Phase Equilibria and Crystal Chemistry in Portions of the System SrO-CaO-Bi₂O₃-CuO, Part IV—The System CaO-Bi₂O₃-CuO

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New data are presented on the phase equilibria and crystal chemistry of the binary systems CaO-Bi₂O₃ and CaO-CuO and the ternary CaO-Bi₂O₃-CuO. Symmetry data and unit cell dimensions based on single crystal and powder x-ray diffraction measurements are reported for several of the binary CaO-Bi₂O₃ phases, including corrected compositions for Ca₄Bi₆O₁₃ and €₃₂8₁₂0₅.

The ternary system contains no new ternary phases which can be formed in air at ~700-900 °C.

Key words: calcium bismuth copper oxide; crystal chemistry; experimental phase relations; phase equilibria.

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1. Introduction

The discovery of superconductivity in cuprates by Bednorz and Müller [1], and its confirmation by Takagi et al. [2] as being due to the phase La₂₋ₓBaₓCuO₄, led to a world-wide search for other compounds with higher Tc's. Identification of the superconducting phase Ba₂YCu₃O₆+δ [3], with a critical temperature Tc ~ 90 K [4], has resulted in hundreds of published reports on the properties of this and related phases.

Phases with still higher Tc's were found in the systems SrO-CaO-Bi₂O₃-CuO and BaO-CaO-Ti₂O₃-CuO [5,6]. These phases belong mostly to a homologous series A₂Caₙ₋₁B₂CuₙO₂n₊₄ (A = Sr, Ba; B = Bi, Ti). In the Bi³⁺ containing systems a phase with n = 2 and Tc ~ 80 K is easily prepared. The exact single-phase region of this phase 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 Tc) phases have not been prepared as single-phase bulk specimens (without PbO). We undertook a comprehensive study of phase equilibria and crystal chemistry in the four component system SrO-CaO-Bi₂O₃-CuO in the hope that such a study will define the optimum processing parameters for reproducible synthesis of samples with useful properties.

A prerequisite to understanding the phase equilibria in the four component system is adequate definition of the phase relations in the boundary binary and ternary systems. The ternary system SrO-CaO-CuO was the first to be investigated [7,8], followed by the ternary system SrO-Bi₂O₃-CuO and its binary subsystems [9,10,11,12]. Preliminary versions have been published of the systems CaO-Bi₂O₃-CuO and SrO-CaO-Bi₂O₃ [13], and the details of the system SrO-CaO-Bi₂O₃ will appear in the near future [14]. The experimental details,
phase relations, and crystal chemistry of the binary CaO-Bi₂O₃ and the ternary system CaO-Bi₂O₃-CuO are the subject of this publication.

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., CaO/1/2Bi₂O₃/CuO. The notation 1/2Bi₂O₃ is used so as to keep the metal ratios the same as the oxide ratios. The "shorthand" notation is used to designate the phases with C = CaO, B = 1/2Bi₂O₃ and Cu = CuO. Thus compositions may be listed simply by numerical ratio e.g., the formula Ca₉Bi₆O₁₃ can be written as C₂B₃ or simply 2:3.

2. Experimental Procedures

In general, about 3.5 g specimens of various compositions in binary and ternary combinations were prepared from CaCO₃, Bi₂O₃ and CuO. Neutron activation analyses of the starting materials indicated that the following impurities (in μg/g) were present: in CuO-3.9Cr, 2.8Ba, 28Fe, 410Zn, 0.09Co, 1.9Ag, 0.03Eu, 14Sb; in Bi₂O₃-2.1Cr, 0.0002Sc, 26Fe, 21Zn, 0.6Co, 0.5Ag, 0.0008Eu, 0.25b; in CaCO₃-1.1Cr, 6Ba, 160Sr, 0.0001Sc, 5Fe, 14Zn, 0.14Co, 0.01Ag, 0.0005Eu, 0.025b. 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 dye 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 ~600 to 850 °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 (Ti) and analyzed by x-ray powder diffraction; 2) annealed at a higher or lower temperature (T₂) where a different assemblage of phases was observed; 3) returned to T₁ to demonstrate reversal of the reaction(s) between T₁ and T₂.

All experimental details are given in Tables 1a and 1b. Phase identification was made by x-ray powder diffraction using a high angle diffractometer with the specimen packed into a cavity 0.127 or 0.254 mm deep in a glass slide. The diffractometer, equipped with a theta compensator slit and a graphite diffracted beam monochromator, was run at 1/4° 2θ/min with CuKα radiation at 40 KV and 35 MA. The radiation was detected by a scintillation counter and solid state amplifier and recorded on a chart with 1°/2θ = 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 lactic acid in an organic precursor route to obtain more intimate mixing at low temperatures [9]. This procedure yielded an essentially single phase amorphous precursor for the composition that contains 66.7 mol % Bi₂O₃. At higher Bi contents, pure Bi metal was formed by carbothermic reduction under even the lowest temperature drying procedures in air.

