | 800(Au')                        |
|           |                           |                                  | unk(4.80°)+CuO+SrCO$_3$         |
|           |                           |                                  | 850(Au')                        |
|           |                           |                                  | unk(4.80°)+CuO+SrCO$_3$         |
|           |                           |                                  | 850×2(Au')                      |
|           |                           |                                  | unk(4.80°)+CuO+SrCO$_3$         |
|           |                           |                                  | 875(Au')                        |
|           |                           |                                  | unk(4.40°)+unk(4.80°)+CuO       |
|           |                           |                                  | 900(Au')                        |

*Composition, mole percent

*Temperature of heat treatment; °C

*Visual results of x-ray diffraction

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Table 1a. Experimental data for the ternary system SrO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition, mole percent* | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction
|-----------|-----------------------------|-------------------------------|-------------------|-------------------------------|
|           | SrO | Bi₂O₃ | CuO | Initial | Final |                       |                        |
| #2        |     |       |     | 875    |       | S₂B₂+2:2:1+SC+Sr₄Cu₄+Rav | +3:2:2+S₂B₂          |
|           |     |       |     |        | 900   | S₂B₂+SC+2:2:1+3:2:2+8:4:5 |                     |
|           |     |       |     |        | 900×2 | S₂B₂+SC+2:2:1+3:2:2+8:4:5 |                     |
|           |     |       |     |        | 950   | part.melt                | S₂B₂+Rav+SC          |
| #3L8      |     |       |     | 650    |       | B₂C+SrCO₃+CuO           |                       |
|           |     |       |     |        | 750   | 2:2:1+S₁₃B₂+SC+3:2:2+Sr₄Cu₄ |                     |
|           |     |       |     |        | 850   | 2:2:1+S₁₃B₂+SC+3:2:2+Sr₄Cu₄ |                     |
|           |     |       |     | 450    |       | 8:4:5+2:2:1+SC          |                     |
|           |     |       |     | 850×2  |       | 8:4:5+2:2:1+SC          |                     |
|           |     |       |     | 900×1  |       | 8:4:5+2:2:1+SC          |                     |
|           |     |       |     | 900×4  |       | 8:4:5+2:2:1+SC          |                     |
|           |     |       |     | 925    |       | 8:4:5+SC₄              |                     |
| #4        |     |       |     | 850    |       | comp.melt               | 8:4:5               |
|           |     |       |     | 1250h  |       | 900(h₃)                 | 8:4:5               |
|           |     |       |     |        |       | 925(h₅)                 | 8:4:5               |
| #1        | 45  | 20    | 35  | 850    |       | 875×7                   | SC+3:2:2+Sr₄Cu₄     |
|           |     |       |     |        | 875   | 900                     | SC+Rav+S₁₃B₂+8:4:5  |
|           |     |       |     |        |       | 900×3                   | SC+3:2:2           |
| #2        |     |       |     | 875    |       | 900                     | 3:2:2+SC+2:2:1     |
| #3        | SC:SB₂ | 3.5:1.0 |     | 800    |       | 875×1                   | SC+Sr₄Cu₄         |
|           |     |       |     |        |       | 875×6                   | SC+2:2:1+8:4:5     |
|           | 45  | 45    | 10  | 700    |       | 875                     | S₁₃B₂+2:2:1        |
|           |     |       |     | 800    |       |                         |                    |
|           |     |       |     | 850    |       |                         |                    |
|           | 45  | 35    | 20  | 700    |       | 875                     | 2:2:1+S₁₃B₂+SC     |
|           |     |       |     | 800    |       | 900                     | 2:2:1+S₁₃B₂+SC     |
|           |     |       |     | 850    |       | 875                     | 2:2:1+S₁₃B₂+SC     |
| 44.44     | 33.33 | 22.22 |     | 700    |       | 875                     | 2:2:1+S₁₃B₂+SC     |
|           |     |       |     | 850    |       | 875                     | 2:2:1+S₁₃B₂+SC     |
|           |     |       |     | 875    |       | 900                     | 2:2:1+S₁₃B₂+SC     |
|           |     |       |     | 900    |       | 2:2:1+S₁₃B₂+SC          |                    |
### Table 1a. Experimental data for the ternary system SrO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition, mole percent* | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction$^c$ |
|-----------|--------------------------|-----------------------------------|-------------------|---------------------------------|
|           | SrO                  Bi₂O₃  CuO | Initial  Final                |                   |                                 |
| 43.75     | 25.00                  31.25 | 700 750                            |                   |                                 |
|           |                        | 875 | 3:2:2+SC+Sr₆Cu₂₁+Sr₂B₂          | 3:2:2+SC+Sr₆Cu₂₁+2:2:1_{a} |
|           |                        | 900 | 3:2:2+SC+Sr₆Cu₂₁+2:2:1_{a}      | 3:2:2+SC+Sr₆Cu₂₁   |
| 43.62     | 32.98                  23.40 | 700 750                            |                   |                                 |
|           |                        | 875 | 2:2:1+3:2:2+Sr₆Cu₂₁+SC          | 2:2:1+3:2:2+SC+8:4:5_{a} |
| 43        | 37                     20    | 700 800                            |                   |                                 |
|           |                        | 875 | 2:2:1+SC+Sr₂B₂                 | 2:2:1+SC+Sr₂B₂    |
| 42.86     | 32.65                  24.49 | 700 750                            |                   |                                 |
|           |                        | 875 | 2:2:1+3:2:2+Sr₆Cu₂₁+SC          | 2:2:1+3:2:2+Sr₆Cu₂₁+SC |
| #1        | 42.86 (3:2:2)          | 28.57 28.57                      | 700 850            |                                 |
|           |                        | 850 | 2:2:1+3:2:2+Sr₂Cu₂₁+3:2:2+Sr₂B₂ | 2:2:1+SC+Sr₆Cu₂₁| 3:2:2+Sr₆Cu₂₁+3:2:2+Sr₂B₂ |
|           |                        | 875 | 2:2:1+3:2:2+Sr₂Cu₂₁+3:2:2+Sr₂B₂ | 2:2:1+3:2:2+Sr₂Cu₂₁+SC |
|           |                        | 900×3(An)                         |                   |                                 |
|           |                        | 900×6(An)                         |                   |                                 |
|           |                        | 900×8(An)                         |                   |                                 |
| #2        |                        | 700 750                            |                   |                                 |
|           |                        | 850 | 2:2:1+SC+Sr₆Cu₂₁+3:2:2+Sr₂B₂    | 2:2:1+3:2:2+SC+8:4:5_{a} |
|           |                        | 900 | 2:2:1+3:2:2+SC+8:4:5_{a}        | 2:2:1+3:2:2+Sr₂B₂  |
|           |                        | 900×2                             |                   |                                 |
|           |                        | 925(O₂)[2]                         |                   |                                 |
|           |                        | 925×2(O₂)[2]                      |                   |                                 |
|           |                        | 950(O₂)[2]                         |                   |                                 |
|           |                        | part.melt                         |                   |                                 |
| #3L⁺      |                        | 900×2                             |                   |                                 |
|           |                        | 900×3                             |                   |                                 |
| 42.5      | 47.5                   10     | 800                                |                   |                                 |
|           |                        | 875 | S₃B₂+Rav                       | 2:2:1+3:2:2+SC     |
|           |                        | 925 | comp.melt                      | 2:2:1+3:2:2+SC     |
| 42.16     | 32.35                  25.49 | 700 750                            |                   |                                 |
|           |                        | 875 | 2:2:1+3:2:2+Sr₆Cu₂₁+SC          | 2:2:1+3:2:2+Sr₂Cu₂₁+SC |
|           |                        | 900 | 2:2:1+3:2:2+Sr₆Cu₂₁+SC          | 2:2:1+3:2:2+Sr₂Cu₂₁+SC |
| 42        | 40                     18     | 700 850                            |                   |                                 |
|           |                        | 875 | 2:2:1+3:2:2+Sr₆Cu₂₁+SC          | 2:2:1+3:2:2+Sr₆Cu₂₁+SC |

*Composition in mole percent; °C = temperature of heat treatment; x-ray diffraction refers to results of x-ray diffraction analysis.
Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | SrO   | Bi$_2$O$_3$ | CuO  | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction$^c$ |
|-----------|-------|-----------|------|----------------------------------|--------------------|----------------------------------|
|           |       |           |      | Initial | Final |                                 |                                 |
| 42        | 41    | 41        | 17   | 700     | 850   | 875                              | 2:2:1+SrB$_2$+SrB$_2$           |
| 42        | 38    | 20        |      | 700     | 800   | 850                              | 875                              | 2:1:1+Sr$_2$C$_{24}$+SC         |
|           |       |           |      |         |       | 900                              | 2:2:1+SC                         |
| 41.67     | 33.33 | 25.00     |      | 700     | 750   | 850                              | 875                              | 2:2:1+3:2:2+Sr$_4$C$_{24}$       |
|           |       |           |      | 900×2   |       |                                   | 2:2:1+3:2:2+Sr$_4$C$_{24}'$      |
|           |       |           |      | 900(O$_2$) |       |                                   | 2:2:1+3:2:2+Sr$_4$C$_{24}'$      |
|           |       | 925(Au$^+$) | part.melt | Rav+SC$_{24}$ |       | 2:2:1+3:2:2+Sr$_4$C$_{24}$       |
|           |       | 925(O$_2$) | no melting |         |       | 2:2:1+3:2:2+Sr$_4$C$_{24}$       |
| 41        | 44    | 15        |      | 700     | 850   | 875                              | 2:2:1+Rav+SrB$_2$               |
|           |       |           |      | 900     |       |                                   | 2:2:1+SrB$_2$+Rav               |
| 41        | 43    | 16        |      | 700     | 850   | 875                              | 2:2:1+SrB$_2$+Rav               |
|           |       |           |      | 900     |       |                                   | 2:2:1+SrB$_2$                   |
| 41        | 42    | 17        |      | 700     | 850   | 875                              | 2:2:1+SrB$_2$                   |
|           |       |           |      | 900     |       |                                   | 2:2:1+SrB$_{24}$               |
| 41        | 41    | 18        |      | 700     | 850   | 870                              | 2:2:1+SrB$_{24}$               |
|           |       |           |      | 900     |       |                                   | 2:2:1+Sr$_2$C$_{24}$r           |
|           |       | 925      | part.melt | Rav+2:2:1 |       | 2:2:1+Sr$_2$C$_{24}$r           |
| 41        | 40    | 19        |      | 700     | 850   | 870                              | 2:2:1                          |
|           |       |           |      | 900     |       |                                   | 2:2:1+Sr$_2$C$_{24}$r           |
|           |       | 900(Au$^+$) |         | 2:2:1+Sr$_2$C$_{24}$r |       | 2:2:1+Rav                       |
| 41        | 39    | 20        |      | 700     | 850   | 875                              | 2:2:1+Sr$_2$C$_{24}$r           |
|           |       |           |      | 900     |       |                                   | 2:2:1+Sr$_2$C$_{24}$r           |
Table Ia. Experimental data for the ternary system SrO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition, mole percenta | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffractionb |
|-----------|-----------------------------|----------------------------------|-------------------|------------------------------|
|           | SrO                         | Initial − Final                  |                   |                              |
| 40.67     | 40.32                       | 19.00                            |                   |                              |
| 1.00:0.45:1.00 |                        | 880                             | 880×5             | 2:2:1 + Rav                 |
|           |                             |                                  |                   |                              |
| 40.5      | 49.5                        | 10.0                             |                   |                              |
|           |                             | 750                             | 800               | Rav + S₂B₂ + Tet             |
|           |                             |                                  | 850               | Rav + S₂B₂ + Tet             |
|           |                             |                                  | 875               | Tet + Rav + 2:2:1            |
| 40.5      | 40.5                        | 19.0                             |                   |                              |
|           |                             | 700                             | 850               | R₂B₂ + S₂B₂ + Rav            |
|           |                             |                                  |                   |                              |
| #1        | 40                          | 40                              | 20                |                              |
|           |                             | 650                             | 750               | Rav + S₂B₂                   |
|           |                             |                                  | 800               | 2:2:1 + S₂B₂ + Rav           |
|           |                             |                                  | 850               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
|           |                             |                                  | 870               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
|           |                             |                                  | 900               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
|           |                             |                                  |                   |                              |
| #2        | 650                         | 750                             | 800               | Rav + S₂B₂                   |
|           |                             |                                  | 850               | 2:2:1 + S₂B₂ + Rav           |
|           |                             |                                  | 870               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
|           |                             |                                  |                   |                              |
| #3        | SC:SB₂                      | 1:1                             | 850×1             | Rav + SC + 2:2:1 + S₂B₂ + S₂B₂ + Rav₉|
|           |                             |                                  | 850×2             | 2:2:1 + Rav + SCu + S₂C₉   |
| #4        | SC:SB₂                      | 1:1                             | 650               | Rav + S₂B₂                   |
|           |                             | 750                             | 800               | 2:2:1 + S₂B₂ + Rav           |
|           |                             |                                  | 875               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
|           |                             |                                  | 925               | 2:2:1 + S₂B₂ + Rav + Rav₉   |
| #5        | S₂B₂CuO                     | 1:1                             | 880               | Rav + 2:2:1                  |
|           |                             |                                  | 880×5             | 2:2:1 + Rav                  |
|           |                             |                                  | 900(Q₂)           | Rav + 2:2:1                  |
|           |                             |                                  | 950               | comp.melt                    |
|           |                             |                                  | 875               | 2:2:1 + Rav                  |
|           |                             |                                  | 900-PO₃          | 2:2:1 + Rav"                 |
|           |                             |                                  | 0.15             | 2:2:1 + Rav "                |

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Table 1a. Experimental data for the ternary system SrO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition, mole percent | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction |
|-----------|--------------------------|----------------------------------|-------------------|-----------------------------|
|           | SrO          Bi₂O₃        CuO | Initial Final                    |                   |                             |
| #6        | 800(O₂)      850(O₂)      900(O₂) |                      | Rav + 2:2:1       |                             |
| #7        | 850          1250 a        comp.melt | Rav + S₂B₂          | Rav + 2:2:1       |
|           | 800          850           900        |                      | Rav + 2:2:1         | Rav + 2:2:1                 |
|           | 900          900 × 2       900 × 3   |                      | Rav + 2:2:1         | Rav + 2:2:1                 |
|           | 900(O₂)      925(O₂)      |                      | Rav + 2:2:1         | Rav + 2:2:1                 |
| 40        | 20           40            | 650                    | Rav + 2:2:1 + CuO + S₂B₂ + X |                           |
|           | 750          800           850        |                      | 2:2:1 + Sr₆C₆ + SC |                           |
|           | 900          650           750        |                      | 2:2:1 + 3:2:2 + Sr₆C₆ + Sr₆C₆ |                       |
| 38        | 42           20            | 880 × 1               | Rav + 2:2:1       |                             |
| S₃B₂Tet:CuO | 1.00:0.45:1.00 |                          |                   |                             |
| 37        | 44           19            | 700                    | Rav + 2:2:1       |                             |
|           | 850          900           |                      | Rav + 2:2:1       |                             |
| 37        | 43           20            | 700                    | Rav + 2:2:1       |                             |
|           | 850          900           |                      | Rav + 2:2:1       |                             |
| 36.66     | 53.33        10.00         | 700                    | Rav + SB₂ + S₂B₂  |                             |
|           | 750          850           |                      | Rav + SB₂ + Tet   |                             |
|           | 875          part.melt     |                      | Rav + SB₂ + Tet   |                             |
| 36.66     | 36.66        26.66         | 650                    | Rav + S₂B₂ + CuO  |                             |
|           | 750          800           850        |                      | 2:2:1 + Rav + CuO + Sr₆C₆ |                       |
|           | 870          900           |                      | 2:2:1 + Rav + CuO + Sr₆C₆ |                       |
| 36.15     | 44.50        19.35         | 880                    | Rav + S₂B₂ + SC   |                             |
| S₂B₂-5Bi₂O₅SC | 0.700:1.4444:1.0000 |                          |                   |                             |
|           | 880          880 × 5       |                      | Rav + 2:2:1       |                             |

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Table 1a. Experimental data for the ternary system SrO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition, mole percent | Temperature of heat treatment; °C | Visual observation | Results of x-ray diffraction |
|-----------|--------------------------|----------------------------------|--------------------|------------------------------|
|           | SrO          | Bi₂O₃ | CuO | Initial | Final | |
| 36        | 45           | 19    |     | 700     | 850   | 900 | Rav+2:2:1 |
| #1        | 36           | 44    | 20  | 700     | 850   | 875X7 | Rav+2:2:1 |
|           |              |       |     |         |       | 880(Au') | Rav |
|           |              |       |     |         |       | 880X2(Au') | Rav |
|           |              |       |     |         |       | 900X3  | Rav |
| #2        | Tet:CuO      | 800   |     | 875     | 875X5 | Rav |
|           | 9:5          |       |     |         |       | Rav |
| #3        | Rhomb:SC     | 875X5 |     | 950     | 875   | Rav+2:2:1 |
|           | 1.00:1.25    |       |     |         |       | comp.melt |
| 35.29     | 43.14        | 21.57 |     | 800     | 875   | Rav+CuO |
|           | Tet:CuO      | 9:0:5.5 |     | 875     | 875X5 | Rav+CuO |
| 35        | 48           | 17    |     | 700     | 850   | 875 | Rav+Rhomb
| 35        | 47           | 18    |     | 700     | 830   | 875 | Rav+Rhomb
| 35        | 46           | 19    |     | 700     | 850   | 875 | Rav+Rhomb |
| 35        | 45           | 20    |     | 700     | 850   | 875 | Rav+Rhomb |
| 35        | 5            | 60    |     | 700     | 850   | 900 | Sr₃Cu₂+Rav+CuO |
| 34.66     | 55.33        | 10.00 |     | 700     | 750   | 800 | SB₂+Rav |
|           |              |       |     |         |       | 850 | SB₂+Rav |
|           |              |       |     |         |       | 875 | part.melt |
| 34        | 47           | 19    |     | 700     | 800   | 875 | Rav |
### Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition, mole percent $^a$ | Temperature of heat treatment; °C $^b$ | Visual observation | Results of x-ray diffraction $^c$ |
|-----------|-------------------------------|----------------------------------------|-------------------|----------------------------------|
|           | SrO  | Bi$_2$O$_3$ | CuO | Initial | Final |                          |                                  |
| #1        | 33.33 | 33.33 | 33.33 | 800(12hr) | 900(2hr)$^a$ | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| #2        | 650   | 750   | 800   | 870     | 900   | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| #3        | 5$\frac{1}{2}$Bi$_2$O$_3$:SC | 1:1 | 800   | 850     |       | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| #4        | 5$\frac{1}{2}$Bi$_2$O$_3$:SC | 1:1 | 650   | 750     | 800   | 875             | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| 33        | 47    | 20    | 700   | 850     | 875   | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| #5        | 48    | 20    | 880×1 | 880×5   |       | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| #6        | 46    | 22    | 880×2 | 880×5   |       | Rav+CuO+2:2:1+S$_{14}$C$_{24}$ |
| 31.842    | 5.000 | 63.158| 700   | 850     | 900   | S$_{14}$C$_{24}$+Rav+CuO  |
| 31.33     | 58.66 | 10.00 | 700   | 750     | 850   | Rhomb+Rav          | 875 comp.melt Rhomb+Rav         |
| #1        | 30.75 | 47.25 | 22.00 | 750     | 900   | Slight melt        | Rav+Rhomb                      |

$^a$ Composition as mole percent.
$^b$ Temperature of heat treatment in °C.
$^c$ Results of x-ray diffraction.
Table 1a. Experimental data for the ternary system SrO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition, mole percent$^a$ | Temperature of heat treatment; °C | Visual | Results of x-ray diffraction$^d$ |
|-----------|-----------------------------|----------------------------------|-------|----------------------------------|
|           | SrO | 1/2Bi$_2$O$_3$ | CuO | Initial | Final | observation | |
| #2        |     |                |     | 700    | 850   |             | 875 | Rav   |
| 30        | 30  | 50             | 20  | 1.8888:0.5000:1.0000 | 880 | 880×5 | Rav+Rhomb |
|           | 880×2 | Rav+Rhomb  |
| 30        | 47  | 23             |     | 1.6715:0.3043:1.0000 | 880×2 | 880×5 | Rav+CuO+Rhomb |
|           | Rav+CuO+Rhomb  |
| 30        | 45  | 25             |     | 1.5555:0.2000:1.0000 | 880×2 | 880×5 | Rav+CuO |
|           | Rav+CuO  |
| 28        | 48  | 24             |     | 1.0000:1.7963:0.1667 | 880×2 | 880×5 | Rhom+Rav+CuO$_y$ |
|           | Rhom+Rav+CuO$_y$  |
| 20.0      | 46.5 | 33.5 | 650 | 750 | 800 | 850 | consid.melt | Rav+Rhomb+CuO$_y$ |
| 10.00     | 56.66 | 33.33 | 700 | 750 | 800 | Rhomb+Bi$_2$C+CuO |
|           | Rhomb+Bi$_2$C+CuO  |

* Starting materials: SrCO$_3$, Bi$_2$O$_3$, CuO, except when listed in italics. Compositions given in italics were formulated from the listed prereacted compounds or compositions. S.B. = Sr$_{1240}$Bi$_{1222}$O$_{394}$, Rhomb = SrBi$_{122}$O$_{312}$, Tet = SrBi$_{12}$O$_{24}$.

$^d$ Specimens were given all previous heat treatments listed in the initial column, sequentially, and held at temperature 16-24 h, with grinding in-between, for the number of times shown and then reheated at the final temperature overnight. Specimens were heated as pellets on Au foil or MgO single crystal plates, except as indicated. In general, only a small portion of the specimen used for the initial (calcined) heat treatments was used to make sequential “final” heat treatments. Q = quenched.

$^d$ Compounds are listed in order of estimated amounts, most prevalent first.

tr = trace, just barely discernible
B$_2$C = Bi$_2$CuO$_4$
S$_2$C = Sr$_2$CuO$_3$
SC = SrCu$_2$O$_3$
Sr$_2$Cu$_4$ = Sr$_2$Cu$_2$O$_4$
Rhom = rhombohedral solid solution
SB$_2$ = SrBi$_2$O$_4$
Tet = Tetragonal solid solution near SrBi$_{12}$O$_{24}$
S$_2$B$_2$ = Sr$_2$Bi$_2$O$_5$
S$_3$B$_2$ = Sr$_3$Bi$_2$O$_6$
S$_3$B = Sr$_3$Bi$_2$O$_6$
2:2:1 = Sr$_2$Bi$_2$Cu$_4$O$_8$
Rav = Raveau-type solid solution, ~Sr$_{1.8-2.2}$Bi$_{3.2-4.2}$CuO$_2$
8:4:5 = Sr$_8$Bi$_4$Cu$_4$O$_{19-20}$
3:2:2 = Sr$_3$Bi$_2$CuO$_6$
X, unk = phases of unknown composition

"7:2:2" = unknown phase, probably oxycarbonate with diffraction peaks a ~18.40° and ~21.27° 2θ

*=unknown phase, probably an oxycarbonate, with diffraction peaks a 4.40° and 5.68° plus major peaks at 30.50° and 32.45° 2θ
Footnotes to table 1a—Continued

*d* These specimens are numbered when more than one batch of a given oxide ratio were prepared.