Specimens for solidus and liquidus determinations in the CaO-CuO system were prepared by dissolving mixtures of cupric nitrate and calcium nitrate in distilled water and then drying. The specimens were calcined two or three times between 500 and 700 °C with intermittent grinding. Samples of Ca₁₋ₓCu₂O were heated in a horizontal tube furnace for 36 to 120 h in air or in oxygen. In determining the exact stoichiometry of the compound previously reported as "CaCuO₂" [7], however, a citrate synthesis route was used [15]. Dried
anhydrous calcium carbonate and basic cupric carbonate \((\text{Cu(OH)}_2: \text{CuCO}_3)\) were dissolved in dilute nitric acid and complexed with excess citric acid monohydrate. After drying, the resulting friable, low-density material was calcined at 700 °C either in air or in a flowing oxygen atmosphere until x-ray diffraction revealed the presence of fewer than three phases. It took 18 to 84 h for these synthesis reactions to reach completion.

Table 1a. Experimental data for the system \(\text{CaO-Bi}_2\text{O}_3-\text{CuO}\)

| Spec. no. | Composition mole percent | Heat treatment\(^a\) | Phys. obs. | Results of x-ray diffraction\(^d\) |
|-----------|--------------------------|----------------------|------------|----------------------------------|
|           | CaO \(1/2\)Bi\(2\)O\(_3\) CuO | Initial | final | Temperature | Time h |                               |
| 100       | 0                        | 0                   | 500       | CaCO\(_3\) | Ca\(_2\)Cu                        |
|           |                          |                     | 600       | CaO + CaCO\(_3\) |                                |
|           |                          |                     | 600 × 2   | CaO |                                |
| 66.7      | 0                        | 33.3                | 700       | Ca\(_2\)Cu |                                |
|           |                          |                     | 850       | CaO + CuO + C\(_{1-x}\)Cu |                                |
|           |                          |                     | 1000 × 3  | CuO + CaO + C\(_2\)Cu |                                |
| 60        | 0                        | 40                  | 500       | CaO + CuO |                                |
|           |                          |                     | 750 × 2   | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 750       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 745       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 800 × 2   | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 875 × 2   | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 950       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 980       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 990       | C\(_2\)Cu + CaO + C\(_2\)Cu |                                |
|           |                          |                     | 990       | C\(_2\)Cu + C\(_2\)Cu |                                |
|           |                          |                     | 1000      | C\(_2\)Cu + C\(_2\)Cu |                                |
|           |                          |                     | 1000 × 2  | C\(_2\)Cu + C\(_2\)Cu |                                |
|           |                          |                     | 1000 × 3  | C\(_2\)Cu + C\(_2\)Cu |                                |
|           |                          |                     | 1007      | C\(_2\)Cu + Cu(OH)\(_2\) |                                |
|           |                          |                     | 1011      | C\(_2\)Cu + Cu(OH)\(_2\) |                                |
|           |                          |                     | 1014      | C\(_2\)Cu + Cu(OH)\(_2\) |                                |
| 50        | 0                        | 50                  | 450       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_2\)Cu + CuO |                                |
|           |                          |                     | 800       | C\(_2\)Cu + CuO |                                |
| #1        | ppt. hydrox-carb.        | 450                 | 6.0       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 800       | C\(_{1-x}\)Cu + CuO |                                |
| #2        | ppt. hydrox-carb.        | 500                 | 550       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 600       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 650       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 700       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 740       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 760       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 780       | C\(_{1-x}\)Cu + CuO |                                |
|           |                          |                     | 800       | C\(_{1-x}\)Cu + CuO |                                |
Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment⁵<sup>b</sup> | Phys. obs.⁶<sup>a</sup> | Results of x-ray diffraction⁷<sup>d</sup> |
|-----------|--------------------------|-------------------------------|------------------------|------------------------------------------|
|           | CaO 1/2Bi₂O₃ CuO | Initial temp °C | final Time h |                                          |
| #3        |                           |                               |                       |                                          |
|           | 600                       |                               |                       |                                          |
|           | 600 × 2                   |                               |                       |                                          |
|           | 600 × 3                   |                               |                       |                                          |
|           | 600 × 4                   |                               |                       |                                          |
|           | 675                       |                               |                       |                                          |
|           | 675 × 5                   |                               |                       |                                          |
|           | 675 × 11                  |                               |                       |                                          |
|           | 675 × 16                  |                               |                       |                                          |
|           | 675 × 21                  |                               |                       |                                          |
|           | 675 × 26                  |                               |                       |                                          |
|           | 675 × 31                  |                               |                       |                                          |
|           | 675 × 36                  |                               |                       |                                          |
|           | 750 × 2                   |                               |                       |                                          |
|           | 850                       |                               |                       |                                          |
|           | 900                       |                               |                       |                                          |
|           | 600                       |                               |                       |                                          |
|           | 750                       |                               |                       |                                          |
|           | 900                       |                               |                       |                                          |
|           |                           | 675 70                        |                       |                                          |
|           |                           | 675 × 4                       |                       |                                          |
| #4        | nitrate                  | 500                           |                       |                                          |
|           |                           | 600                           |                       |                                          |
|           |                           | 995 1.0                       |                       | C₂Cu + CuO + Cu₂O + Cu₂Cu₂r              |
|           |                           | 1007 10.0                     |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂Cu₂r            |
|           |                           | 1011 1.0                      |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂Cu₂r            |
|           |                           | 1013 1.0                      |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂Cu₂r            |
|           |                           | 1007 10                       |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂Cu₂r            |
|           |                           | 1013 24                       |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂Cu₂r            |
|           |                           | 1014 0.5                      |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1018 0.5                      |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1022 0.5                      |                       | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1028 0.5                      | n.m.                  | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1032 0.5                      | p.m.                  | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1036 0.5                      | p.m.                  | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
|           |                           | 1040 0.5                      | p.m.                  | C₂Cu + Cu₂O + Cu₂O + Cu₂O + Cu₂Cu₂r     |
| #5        | citrate                  | 700 22                        |                       | C₁₋₂Cu + CuO                           |
|           |                           | 700 18-O₂                     |                       | C₁₋₂Cu + CuO                           |
|           |                           | 700 18                        |                       | C₁₋₂Cu + CuO                           |
|           |                           | 700 78-O₂                     |                       | C₁₋₂Cu + CuO                           |
|           |                           | 47.37 52.63                   |                       | C₁₋₂Cu + CuO                           |
|           | (9:10) citrate           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
| 45.45     | 0                         | 54.54                         |                       |                                          |
|           | (5:6) citrate            |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
| 45.33     | 0                         | 54.67                         |                       |                                          |
|           | citrate                  | 700 86-O₂                     |                       | C₁₋₂Cu                                  |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |
| 45.20     | 0                         | 54.80                         |                       |                                          |
|           | citrate                  | 700 24-O₂                     |                       | C₁₋₂Cu                                  |
|           |                           |                               |                       |                                          |
|           |                           |                               |                       |                                          |