*e* Specimens were heated in 70Ag/30Pd tubes, which caused the appearance of unknown phases due to reaction with the tube.

*f* Specimens were contained in 3-mm diameter Au tubes. Excessive heat treatment in such tubes resulted in appreciable loss of Cu to the surrounding Au tube.

*g* L=Specimen prepared by an organic precursor route utilizing lactic acid.

*h* The specimen was melted in an Al2O3 crucible and poured onto an Al chill plate.

*i* Specimen heated in one atmosphere pure oxygen instead of in air.

*j* Increase in amount of S3B2 relative to 3:2:2; indicates that the 3:2:2 phase is not favored by higher oxygen partial pressure.

*k* Specimen cooled from 925 to 889 °C at 1 °C/h.

*l* Amount of 2:2:1 phase not increased.

*m* Specimen heated in atmosphere of mixed Argon/Oxygen with the partial pressure of oxygen equal to 0.15 atm; amount of 2:2:1 phase greatly increased.

*n* Amount of 2:2:1 phase increased relative to previous heat treatment.

*p* This specimen was prepared as described in reference [30].

Table 1b. Experimental conditions for crystal growth experiments

| Charge       | Flux     | Container   | Temperature cycle | Results          |
|--------------|----------|-------------|-------------------|------------------|
| Sr0:1/2Bi2O3 | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h |                  |
| 4:1          | 98 wt%   | 2 wt%       |                   |                  |
| Sr0:1/2Bi2O3 | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h |                  |
| 4:1          | 90 wt%   | 10 wt%      |                   |                  |
| Sr0:1/2Bi2O3 | (KNa)Cl  | sealed small diameter Au | 1025—650 °C | @ 5 °C/h        |
| 4:1          | 80 wt%   | 20 wt%      |                   |                  |
| Sr4Bi2O5     |          | open small  diameter Au | 925—900 °C | @ 0.3 °C/h      |
| Sr4Bi2O5     | (KNa)Cl  | sealed small diameter Au | 900 °C 16 h |                  |
| 98 wt%       | 2 wt%    |             |                   |                  |
| Sr4Bi2O5     | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h |                  |
| 98 wt%       | 2 wt%    |             |                   |                  |
| Sr4Bi2O5     | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h | S3B oxychloride |
| 90 wt%       | 10 wt%   |             |                   |                  |
| Sr4Bi2O5     | (KNa)Cl  | sealed small diameter Au | 1025—650 °C | @ 5 °C/hr       |
| 80 wt%       | 20 wt%   |             |                   | S3B2 xths       |
|               |          |             |                   | hydrate after long exposure to air |
| Sr4Bi2O5     | (KNa)Cl  | sealed small diameter Au | 925—650 °C |                  |
| 80 wt%       | 20 wt%   |             |                   | @ 4 °C/h        |
| SrO:1/2Bi2O3 | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h |                  |
| 2:1          | 98 wt%   | 2 wt%       |                   |                  |
| SrO:1/2Bi2O3 | (KNa)Cl  | sealed small diameter Au | 800 °C 16 h |                  |
| 2:1          | 90 wt%   | 10 wt%      |                   |                  |
| Sr2Bi2O5     |          | sealed small diameter Pt | 925 °C 162 h | S3B2 xths       |
|               |          |             |                   | Partially melted|
Table 1b. Experimental conditions for crystal growth experiments—Continued

| Charge          | Flux          | Container | Temperature cycle | Results          |
|-----------------|--------------|-----------|-------------------|------------------|
| Sr₂Bi₂O₃       | sealed small | 1025→950 °C @ 1 °/h | b.c. Tet         |
| Sr₂Bi₂O₃       | sealed small | 1025→900 °C @ 1 °/h | b.c. Tet         |
| Sr₂Bi₂O₃       | sealed small | 1025→900 °C @ 1 °/h; 875 °C-225 h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 900→640 °C @ 3 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 900→660 °C @ 3 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 900→660 °C @ 3 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed large | 900→760 °C @ 3 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed large | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂Bi₂O₃       | (KNa)Cl      | sealed small | 800→645 °C @ 1 °/h | S₂B₂          |
| Sr₂O₁/2Bi₂O₃:CuO | (KNa)Cl      | sealed small | 900 °C 16 h      | xtals soluble in H₂O |
| Sr₂O₁/2Bi₂O₃:CuO | (KNa)Cl      | sealed small | 900 °C 16 h      | xeels soluble in H₂O |
| Sr₂O₁/2Bi₂O₃:CuO | (KNa)Cl      | sealed large | 950→615 °C @ 1 °/min |          |
| Sr₂O₁/2Bi₂O₃:CuO | (KNa)Cl      | sealed small | 900 °C 16 h      | partially melted needlelike xeels of 8:4:5 |
| Sr₂O₁/2Bi₂O₃:CuO | 2NaF:SrF₂   | sealed small | 900→650 °C @ 3 °/h | Partially melted Rav |
| Sr₂O₁/2Bi₂O₃:CuO | Ag/Pd small  | 950→800 °C @ 1 °/h |                |
### Table 1b. Experimental conditions for crystal growth experiments—Continued

| Charge                  | Flux          | Container   | Temperature cycle | Results                                   |
|------------------------|---------------|-------------|-------------------|-------------------------------------------|
| Sr$_2$Bi$_2$Cu$_2$O$_8$ | (KNa)Cl       | sealed small diameter Au | 900 °C 16 h       | crystals not soluble in H$_2$O              |
| 90 wt%                 | 10 wt%        |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | Ag/Pd small   |             |                   |                                            |
| 42.5:47.5:10           | diameter tube |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | sealed small  |             |                   |                                            |
| 41:41:18               | diameter Au   |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | open small    |             |                   |                                            |
| 41:40:19               | diameter Au   |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | Ag/Pd small   |             |                   |                                            |
| 40.5:49.5:10           | diameter tube |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | Pt small      |             |                   |                                            |
| 42:58                  | diameter tube |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | sealed small  |             |                   |                                            |
| 40.5:40.5:19           | diameter Au   |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | sealed small  |             |                   |                                            |
| 50.86:49.14            | diameter Au   |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | (KNa)Cl       | sealed small diameter Au | 900 °C 16 h       | completely melted                           |
| 90 wt%                 | 10 wt%        |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | NaF:KF        | sealed small diameter Au | 900 °C 3 d         | Rav                                        |
| 98 wt%                 | 2 wt%         |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | NaF:KF        | sealed small diameter Au | 900°C-650 °C      | Rav                                        |
| 90 wt%                 | 10 wt %       |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | 2NaF:SrF$_2$  | sealed small diameter Au | 850°C-650 °C      | Rav                                        |
| 90 wt%                 | 10 wt %       |             |                   |                                            |
| Sr$_2$Bi$_2$Cu$_2$O$_6$ | 2NaF:CaF$_2$  | sealed small diameter Au | 900°C-650 °C      | Rav                                        |
| 90 wt%                 | 20 wt%        |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | (KNa)Cl       | sealed small diameter Au | 1025°C-650 °C    |                                            |
| 3 : 2 : 3              |               |             |                   |                                            |
| 80 wt%                 | 20 wt%        |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | Ag/Pd small   |             |                   |                                            |
| 36 : 44 : 20           | diameter tube |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | large         |             |                   |                                            |
| 1 : 1 : 1              | diameter Pt   |             |                   |                                            |
| SrO:1/2Bi$_2$O$_3$:CuO | (KNa)Cl       | sealed small diameter Au | 1025°C-650 °C    |                                            |
| 1 : 1 : 1              |               |             |                   |                                            |
| 80 wt%                 | 20 wt%        |             |                   |                                            |
temperatures well below melting. Partial melting was assumed to have occurred when the x-ray powder diffraction pattern of a quenched specimen indicated an abrupt change in the phase fraction of a second phase. Both SrCuO\(_2\) and Sr\(_2\)CuO\(_3\) melt incongruently: SrCuO\(_2\) melts to liquid plus Sr\(_2\)CuO\(_3\) at \(\sim\) 1085 °C, and Sr\(_2\)CuO\(_3\) melts to liquid plus SrO at \(\sim\) 1225 °C. The phase equilibria diagram constructed from the data in table 1 and the previously reported experiments [16] is shown in figure 2.

### 3.3 The System SrO-Sr\(_2\)CuO\(_3\)

The phase equilibria diagram for the system SrO-Sr\(_2\)CuO\(_3\) was reported in [27] and redrawn as figure 6428 in PDFC [22] and figure 3 (where the scale is changed to \(\text{Bi}_2\text{O}_3:\text{CuO}\) instead of the original \(\text{Bi}_2\text{O}_3:\text{CuO}\) to be consistent with the other phase diagrams in this report). Considerable effort was made to study the phase relations of this binary. Complete experimental results are published in [28], and the results are shown in figures 4a and 4b.
Table 3. X-ray powder diffraction data for Sr$_{16}$Cu$_{24}$O$_{41}$

| $d$ (Å) | Rel $I$ (%) | $2\theta$ obs | $2\theta$ calc$^a$ | $hkl$ |
|---------|-------------|---------------|-------------------|------|
| 6.68    | 2           | 13.25         | 13.22             | 020  |
| 5.72    | <1          | 15.48         | 15.45             | 200  |
| 4.352   | 2           | 20.39         | 20.38             | 220  |
| 3.596   | 6           | 24.74         | 24.75             | 111  |
| 3.347   | 12          | 26.61         | 26.61             | 040  |
| 3.021$^b$ | 1          | 29.55         |                   |      |
| 2.8879  | 100         | 30.94         | 30.91             | 240  |
| 2.8608  | 66          | 31.24         | 31.22             | 131  |
| 2.6853  | 52          | 33.34         | 33.30             | 311  |
| 2.6339  | 10          | 34.01         | 34.00             | 420  |
| 2.6049$^b$ | 1         | 34.40         |                   |      |
| 2.4245$^b$ | 1         | 37.05         |                   |      |
| 2.3364  | 38          | 38.50         | 38.47             | 331  |
| 2.2834$^a$ | 1         | 39.43         |                   |      |
| 2.2324  | 1           | 40.37         | 40.39             | 060  |
| 2.1742  | 42          | 41.47         | 41.47             | 151  |
| 2.0801  | 1           | 43.47         | 43.48             | 260  |
| 1.9878$^b$ | 3         | 45.60         |                   |      |
| 1.9718  | 13          | 45.99         | 45.96             | 002  |
| 1.9582  | 6           | 46.33         |                   |      |
| 1.9103  | 14          | 47.56         | 47.55             | 600  |
| 1.8920  | 6           | 48.05         | 48.04             | 022  |
| 1.8657  | 2           | 48.77         | 48.78             | 202  |
| 1.8361  | 17          | 49.61         | 49.57             | 620  |
| 1.8108  | 46          | 50.35         | 50.32             | 531  |
| 1.7975  | 3           | 50.75         | 50.76             | 222  |
| 1.7610  | 2           | 51.88         | 51.87             | 460  |
| 1.7413$^b$ | 2         | 52.51         |                   |      |
| 1.7096$^b$ | 2         | 53.56         |                   |      |
| 1.7026  | 3           | 53.80         | 53.81             | 171  |
| 1.6733  | 15          | 54.82         | 54.81             | 080  |
| 1.6599  | 2           | 55.30         | 55.32             | 640  |
| 1.6290  | 16          | 56.44         | 56.42             | 642  |
| 1.5934  | 9           | 57.82         | 57.82             | 551  |
| 1.5789  | 2           | 58.40         | 58.39             | 422  |
| 1.5606  | 13          | 58.78         | 58.79             | 371  |
| 1.5542$^b$ | 1         | 59.42         |                   |      |
| 1.5117$^b$ | 1         | 61.27         |                   |      |
| 1.5037  | 1           | 61.63         | 61.65             | 711  |
| 1.4783  | 4           | 62.81         | 62.82             | 062  |
| 1.4624  | 11          | 63.57         | 63.59             | 442  |
| 1.4518  | 9           | 64.09         | 64.11             | 660  |
| 1.4422$^b$ | 3         | 64.57         |                   |      |
| 1.4327  | 15          | 65.05         | 65.05             | 731  |
| 1.4017  | 5           | 66.67         | 66.69             | 820  |
| 1.3731  | 11          | 68.25         | 68.28             | 602  |
| 1.3450  | 4           | 69.88         | 69.90             | 622  |

$^a$ Calculated from an orthorhombic unit cell, $a=11.466(2)$; $b=13.389(2)$ and $c=3.9458(6)$ Å.

$^b$ Superstructure peak.

(compare with fig. 3). The major differences between our new diagram and the one presented in [27] are: 1) the occurrence of a new compound which is estimated to have the stoichiometry Sr$_6$Bi$_2$O$_9$ (fig. 4a); 2) the presence of a high temperature polymorph of SrBi$_2$O$_4$ (fig. 4b) which becomes stable between 800 and 825 °C and melts incongruently at 940±5 °C; and 3) the determination of melting relations in the region of 20–50 mol percent SrO.
Figure 1. X-ray powder diffraction pattern of Sr$_4$Cu$_{24}$O$_{41}$ (cooled from 925 °C). *Superstructure peaks.

Figure 2. Phase diagram for the system SrO-CuO •-not melted, ○-partially melted, O-completely melted.
3.3.1 Rhombohedral Solid Solution (Sillen Phase-Rhomb) The rhombohedral solid solution was first reported by Sillen [29] and it was later shown by Levin and Roth [30] that the solidus temperature is increased when SrO is added to face-centered-cubic (fcc) $\text{Bi}_2\text{O}_3$, or when it is added to the rhombohedral solid solution phase. Melting relations in the SrO-rich region of the Sillen phase field were previously [27] represented schematically (by dashed lines) as a melting loop, but the experiments reported in [28] indicate a congruent melting point between 25-30 mol% SrO and 950-960 °C. Guillermo et al. [27] reported that a phase transition occurred from one rhombohedral phase to another, but as this has not been confirmed by quench data, such possible polymorphism is ignored in the present work. X-ray diffraction data for this phase are well established [27] and will not be summarized here.

3.3.2 $\text{SrBi}_2\text{O}_4$ (SB$_2$) $\text{SrBi}_2\text{O}_4$ appears to have both high- and low-temperature polymorphs with a transition point at about 825 °C. The high-temperatures form melts incongruently to liquid plus the tetragonal solid solution (next section) between 940 and 945 °C. In the high to low-temperature transition, sharp x-ray diffraction peaks in a powder pattern of the low-temperature phase become broad and diffuse when specimens are quenched from about 825-940 °C. Also, a few maxima (e.g., 202) that are present in patterns from the low-temperature phase have drastically reduced intensities in patterns from samples that were quenched from above 825 °C. The indexed x-ray powder diffraction data for low-$\text{SrBi}_2\text{O}_4$ are listed in table 4. The patterns for both low-temperature and high-temperature $\text{SrBi}_2\text{O}_4$ are shown in figure 5. The observed broadening of diffraction maxima in the pattern from the quenched sample suggests that the high-temperature polymorph, perhaps orthorhombic, was not successfully quenched. The presence of broad rather than sharp peaks suggests a small domain size in samples quenched from above 825 °C.

Very small single crystals of low-temperature $\text{SrBi}_2\text{O}_4$ were prepared (table 1b) by heating a pre-reacted powder sample of $\text{SrBi}_2\text{O}_4$ plus a 1:1 NaCl:KCl flux (80/20 flux/charge ratio) in a sealed Pt tube. The specimen was heated to 740 °C and cooled to 570 °C at 6 °C/h. After the flux was dissolved with H$_2$O, a very thin flat platelet was
Figure 4a. Phase diagram for the system SrO-\(\frac{1}{2}\)Bi\(_2\)O\(_3\) as reported in [28] ● not melted, ○ partially melted, O completely melted.

Figure 4b. Enlargement of figure 4a showing polymorphism of SrBi\(_2\)O\(_4\).
Table 4. X-ray powder diffraction data for the compound SrBi₂O₄

| d obs(Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl |
|----------|----------|--------|----------|-----|
| 9.64     | 9        | 9.17   | 9.19     | 200 |
| 6.09     | 4        | 14.53  | 14.55    | 001 |
| 5.36     | 1        | 16.54  | 16.56    | 201 |
| 4.813    | 22       | 18.42  | 18.44    | 400 |
| 3.626    | 7        | 24.53  | 24.53    | 401 |
| 3.066    | 6        | 24.67  | 24.69    | 310 |
| 3.454    | 29       | 25.77  | 25.78    | 111 |
| 3.205    | 97       | 27.81  | 27.81    | 600 |
| 3.168    | 100      | 28.15  | 28.16    | 311 |
| 3.040    | 93       | 29.36  | 29.38    | 311 |
| 2.9743   | 15       | 30.02  | 30.03    | 202 |
| 2.9417   | 3        | 30.36  | 30.38    | 601 |
| 2.8326   | 6        | 31.56  | 31.57    | 202 |
| 2.7421   | 13       | 32.63  | 32.63    | 601 |
| 2.6728   | 7        | 33.50  | 33.51    | 511 |
| 2.5454   | 1        | 35.23  | 35.25    | 511 |
| 2.4781   | 7        | 36.22  | 36.23    | 402 |
| 2.4526   | 3        | 36.61  | 36.63    | 111 |
| 2.4051   | 1        | 37.36  | 37.38    | 800 |
| 2.3065   | 19       | 39.02  | 39.03    | 620 |
| 2.2724   | 5        | 39.63  | 39.64    | 312 |
| 2.1782   | 34       | 41.42  | 41.42    | 020 |
| 2.1196   | 22       | 42.62  | 42.59    | 711 |
| 2.0501   | 1        | 44.14  | 44.13    | 021 |
| 2.0291   | 2        | 44.62  | 44.62    | 512 |
| 2.0197   | 3        | 44.84  | 44.86    | 203 |
| 1.9841   | 5        | 45.69  | 45.69    | 420 |
| 1.9686   | 5        | 46.07  | 46.07    | 802 |
| 1.9191   | 19       | 47.33  | 47.35    | 910 |
| 1.8701   | 33       | 48.65  | 48.63    | 911 |
| 1.8427   | 8        | 49.42  | 49.40    | 113 |
| 1.8145   | 17       | 50.24  | 50.25    | 403 |
| 1.8018   | 43       | 50.62  | 50.63    | 620 |
| 1.7909   | 31       | 50.95  | 50.95    | 911 |
| 1.7705   | 16       | 51.58  | 51.57    | 022 |
| 1.7569   | 11       | 52.01  | 52.00    | 222 |
| 1.7318   | 9        | 52.82  | 52.81    | 313 |
| 1.7270   | 8        | 52.98  | 53.00    | 222 |
| 1.7096   | 10       | 53.56  | 53.53    | 513 |
| 1.7058   | 12       | 53.69  | 53.70    | 621 |
| 1.6812   | 3        | 54.54  | 54.54    | 912 |
| 1.6514   | 2        | 55.61  | 55.60    | 603 |
| 1.6357   | 5        | 56.19  | 56.18    | 422 |
| 1.6107   | 6        | 57.14  | 57.12    | 513 |
| 1.5923   | 11       | 57.47  | 57.45    | 122 |
| 1.5831   | 19       | 58.23  | 58.22    | 622 |
| 1.5691   | 7        | 58.80  | 58.77    | 912 |
| 1.5670   | 6        | 58.89  | 58.90    | 10,0 |

*Calculated on the basis of a monoclinic cell, C2/m, a=19.301(2), b=4.3563(5), c=6.1049(7) Å, β=94.85(1)°.

picked and single crystal x-ray precession photographs were taken (fig. 6) of it. The precession data indicate that the phase is C-centered monoclinic, probably C2/m, and unit cell dimensions refined from x-ray powder diffraction data are a=19.301(2), b=4.3563(5), c=6.1049(7) Å, β=94.85(1)°. Larger crystals were obtained from both 80:20 and 50:50 flux/charge ratios by cooling from 800 °C to 645 °C at 1°/h.
3.3.3 The Tetragonal Solid Solution Near SrBi$_2$O$_2$ (Tet) This phase was previously reported [27] with space group I4/m, $a = 13.239(2)$, $c = 4.257(1)$ Å. Experiments during the course of this study agree reasonably well with those previously reported, except for the region near the solidus where we find the single phase region extends to compositions with at least 50 mol percent SrO. The x-ray powder diffraction data was previously reported [27]. Very large single crystals were obtained by cooling the Sr$_2$Bi$_2$O$_5$ composition from above the melting point to ~950 °C.

3.3.4 Sr$_2$Bi$_3$O$_5$(S$_2$B$_4$) The compound Sr$_2$Bi$_3$O$_5$ was reported [27] to be orthorhombic, space group Pcmn with $a = 14.293(2)$, $b = 7.651(2)$ and $c = 6.172(1)$ Å. Although precession photographs collected from very small crystals in the present study show evidence of only $\frac{1}{2}$ the $b$ axis reported in [27] (see fig. 7), much larger crystals showed a very weak superstructure and a doubled $b$-axis. The subcell space group is apparently Cmcm and in this orientation $a = 3.8262(2)$, $b = 14.307(1)$, $c = 6.1713(4)$ Å as obtained from a least-squares refinement of the powder data. The indexed powder data are given in table 5 and illustrated in figure 8. Apparently the superstructure destroys the subcell symmetry of the C-centering, showing such peaks as $(1/2, 16, 0)$ and $(1 1/2, 0, 1)$ resulting in a space group symmetry consistent with Pbnm. Very large single crystals were obtained by cooling the Sr$_2$Bi$_3$O$_5$ composition from above the melting point to ~900 °C, and annealing large fragments at 850 °C—258 h.

3.3.5 Sr$_2$Bi$_3$O$_5$(S$_2$B$_4$) Sr$_2$Bi$_3$O$_5$ melts incongruently between 1200 and 1220 °C. Single crystals are formed in many compositions in the ternary system with CuO when heated above ~900 °C. Apparently, this phase has a large primary phase field in the ternary system. For example, single crystals were obtained from SrO:Bi$_2$O$_3$:CuO 55:35:10 at 900 °C and from SrO:Bi$_2$O$_3$:CuO 57.5:42.5 at 1000 °C. These crystals often react slowly with atmospheric moisture. The best crystals were obtained using an NaCl:KCl flux with 4/1 flux/Sr$_2$Bi$_3$O$_5$ ratio cooled.
from 1025 to 650 °C at 5 °/h (table 1b). These crystals are colorless and easily recognized because of their very low birefringence in polarized light. All these crystals were found (see precession photographs, fig. 9) to be rhombohedral probably R3m, with unit cell dimensions refined from the x-ray diffraction powder data (table 6, fig. 10) \( a = 12.526(1) \), \( c = 18.331(2) \) Å.

3.3.6 \( \text{Sr}_6\text{Bi}_2\text{O}_{19}(\text{S}_3\text{B}) \) Previous workers [27] did not report any binary compound with more than 60 mole percent \( \text{SrO} \); however, \( \text{Sr}_6\text{Bi}_2\text{O}_9 \) appears to be stable between about 750 and 950 °C, and it decomposes between 950 and 975 °C to \( \text{Sr}_3\text{Bi}_2\text{O}_6 + \text{SrO} \). Single crystals were obtained by heating a prereacted specimen plus 1:1 \( \text{NaCl}:\text{KCl} \) flux (flux/charge ratio = 10/90). X-ray precession photographs (fig. 11) indicate an apparently rhombohedral unit cell with \( a = 6.009 \) and \( c = 58.633 \) Å. This appears, however, to be a subcell and even a doubled \( a \)-axis (as suggested by electron diffraction data) does not account for all of the diffraction maxima observed in an x-ray powder diffraction pattern of the prereacted mix (table 7, fig. 12). The crystals may actually be an oxychloride phase and the pseudocell suggested in table 7 does not fit the observed data very accurately. The reaction \( \text{Sr}_6\text{Bi}_2\text{O}_{19} \rightarrow (975 \, ^\circ\text{C}) \rightarrow \text{Sr}_3\text{Bi}_2\text{O}_6 + 3\text{SrO} \) is completely reversible i.e., with material that was decomposed, \( \text{Sr}_6\text{Bi}_2\text{O}_{19} \rightarrow \text{Sr}_3\text{Bi}_2\text{O}_6 + 3\text{SrO} \) at 975 °C, one can perform the back reaction, \( \text{Sr}_3\text{Bi}_2\text{O}_6 + 3\text{SrO} \rightarrow (900 \, ^\circ\text{C}) \rightarrow \text{Sr}_6\text{Bi}_2\text{O}_{19} \) with or without intermediate grinding (and exposure to atmospheric \( \text{CO}_2 \)).

3.4 The System \( \text{SrO}_2: \text{Bi}_2\text{O}_3: \text{CuO} \)

Phase relations in the nominally ternary system are shown in figure 13 and experimental data are reported in table 1. Figure 14 is an enlargement of the triangular region of figure 13 that is delineated by dots. Many of the experiments listed in table 1 yield apparently conflicting and often confusing results, precisely because the experimental system is not strictly ternary in air and/or in contact with various capsule materials such as Au, Pt or 70Ag30Pd. Reproducibility of experiments in this system is exceedingly difficult to achieve, and it is often impossible to reproduce the results published.

Figure 6. X-ray precession photographs for \( \text{SrBi}_2\text{O}_4 \) (a) \( h0l \), (b) \( hll \).
Figure 7. X-ray precession photographs of Sr$_2$Bi$_2$O$_5$: (a) $hk0$, (b) $h0l$ and (c) $hll$. 
Table 5. X-ray powder diffraction data for the compound Sr$_2$Bi$_2$O$_5$

| $d$ (Å) | Rel. Int. (%) | $2\theta$ (°) obs | $2\theta$ (°) calc | hkl |
|--------|--------------|-------------------|-------------------|-----|
| 7.161  | 17           | 12.35             | 12.3              | 020 |
| 4.676  | 15           | 18.96             | 18.98             | 021 |
| 3.697  | 32           | 24.05             | 24.06             | 110 |
| 3.171  | 8            | 28.11             | 28.12             | 111 |
| 3.094  | 100          | 28.84             | 28.83             | 041 |
| 2.9842 | 10           | 29.92             | 29.92             | 130 |
| 2.8319 | 8            | 31.57             | 31.55             | 022 |
| 2.6865 | 23           | 33.33             | 33.32             | 131 |
| 2.3857 | 1            | 37.67             | 37.69             | 060 |
| 2.3684 | 11           | 37.96             | 37.95             | 112 |
| 2.3373 | <1           | 38.49             | 38.50             | 042 |
| 2.2918 | 9            | 39.28             | 39.29             | 150 |
| 2.2254 | 2            | 40.50             | 40.52             | 061 |
| 2.1466 | 26           | 42.06             | 42.09             | 132 |
| 1.9767 | 1            | 45.88             | 45.87             | 023 |
| 1.9122 | 8            | 47.51             | 47.49             | 200 |
| 1.8873 | 2            | 48.18             | 48.19             | 062 |
| 1.8401 | 8            | 49.50             | 49.51             | 152 |
| 1.8030 | 5            | 50.39             | 50.29             | 170 |
| 1.7979 | 8            | 50.74             | 50.75             | 113 |
| 1.7827 | 17           | 51.20             | 51.19             | 043 |
| 1.7712 | 2            | 51.56             | 51.58             | 221 |
| 1.7306 | 7            | 52.86             | 52.86             | 171 |
| 1.6936 | 5            | 54.11             | 54.10             | 133 |
| 1.6873 | 1            | 54.33             | 54.34             | 240 |
| 1.6271 | 17           | 56.51             | 56.51             | 241 |
| 1.5849 | <1           | 56.16             | 58.14             | 222 |
| 1.5570 | 5            | 59.31             | 59.32             | 172 |
| 1.5472 | 7            | 59.72             | 59.71             | 082 |
| 1.5424 | 7            | 59.92             | 59.91             | 004 |

* Calculated on the basis of an orthorhombic unit cell, Cmcm, $a = 3.8262(2)$, $b = 14.307(1)$, $c = 6.1713(4)$ Å.

by others. In some cases this may be because insufficient experimental details were given; however, attempts to reproduce our own experiments have sometimes lead to slightly different results. Experimental results are greatly affected by the factors outlined below.

(1) Compositional changes caused by reaction with Au or other containers;
(2) Volatilization of Bi$_2$O$_5$;
(3) CO$_2$ in some phases at the lower temperatures (e.g., SrCO$_3$ does not decompose in air until about 875 °C);
(4) Oxidation/reduction reactions involving atmospheric O$_2$, CO$_2$, or H$_2$O;
(5) Difficulties related to the very disparate melting behaviors of various compounds and the end members. For example, Bi$_2$O$_3$ melts at ~825 °C but CuO decomposes in air to form Cu$_2$O at about 1020 °C which melts at about 1210 °C. Also, the Sr-cuprates react very slowly at temperatures below the melting points of Bi$_2$O$_3$ and Bi$_2$CuO$_4$. Thus, it was often necessary to prepare specimens from prereacted compounds (or mixtures of compounds) instead of the end members.
(6) Persistence of apparently unstable three phase assemblages within single phase regions. Typically, it is not possible to homogenize single phase ternary samples to the point that all detectable traces of additional phases are eliminated from x-ray powder patterns. Therefore, it should be emphasized that the diagram in figure 13 is a composite of subsolidus data that is neither strictly ternary nor strictly isothermal. The region below the join that connects CuO to the SrO-poor end of the rhombohedral Sillen phase field contains phases which melt below 850 °C, and some phases in the low CuO portion of the system begin to melt between ~875 and 900 °C. Also, specimens of one composition which are near the SrBi$_2$O$_5$:Raveau-solid-solution join showed evidence of melting between 850 and 875 °C. All other compositions start to melt above at least 900 °C and many start melting slightly above 925 °C.
3.4.1 \(\text{Sr}_2\text{Bi}_2\text{CuO}_6(\text{S}_2\text{B}_2\text{C}-2:2:1)\) This compound should nominally be the end member with \(n = 1\) of the homologous series \(\text{Sr}_2\text{Bi}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}\). However, the x-ray powder diffraction pattern for this composition does not match at all with the predicted tetragonal subcell for a compound of this structure type. The predicted type of x-ray pattern is only found in specimens that are grossly deficient in SrO (i.e., compositions corresponding to the Raveau solid solution region—see below). The compound which occurs at approximately \(\text{Sr}_2\text{Bi}_2\text{CuO}_6\) has been characterized by electron diffraction and x-ray powder and single crystal diffraction and the results reported elsewhere [18]. The compound was found to be monoclinic, space group \(C2/m\) (or \(Cm\)) with \(a = 24.493(2)\), \(b = 5.4223(5)\), \(c = 21.959(2)\) Å, \(\beta = 105.40(1)\)°. The actual composition with Sr:Bi:Cu ratio of 2:2:1 always contains a small amount of \(\text{Sr}_4\text{Cu}_{12}\text{O}_{41}\) and probably also some of the Raveau-type phase. Therefore, this compound is shown in figures 13 and 14 as being slightly deficient in CuO (less than 1 mol percent) and having a small homogeneity region. The x-ray powder diffraction data, single crystal precession photographs and electron microscopy data, along with figure 14, were previously published [18]. This phase appears to have a subcell with \(c\)-subcell \((-5.49\text{ Å})\) \(\frac{1}{2}\)-supercell; electron microscopy data for some grains indicate an incommensurate superstructure. The x-ray diffraction data for compositions with only 19 mol percent CuO do not yield satisfactory least-squares refinements. It is possible that the observed incommensurate modulation is an equilibrium phenomenon dependent on composition, although it is equally likely to be due to a non-equilibrium chemical inhomogeneity.

3.4.2 The Raveau-Type Solid Solution (Rav) A two-phase region is shown in figure 14 (after [18]) between the 2:2:1 phase and the region referred to as the Raveau-type solid solution. This nomenclature is used because, structurally, the Raveau-type phase most closely resembles the \(n = 1\) end member of the series \(\text{Sr}_2\text{Bi}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}\) and because Raveau and co-workers were the first to report superconductivity in this system [31]. This phase often forms
Figure 9. X-ray precession photographs of Sr$_3$Bi$_2$O$_6$ (a) $hk\theta$, (b) unscreened $hk\theta$ and (c) $h\theta l$. 
Table 6. X-ray powder diffraction data for the compound Sr₂Bi₂Os₆

| d (Å) | I (%) | 2θ calc* | hkl  |
|-------|-------|----------|------|
| 9.32  | 2     | 9.48     | 9.47 | 101  |
| 6.997 | 2     | 12.64    | 12.63| 012  |
| 6.100 | 4     | 14.51    | 14.49| 003  |
| 4.662 | 16    | 19.02    | 19.00| 202  |
| 4.371 | 14    | 20.30    | 20.29| 113  |
| 4.217 | 8     | 21.05    | 21.03| 104  |
| 4.001 | 11    | 22.20    | 22.20| 211  |
| 3.740 | 9     | 23.77    | 23.76| 122  |
| 3.1326| 100   | 28.47    | 28.48| 220  |
| 3.0394| 85    | 29.36    | 29.38| 205  |
| 2.9694| 6     | 30.07    | 30.08| 131  |
| 2.8582| 4     | 31.27    | 31.27| 312  |
| 2.7861| 3     | 32.10    | 32.09| 223  |
| 2.7454| 2     | 32.59    | 32.58| 116  |
| 2.7347| 2     | 32.72    | 32.74| 125  |
| 2.6013| 7     | 34.45    | 34.46| 042  |
| 2.5150| 8     | 35.67    | 35.67| 134  |
| 2.4024| 1     | 37.40    | 37.42| 232  |
| 2.3588| 26    | 38.19    | 38.19| 045  |
| 2.3329| 2     | 38.56    | 38.54| 404  |
| 2.3265| 2     | 38.67    | 38.68| 315  |
| 2.2420| 3     | 40.19    | 40.19| 018  |
| 2.2073| 5     | 40.85    | 40.85| 413  |
| 2.1797| 63    | 41.39    | 41.38| 045  |
| 2.1552| 2     | 41.88    | 41.90| 051  |
| 2.1111| 2     | 42.80    | 42.79| 502  |
| 2.0377| 2     | 44.42    | 44.43| 241  |
| 2.0011| 11    | 45.28    | 45.29| 422  |
| 1.9767| 6     | 45.87    | 45.90| 333  |
| 1.9376| 7     | 46.85    | 46.86| 511  |
| 1.9062| 4     | 47.67    | 47.68| 152  |
| 1.8832| 12    | 48.29    | 48.27| 407  |
| 1.8711| 7     | 48.62    | 48.62| 416  |
| 1.8230| 9     | 49.99    | 49.99| 318  |
| 1.8087| 24    | 50.41    | 50.44| 600  |
| 1.7893| 46    | 51.00    | 51.00| 425  |
| 1.7753| 9     | 51.43    | 51.44| 431  |
| 1.7512| 3     | 52.19    | 52.19| 342  |
| 1.7367| 40    | 52.66    | 52.66| 0210 |
| 1.7248| 4     | 53.05    | 53.09| 336  |
| 1.7200| 4     | 53.21    | 53.20| 155  |
| 1.6855| 5     | 54.39    | 54.38| 238  |
| 1.6146| 9     | 56.99    | 57.00| 247  |
| 1.5931| 4     | 57.83    | 57.84| 2011 |
| 1.5667| 24    | 58.90    | 58.94| 440  |
| 1.5569| 5     | 59.31    | 59.35| 164  |
| 1.5443| 9     | 59.84    | 59.85| 701  |

*Calculated on the basis of a rhombohedral unit cell a = 12.52(1), c = 18.331(2) Å.
metastably as an almost single-phase product when compositions near the indicated equilibrium single-phase region are synthesized by cooling from a melt. For example, a melt of 2:2:1 composition first crystallizes as the Raveau solid solution and reacts to form the 2:2:1 phase only after subsequent heating and grinding (table 1); similarly, when a mixture of composition 3:2:2 was prepared by a lactate route, the Raveau solid solution was the first crystalline phase to form; but, the 3:2:2 phase replaced it after subsequent heating and grinding (table 1). The crystals formed from melts of Raveau solid solution, or similar compositions (outside the equilibrium Raveau field), are always very platy and micaaceous and form “books” of crystals not well ordered in the direction perpendicular to the plates. They always have one long crystallographic axis of about 26.6 Å and the x-ray powder diffraction data can be roughly fit to a pseudotetragonal subcell with $a = 5.3$ Å. Several unit cells have been reported for this phase, either pseudotetragonal or pseudoorthorhombic [32,33].

Crystals that were picked from various ternary melts (with or without chloride flux) were invariably non-single and appear to have a monoclinic superstructure. The phase formed using 1:1 NaF:KF flux, however, yielded crystals with apparent orthorhombic symmetry and a very strange incommensurate superstructure (fig. 15). Onoda and Sato [34] obtained a monoclinic superstructure for a crystal that was grown from a melt of 1:1:1 composition (Sr:Bi:Cu=1:1:1) which was heated in an Al$_2$O$_3$ crucible. They report a nominal composition for the crystal of Sr:Bi:Cu 4:6:3, well outside the equilibrium single-phase region reported in figures 13 and 14. The unit cell reported for this phase [34] is C-centered monoclinic with $a=26.856$, $b=5.380$, $c=26.908$ Å, $\beta=113.55^\circ$; no data were reported on the extent of contamination from the Al$_2$O$_3$ crucible. A calculated powder pattern based on their structure determination [34] was obtained from M. Onoda (private communication) and these data were used to index the x-ray powder diffraction pattern of the composition with Sr:Bi:Cu ratios of 36:44:20 (near the SrO-rich end of the Raveau solid solution region). All of the superstructure lines observed for this composition can be completely accounted for by $hkl$’s with intensities very similar to those calculated by Onoda. For a C-centered monoclinic cell, the unit cell dimen-
Figure 11. X-ray precession photograph of "Sr₂Bi₂O₇" (a) k0l, (b) hhl and (c) unscreened hkl.
Table 7. X-ray powder diffraction data for the compound Sr$_6$Bi$_2$O$_9$

| $d$ (Å) | Rel $I$ (%) | 2$\theta$ obs | 2$\theta$ calc$^a$ | $hkl$ $^b$ |
|--------|-------------|---------------|-----------------|---------|
| 4.891  | 18          | 18.12         | 18.13           | 0,0,12  |
| 4.777  | 1           | 18.56         |                 |         |
| 4.397  | 1           | 20.18         |                 |         |
| 4.258  | 12          | 20.85         | 20.93           | 018     |
| 4.197  | 6           | 21.15         |                 |         |
| 3.810  | 1           | 23.33         |                 |         |
| 3.589  | 1           | 24.79         |                 |         |
| 3.396  | 3           | 26.22         | 26.13           | 1,0,13  |
| 3.318  | 1           | 26.85         |                 |         |
| 3.271  | 1           | 27.24         |                 |         |
| 3.218  | 1           | 27.70         |                 |         |
| 3.184  | 1           | 28.00         |                 |         |
| 3.092  | 1           | 28.85         |                 |         |
| 3.0105 | 58          | 29.65         | 29.74           | 110     |
| 2.9997 | 61          | 29.76         | 29.79           | 10,16   |
| 2.9859 | 100         | 29.90         |                 |         |
| 2.8779 | 1           | 31.05         |                 |         |
| 2.8493 | 1           | 31.37         |                 |         |
| 2.7283 | 1           | 32.80         |                 |         |
| 2.6437 | 5           | 33.88         | 33.74           | 1,0,19  |
| 2.5615 | 16          | 35.00         | 35.05           | 1,1,12  |
| 2.5357 | 9           | 35.37         |                 |         |
| 2.4827 | 2           | 36.15         |                 |         |
| 2.4436 | 4           | 36.75         | 36.74           | 0,0,24  |
| 2.4075 | 1           | 37.32         |                 |         |
| 2.3829 | 2           | 37.72         |                 |         |
| 2.3672 | 2           | 37.98         |                 |         |
| 2.3383 | 1           | 38.55         |                 |         |
| 2.2974 | 1           | 39.18         |                 |         |
| 2.2603 | 6           | 39.85         | 39.99           | 0,2,13  |
| 2.2308 | 1           | 40.40         |                 |         |
| 2.1272 | 32          | 42.46         | 42.60           | 0,2,16  |
| 2.0953 | 15          | 43.14         |                 |         |
| 2.0452 | 2           | 44.25         |                 |         |
| 2.0146 | 1           | 44.96         |                 |         |
| 1.9952 | 4           | 45.42         |                 |         |
| 1.9845 | 3           | 45.68         |                 |         |
| 1.9550 | 4           | 46.41         |                 |         |
| 1.9502 | 6           | 46.53         |                 |         |
| 1.9415 | 8           | 46.75         |                 |         |
| 1.9337 | 10          | 46.95         |                 |         |
| 1.9054 | 4           | 47.69         |                 |         |
| 1.9006 | 5           | 47.82         |                 |         |
| 1.8629 | 4           | 48.85         |                 |         |
| 1.8452 | 2           | 49.35         |                 |         |
| 1.8118 | 2           | 50.32         |                 |         |
| 1.8001 | 3           | 50.67         |                 |         |
| 1.7509 | 3           | 52.20         |                 |         |
| 1.7364 | 18          | 52.67         |                 |         |
| 1.7218 | 35          | 52.82         | 52.77           | 300     |
| 1.7188 | 21          | 53.25         |                 |         |
| 1.7031 | 2           | 53.78         |                 |         |
| 1.6838 | 2           | 54.45         |                 |         |
| 1.6557 | 2           | 55.45         |                 |         |
| 1.6354 | 9           | 56.20         |                 |         |
| 1.6295 | 4           | 56.42         |                 |         |
| 1.6156 | 3           | 56.95         |                 |         |
| 1.5984 | 1           | 58.02         |                 |         |
| 1.5802 | 2           | 58.35         |                 |         |
| 1.5600 | 2           | 59.18         |                 |         |

$^a$ Calculated on the basis of a rhombohedral subcell with $a = 6.009$, $c = 58.663$ Å.

$^b$ Based on the intensities observed in single crystal precession photographs, figure 11.
Figure 12. X-ray powder diffraction pattern of Sr$_4$Bi$_2$O$_3$ (heated to 975 °C then cooled to 900 °C, held for 24 h and cooled to room temperature).

sions obtained by least-squares analysis of this x-ray powder data (table 8, fig. 16) are $a = 26.889(9)$, $b = 5.384(2)$, $c = 26.933(8)$ Å, $\beta = 113.67(3)^\circ$.

It should be noted, however, that powder patterns for more Bi-rich Raveau-type solid solutions display superstructure peaks which deviate widely from those observed for the 36:44:20 composition. At present it is not known if this is truly a region of solid solution or a collection of smaller regions (separated by two and/or three phase fields) in which several structurally related phases are stable. New specimens are currently being prepared at very close intervals in this Raveau-type region in order to determine the true crystal chemistry of this important "phase." These results will be reported in the near future [35].

The Raveau solid solution region extends along a line with approximately 20 mol percent CuO according to the formula Sr$_{1.8-x}$Bi$_{2.2+x}$CuO$_2$ with $-0.0 < x < -0.15$. This is slightly at odds with the results of Saggio et al. [36] who reported the formula Sr$_{1.8+x}$Bi$_{2.2-x}$CuO$_2$ with $0.0 < x < 0.08$ which corresponds to negative values of $x$ in our formula. Their samples were annealed at 800 °C and premixed with 0.5 weight percent Li$_2$CO$_3$. It is not known if the differences between their results and ours are due to the temperature difference, the time of "equilibration," or to the presence of Li$_2$CO$_3$. They also report [36] that only the high SrO end of the solid solution exhibits superconductivity based on the data of Akimitsu et al. [37] which were obtained from specimens that were heated twice at 880 °C for 12 h. This preparation should probably have yielded results similar to ours, but we failed to find evidence of superconductivity at temperatures above 10 K. It is possible that superconductivity only occurs in metastable Raveau-type solutions that have compositions which lie outside the equilibrium "single phase" field.

The Raveau-type solid solution also exhibits non-stoichiometry with respect to its CuO concentration. The solid solution region corresponds approximately to the formula Sr$_{1.8-x}$Bi$_{2.2+x}$Cu$_{12+x/2}$O$_7$. Of course, there is no a priori reason why the CuO concentration must be structurally controlled by the Sr/Bi ratio.

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Figure 13. Phase diagram for the system SrO-Bi2O3-CuO. •-compositions studied, ○-compounds. This diagram represents subsolidus conditions, although Bi2O3 melts at 825 °C and therefore partial melting occurs below 875 °C in most compositions below the join CuO-Rhomb. In addition, some melting was found at 875 °C for the composition 34:66:55:33:10.

Chakoumakos et al. [38] reported the results of a study of Raveau-type single crystals that were grown under oxygen from CuO-rich melts in crucibles of various compositions. Incommensurate superstructure peaks (related to orthorhombic symmetry) were found to vary systematically with the SrO content. Superconductivity was found to be related to excess oxygen and to the concentration of impurities including Al2O3. The superstructure peaks occurred with modulation of ~1/5b* plus a c* component varying from 0.29c* to 0.65c* (where * represents the reciprocal vector direction). The observed formula for these crystals was reported as Bi2Sr2-xCuO6_{1+y}. These crystals (and most if not all melt-grown, Raveau-type crystals) are probably metastable since they have compositions well outside the equilibrium range shown in figures 13 and 14. It should be noted, however, that Chakoumakos et al. grew their crystals under oxygen rather than air, so the relevant single-phase region may be similar but will not be identical to that in figures 13 and 14.

3.4.3 Sr4Bi2Cu2O6_3 Sr4Bi2Cu2O6_3 (S8B4C5-8:4:5) This phase was apparently first described [39] as a compound with the composition Sr4Bi2Cu2O6_{1+z} (Sr:Bi:Cu=2:1:1); however, an examination of the reported unindexed x-ray powder diffraction data indicate that modest amounts of both S3B2 and SC were present in this sample. All of our experiments with the 2:1:1 composition yielded three phases when equilibrated in air at subsolidus temperatures, although the minority phases that were observed depended upon the heat treatment (table 1). Small single crystals of this new phase were obtained from a specimen of 2:1:1 that was mixed with 10 weight percent 1:1 NaCl:KCl flux and sealed in a gold tube that was heated at 900 °C for 1 h then cooled to 650 °C at 3 °C/h. The crystals are needle-like suggesting that one crystallographic axis is
Figure 14. An enlargement of the triangular region of the phase diagram in figure 13 that is delineated by dots.

probably much shorter than the others, and x-ray precession photographs (fig. 17) revealed that it is orthorhombic (space group Fmmm) with a, b, c parameters of approximately 33.98, 24.02, 5.364 Å, respectively. The crystal structure of this phase has been solved by Fuertes et al. [40] who describe its chemistry as Bi₄Sr₈Cu₅Oₓ₊ₓ, and its unit cell as orthorhombic with a = 33.98 Å, b = 24.02 Å, c = 5.364 Å. Obviously, the diffraction data in figure 17 indicate that this is the same phase as the one reported in [39,40].

Single-phase specimens of Sr₈Bi₄Cu₅Oₓ₊ₓ were only obtained in this laboratory when the starting materials were annealed in one atmosphere of oxygen. The unit cell refined from the data obtained from the 8:4:5 specimen (table 9, fig. 18) is orthorhombic Fmmm with a = 33.991 Å, b = 24.095 Å, c = 5.3677 Å. Clearly the published structure of this phase [40] requires more than the 19 oxygen atoms per formula unit that are implied by an 8:4:5 ratio. The smaller unit cell obtained by [40] was also found in the present work when an 8:4:5 specimen was melted in an Al₂O₃ crucible (as were the crystals reported by [40]) poured onto an Al plate and annealed in air or oxygen. Attempts to supply the excess oxygen by the substitution of some La⁺³ for some of the Sr⁺² as suggested by R. J. Cava (private communication) was only partially successful, never resulting in a completely single-phase specimen when heated in air.

3.4.4 Sr₂Bi₂Cu₄O₈ (S₃B₂C₂:3:2:2) Extrapolation based on the general formula for the homologous series of Bi-containing high-Tc phases, AₓCa₁₋ₓBiₓ₂Cu₄Oₓ₊ₓ, predicts the formula Sr₂CaBi₂Cu₂O₈ (2:1:2:2) for the phase with n = 2, and a c-axis of ~30.6 Å which implies d(002)
Figure 15. X-ray precession photographs of an orthorhombic/incommensurate Raveau solid solution phase that was grown in 1:1 NaF:KF flux. Original composition = Sr$_2$Bi$_2$CuO$_6$ (a) $hk\ell$, (b) $h\ell\ell$, (c) $0k\ell$ and (d) $hk\ell$. 
Table 8. X-ray powder diffraction data for the Raveau-type phase at the composition $Sr_{1.6}Bi_{2.2}Cu_{0.6}$

| $d_{\text{obs}}$(Å) | Rel /(%$) | $2\theta$ obs | $2\theta$ calc | $hkl$ |
|----------------------|------------|----------------|----------------|--------|
| 12.35                | 6          | 7.15           | 7.17           | 200    |
| 6.16                 | 1          | 14.37          | 14.38          | 400    |
| 5.47                 | 1          | 16.20          | 16.17          | 401    |
| 5.26                 | 3          | 16.83          | 16.84          | 110    |
| 4.50                 | 1          | 19.70          | 19.70          | 310    |
| 4.348                | 2          | 20.41          | 20.44          | 307    |
| 4.183                | 2          | 21.22          | 21.22          | 114    |
| 4.105                | 34         | 21.63          | 21.63          | 600    |
| 3.761                | 2          | 23.64          | 23.62          | 313    |
| 3.632                | 4          | 24.49          | 24.45          | 514    |
| 3.457                | 58         | 25.75          | 25.76          | 515    |
| 3.384                | 1          | 26.32          | 26.32          | 115    |
| 3.239                | 4          | 27.52          | 27.50          | 516    |
| 3.220                | 6          | 27.68          | 27.70          | 801    |
| 3.092                | 24         | 28.85          | 28.85          | 714    |
| 3.081                | 66         | 28.96          | 28.96          | 800    |
| 3.013                | 100        | 29.63          | 29.62          | 715    |
| 2.9427               | 5          | 30.35          | 30.32          | 710    |
| 2.9380               | 5          | 30.40          | 30.41          | 209    |
| 2.9025               | 11         | 30.78          | 30.81          | 716    |
| 2.7929               | 3          | 32.02          | 32.05          | 514    |
| 2.7462               | 2          | 32.58          | 32.54          | 316    |
| 2.6924               | 58         | 33.25          | 33.24          | 40,10  |
| 2.6317               | 2          | 34.04          | 34.05          | 20,10  |
| 2.5831               | 7          | 34.70          | 34.68          | 915    |
| 2.5560               | 2          | 35.08          | 35.11          | 10,1   |
| 2.4623               | 15         | 36.46          | 36.45          | 10,0   |
| 2.4481               | 5          | 36.68          | 36.71          | 4,11   |
| 2.4182               | 5          | 37.15          | 37.15          | 6,11   |
| 2.3565               | 5          | 38.16          | 38.12          | 10,1   |

* Oxygen content not certain.
* Calculated from monoclinic unit cell $a=26.889(9)$, $b=5.384(2)$, $c=26.933(3)$ Å, $\beta=113.67(3)^\circ$.
* Indexed based on single crystal $F_{\text{obs}}$ data received from M. Onoda [34].

~5.78° $2\theta$ for CuKα radiation. It is known that Sr$^{2+}$ can substitute for some of the Ca$^{2+}$ up to at least 3:3:4:4 [40]. If all the Ca$^{2+}$ were replaced by Sr$^{2+}$, the chemical formula would degenerate to 3:2:2 or $Sr_{3}Bi_{2}Cu_{2}O_{6}$; but, attempts to synthesis the $n=2$ phase at this composition have failed. The presence of a small peak at ~5.75° $2\theta$ was noted during the first low temperature calcination of specimens prepared by decomposition of lactate precursor powders with 3:2:2 composition. However, the peak at ~5.75° $2\theta$ disappears after subsequent heat treatments which suggests that it is associated with a metastable phase.

Compositions of 3:2:2 prepared by conventional solid state techniques yield a new phase that has an x-ray powder diffraction pattern (table 10, fig. 19) which resembles both the Raveau-type solid solution and the 2:2:1 phase in some respects. The low angle peak occurs at about the same value as for the Raveau solid solution ($d \sim 12.35$ Å, $2\theta \sim 7.15^\circ$), but there is a very small peak at a $d$-value of twice that ($d \sim 24.7$ Å, $2\theta \sim 3.58^\circ$). The strong (113) Raveau-type tetragonal subcell peak at ~25.75° $2\theta$ is not present and, instead, a strong peak occurs at ~26.85° $2\theta$, similar to the 2:2:1 compound. In addition, there are considerable differences between...
Figure 16. X-ray powder diffraction pattern of the Raveau phase from the composition Sr$_9$Bi$_3$Cu$_5$O$_{30.5}$±x (cooled from 875 °C).

this pattern and both the Raveau solid solution and Sr$_2$Bi$_2$CuO$_6$, which indicate that Sr$_2$Bi$_2$Cu$_2$O$_3$ is a unique phase. As yet, no single crystals of this phase have been synthesized. The pattern in figure 19 shows the presence of a small amount of Sr$_{14}$Cu$_2$O$_{11}$, indicating some probable nonstoichiometry in the composition. The diffraction maxima in this pattern have been indexed with comparison to the 2:2:1 and Raveau solid solution with a C-centered monoclinic unit cell, $a = 24.937(7)$, $b = 5.395(2)$, $c = 19.094(7)$ Å, and $\beta = 96.97(3)^\circ$. This commensurate cell probably represents only a subcell of an incommensurate non-stoichiometric phase.

3.4.5 Miscellaneous Phases of Unknown Composition Two phases high in SrO content at approximate Sr:Bi:Cu ratios of 9:4:1 and 7:2:2 were reported by Saggio et al. [36], and two different phases at 4:2:1 and 2:1:1 were reported by Casais et al. [39]. Of these, we only found evidence for the phase reported at 7:2:2 composition, and then only at temperatures below 875 °C. The Saggio et al. data [36] are complicated by their use of the 0.5 wt% Li$_2$CO$_3$ "as a mineralizer." Peaks corresponding to the $d$-spacings reported for the composition 9:4:1 were not present in our specimens except when we included 0.5 wt% Li$_2$CO$_3$ and the binary phase Sr$_2$Bi$_2$O$_3$ (that was not reported by Saggio et al. [36]) is only present when Li$_2$CO$_3$ is absent. We therefore conclude that the "9:4:1-phase" is not present in the ternary system. Some of the low-angle $d$-spacings reported for the "7:2:2-phase" ($4.82 \AA = 18.40^\circ 2\theta$ and $4.17 \AA = 21.27^\circ 2\theta$) in samples that were heated at 800 °C were observed in patterns from samples that we heated at temperatures below ~875 °C (table 1). Because SrCO$_3$ does not decompose until ~875 °C, these results suggest the presence of one or more oxycarbonate phases. The first two $d$-spacings as well as the strongest peak reported as a "4:2:1" phase [38] ($d = 4.91, 4.25$ and $3.04 \AA$) are apparently due to the phase Sr$_3$Bi$_2$O$_5$(Sr,B).

In summary, we interpret the evidence for these four reported phases as follows:

9:4:1-mostly due to reaction with Li$_2$CO$_3$;
7:2:2-multiphase due to reaction with Li$_2$CO$_3$ plus a Sr:Bi:Cu-oxycarbonate;
Figure 17. X-ray precession photographs of 8:4:5 (a) h0l, (b) 0kl, (c) hkl and (d) hkl.
Table 9. X-ray powder diffraction data for the compound Sr₂Bi₂Cu₃O₈₊₄⁺<sub>a</sub>.

| d (Å) | Rel I (%) | 2θ obs | 2θ calc<sub>b</sub> | hkl<sub>c</sub> |
|-------|-----------|--------|---------------------|----------------|
| 17.05 | 3         | 5.18   | 5.20                | 200            |
| 12.08 | 3         | 7.31   | 7.33                | 020            |
| 9.85  | 1         | 8.97   | 8.99                | 220            |
| 5.668 | <1        | 15.62  | 15.63               | 600            |
| 4.425 | 2         | 20.05  | 20.05               | 131            |
| 4.253 | 2         | 20.87  | 20.89               | 800            |
| 4.153 | 2         | 21.38  | 21.39               | 511            |
| 4.015 | 4         | 22.12  | 22.12               | 060            |
| 3.911 | 3         | 22.72  | 22.73               | 260            |
| 3.729 | 13        | 23.84  | 23.83               | 531            |
| 3.559 | 1         | 25.00  | 24.98               | 711            |
| 3.418 | 2         | 26.05  | 26.04               | 351            |
| 3.288 | 33        | 27.10  | 27.12               | 731            |
| 3.173 | 23        | 28.10  | 28.11               | 551            |
| 3.011 | 27        | 29.65  | 29.64               | 080            |
| 2.9665| 4         | 30.10  | 30.11               | 280            |
| 2.8861| 100       | 30.96  | 30.95               | 171            |
| 2.8317| 11        | 31.57  | 31.56               | 12,0           |
| 2.7569| 2         | 32.45  | 32.44               | 12,2,0         |
| 2.6837| 35        | 33.36  | 33.36               | 002            |
| 2.6498| 1         | 33.80  | 33.78               | 202            |
| 2.6182| 3         | 34.22  | 34.20               | 022            |
|       | 4         |        |                     | 34.40<sup>d</sup> |
| 2.5903| 1         | 34.60  | 34.62               | 222            |
| 2.4881| 2         | 36.07  | 36.07               | 771            |
| 2.4264| 27        | 37.02  | 37.00               | 14,0           |
| 2.4080| 24        | 37.31  | 37.29               | 0,10,0         |
| 2.3793| 3         | 37.78  | 37.77               | 14,2,0         |
| 2.3417| 1         | 38.41  | 38.42               | 11,5,1         |
| 2.3145| 1         | 38.88  | 38.88               | 12,6,0         |
| 2.2571| 2         | 39.91  | 39.93               | 13,3,1         |
| 2.2303| 1         | 40.41  | 40.39               | 062            |
| 2.2125| 1         | 40.75  | 40.75               | 262            |
| 2.1485| 2         | 42.02  | 42.02               | 791            |
| 2.1244| 4         | 42.52  | 42.52               | 16,0,0         |
| 2.1135| 3         | 42.75  | 42.77               | 13,5,1         |
| 2.0639| 14        | 43.83  | 43.84               | 12,8,0         |
| 2.0077| 14        | 45.12  | 45.12               | 0,12,0         |
| 2.0036| 14        | 45.22  | 45.22               | 082            |
| 1.9474| 24        | 46.60  | 46.58               | 12,0,2         |
| 1.9443| 23        | 46.68  | 46.70               | 5,11,1         |
| 1.9164| 20        | 47.40  | 47.42               | 15,5,1         |
| 1.8909| 2         | 48.08  | 48.10               | 14,8,0         |
| 1.8715| 21        | 48.61  | 48.61               | 7,11,1         |
| 1.8351| 8         | 49.64  | 49.63               | 12,10,0        |
| 1.8001| 19        | 50.67  | 50.66               | 14,0,2         |
| 1.7935| 21        | 50.87  | 50.89               | 0,10,2         |
| 1.7875| 12        | 51.05  | 51.08               | 9,11,1         |
| 1.7525| 3         | 52.15  | 52.14               | 12,6,2         |
| 1.7494| 4         | 52.25  | 52.24               | 1,13,1         |
| 1.7264| 3         | 53.00  | 53.02               | 513            |
| 1.7099| 9         | 53.55  | 53.54               | 14,10,0        |
| 1.6967| 7         | 54.00  | 54.01               | 5,13,1         |
| 1.6915| 7         | 54.18  | 54.18               | 533            |
| 1.6604| 10        | 55.28  | 55.28               | 19,3,1         |
| 1.6478| 27        | 55.74  | 55.73               | 7,13,1         |
| 1.6437| 21        | 55.89  | 55.90               | 733            |
| 1.6359| 10        | 56.18  | 56.18               | 12,8,2         |
| 1.6288| 5         | 56.45  | 56.46               | 555            |
| 1.6007| 25        | 57.53  | 57.53               | 19,5,1         |
| 1.5851| 26        | 58.15  | 58.14               | 753            |
| 1.5453| 13        | 59.80  | 59.79               | 14,8,2         |

<sup>a</sup> Oxygen content based on structure derived by [40].
<sup>b</sup> Calculated by least-square analysis from orthorhombic unit cell, Fmmm, a = 33.991(3), b = 24.095(2), c = 5.3677(5) Å.
<sup>c</sup> Indexed with the aid of the single crystal precession photographs, figure 17 and intensities calculated from the published structure [40].
<sup>d</sup> Sr₂CuO₄.
4:2:1-Sr$_2$Bi$_4$O$_9$ + other phases; and
2:1:1-Sr$_2$Bi$_4$Cu$_5$O$_{19+x}$ + S$_2$B$_2$ + SC

On heating above about 850 °C, the diffraction maxima characterizing the 7:2:2 “phase” start to disappear and are ultimately replaced by at least one other strong maximum at ~30.25° 2θ the origin of which is still unknown. At the 3:1:1 composition (table 1) the 7:2:2-type phase is very prevalent at 750 and 800 °C; however, as it starts to decompose at 850 °C, another peak arises at ~11.00° 2θ which persists even at 900 °C after the first heat treatment but finally disappears after three overnight anneals. The origin of this ~11.00° peak is also unknown but it appears to indicate a metastable phase that forms during decarbonation and subsequently decomposes.

At the 2:1:1 and 8:4:5 compositions it was found that preliminary low-temperature annealing was actually detrimental to the formation of an equilibrium assemblage. Apparently, an oxycarbonate phase characterized by small peaks at 2θ=4.40° and 5.60° with strong peaks at 30.50° and 32.45° is formed first with repeated heating at 750°C; further heat treatments at 800 °C produce a new peak at ~4.80° as the 4.40° peak gradually disappears. These are gradually replaced by peaks from the 2:2:1 and Raveau solid solution plus SrCuO$_3$, but the 8:4:5 phase which should form is not found. Note, however, that when this sample was put in an Al$_2$O$_3$ crucible, melted and reheated at 900 °C, the 8:4:5 phase did form. Apparently, the formation of these oxycarbonates blocks the nucleation of 8:4:5.

Four ternary phases were reported in this system by Ikeda et al. [42]. These are essentially the same phases as those reported here, although the compositions do not always agree. The formula given for the Raveau phase solid solution differs somewhat from that used here. The formula for Sr$_2$Bi$_2$CuO$_6$ is given as Sr$_{16}$Bi$_{17}$Cu$_2$O$_{20}$, considerably deficient in SrO and occurring in the region clearly shown by our work to contain three phases. The x-ray diffraction pattern shown for their Sr$_2$Bi$_2$CuO$_6$ clearly shows evidence of the Sr$_{16}$Bi$_{17}$Cu$_2$O$_{20}$ phase, as do our own patterns of this composition. Unit cell dimensions and symmetry given by Ikeda et al. [42] and Saggio et al. [36] for their ternary phases are clearly based on intuition rather than single crystal data and should be considered suspect.
Table 10. X-ray powder diffraction data for the compound Sr₂Bi₂Cu₂O₈⁺

| d (Å)  | Rel. (%) | 2θ (°) | 2θ calc | hkl |
|--------|----------|--------|---------|-----|
| 24.7°  | 1        | 3.57   |         |     |
| 12.35  | 3        | 7.15   | 7.14    | 200 |
| 5.26   | 2        | 16.84  | 16.81   | 110 |
| 5.12   | 1        | 17.32  | 17.33   | 111 |
| 4.120  | 10       | 21.55  | 21.52   | 600 |
| 4.064° | 2        | 21.85  |         |     |
| 3.992  | 2        | 22.25  | 22.22   | 113 |
| 3.625  | 9        | 24.54  |         | 602 |
| 3.573  | 2        | 24.90  | 24.92   | 114 |
| 3.315  | 48       | 26.87  | 26.86   | 604 |
| 3.124  | 11       | 28.55  | 28.63   | 115 |
| 3.095  | 33       | 28.82  | 28.83   | 800 |
| 3.053  | 2        | 29.20  | 29.23   | 802 |
| 3.043  | 2        | 29.33  | 29.32   | 813 |
| 2.9220 | 100      | 30.57  | 30.57   | 803 |
| 2.8031 | 1        | 31.90  | 31.79   | 315 |
| 2.7082 | 26       | 33.05  | 33.06   | 007 |
| 2.6963 | 60       | 33.20  | 33.19   | 020 |
| 2.6324 | 4        | 34.03  | 34.04   | 714 |
| 2.5581 | 2        | 35.05  | 35.07   | 222 |
| 2.5518 | 2        | 35.14  | 35.11   | 803 |
| 2.5281 | 3        | 35.48  | 35.56   | 222 |
| 2.4748 | 20       | 36.27  | 36.26   | 100 |
| 2.4384 | 16       | 36.83  | 36.85   | 912 |
| 2.3933 | 3        | 37.55  | 37.55   | 317 |
| 2.2571 | 3        | 39.91  | 39.91   | 317 |
| 2.0993 | 2        | 43.05  |         |     |
| 2.0629 | 5        | 43.85  |         |     |
| 2.0334 | 34       | 44.52  |         |     |
| 1.9877 | 4        | 45.60  |         |     |
| 1.9815 | 3        | 45.75  |         |     |
| 1.9125 | 41       | 47.50  |         |     |
| 1.8919 | 2        | 48.05  |         |     |
| 1.8539 | 2        | 49.10  |         |     |
| 1.8239 | 13       | 49.96  |         |     |
| 1.8090 | 14       | 50.40  |         |     |
| 1.7908 | 3        | 50.95  |         |     |
| 1.7875 | 2        | 51.05  |         |     |
| 1.7360 | 5        | 52.68  |         |     |
| 1.7232 | 3        | 53.10  |         |     |
| 1.6857 | 18       | 54.38  |         |     |
| 1.6532 | 12       | 55.54  |         |     |
| 1.6388 | 4        | 56.07  |         |     |
| 1.6279 | 18       | 56.48  |         |     |
| 1.5971 | 24       | 57.67  |         |     |
| 1.5744 | 19       | 58.58  |         |     |
| 1.5620 | 8        | 59.09  |         |     |
| 1.5475 | 6        | 59.70  |         |     |

a Heated to 925 °C in flowing O₂ on Au foil. Total oxygen content uncertain.
b Calculated on the basis of a C-centered monoclinic cell with a = 24.937(7),
b = 5.395(2), c = 19.094(7) Å, β = 96.97(3)°.
c Superstructure peaks.

3.4.6 Deduction of Ternary Compatibility (Alkemade) Lines This ternary system is remarkable for the gross irreproducibility of the experimental results. Attainment of equilibrium for each of the ternary compounds that we represent as stable is very difficult and time consuming. Nevertheless, equilibrium can generally be more easily achieved in ternary combinations furthest from the compositions of the stable ternary phases. For this reason the deduction of the compatibility joins is some-
what more reliable than one might suppose based on the difficulties inherent in determining the true compositions of the ternary phases.

Some generalizations can be made concerning both the data in table 1 and the interpretations behind our construction of figures 13 and 14. Because there is a two phase region involving CuO and the rhombohedral Sillen-phase solid solution, the compound Bi$_2$CuO$_4$ and the low melting eutectics of the Bi$_2$O$_3$-CuO binary system are not involved in most of the ternary equilibria. Also, CuO is in equilibrium with most or all of the compositions comprising the Raveau-type solid solution region. Therefore, the 1:1:1 composition (reported by Raveau [31] as superconducting) is in the middle of a ternary phase field bounded by CuO, Raveau solid solution and Sr$_4$C$_2$. The compound Sr$_4$Cu$_5$O$_{14}$ is in equilibrium with all three of the ternary phases related to the structurally homologous series A$_2$Ca$_{1-n}$Bi$_2$Cu$_n$O$_{2n+4}$: Sr$_2$Bi$_2$CuO$_{6}$, Sr$_3$Bi$_2$Cu$_4$O$_8$ and Sr$_{1.8-n}$Bi$_{3.2+n}$Cu$_{1.2+n/2}$O$_{3}$ (i.e., 2:2:1, 3:2:2 and the Raveau solid solution), but not with the structurally dissimilar phase Sr$_4$Bi$_4$Cu$_3$O$_{19+z}$ (8:4:5) or any of the SrO-Bi$_2$O$_3$ binary phases. The compound SrCuO$_2$ is in equilibrium with all three of the ternary compounds except for the Raveau-type solid solution while Sr$_2$CuO$_3$ is compatible only with the two high SrO content binary phases but not with any of the ternary phases. Joins describing compatibility conditions for the 8:4:5 and 3:2:2 phases are left as dashed lines because of the difficulty in determining equilibrium three phase assemblages.

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