Footnotes:
⁵<sup>b</sup> Heat treatment: "°C" indicates temperature in °C; "X" indicates time in hours.
⁶<sup>a</sup> Phys. obs.: "m" indicates mass measurements; "n.m." indicates no mass measurements.
⁷<sup>d</sup> Results of x-ray diffraction: "CuO + Cu₂O + Cu₂Cu₂r" indicates the presence of CuO, Cu₂O, and Cu₂Cu₂r.
### Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obs. | Results of x-ray diffraction* |
|-----------|-------------------------|----------------|------------|------------------------------|
|           | CaO 1/2Bi₂O₃ CuO       | temp °C        |            |                              |
|           |                         | Initial final  | Time h     |                              |
| 44.95     | 0 citrates              | 700 16 700 24-O₂ |            | C₁₋ₓCu + CuOₓ              |
| 44.70     | 0 citrates              | 700 16 700 24-O₂ |            | C₁₋ₓCu + CuO              |
| 40        | 0 citrates              | 700 60 700 18-O₂ |            | C₁₋ₓCu + CuO              |
| 33.3      | 0 66.7                  | 800 875 × 2   |            | C₂Cu + CuO                 |
|           |                         | 965 25.0      |            | C₂Cu + CuO                 |
|           |                         | 1000 19.0     |            | C₂Cu₂₂ + C₂Cu + CuO        |
|           |                         | 1000 × 2      |            | C₂Cu₂₂ + C₂Cu + CuO        |
| #1        | nitrates                | 500           |            | CuO + CaO                  |
|           |                         | 750           |            | CuO + CaO                  |
|           |                         | 700           |            | CuO + CaO                  |
|           |                         | 750 × 2       |            | CuO + CaO + C₃Cu           |
|           |                         | 990           |            | CuO + C₃Cu                 |
|           |                         | 500           | 980 16.0   | CuO + C₃Cu                 |
|           |                         |              | 990 22.0   | CuO + C₃Cu                 |
|           |                         |              | 1000 16.0  | C₂Cu₂₂ + CuO + C₂Cu        |
|           |                         |              | 1010 0.5   | C₂Cu₂₂ + C₂Cu₂₂ + C₂Cuₓ     |
|           |                         |              | 1014 0.5   | C₂Cu₂₂ + C₂Cu + C₂Cu        |
|           |                         |              | 1016 24.0  | C₂Cu₂₂ + C₂Cu + C₂Cu        |
| #2        | citrates                | 700           | 86-O₂      |                              |
| #1        | 25 0 75                 | 600           |            | CuO + C₃Cu                 |
|           |                         | 750           |            | CuO + C₃Cu                 |
|           |                         | 950           |            | CuO + C₃Cu                 |
|           |                         | 975           |            | CuO + C₃Cu                 |
|           |                         | 1000          |            | C₂Cu₂₂ + CuO + C₂O₂ + C₃Cu |
|           |                         | 1025          |            | C₂Cu₂₂ + CuO + C₂O₂ + C₃Cu |
| #2        | nitrates                | 500           |            | CuO + CaO                  |
|           |                         | 450           |            | CuO + CaO                  |
|           |                         | 500           | 72-O₂      | CuO + CaO                  |
|           |                         | 600           | 72-O₂      | CuO + C₁₋ₓCu               |
|           |                         | 750           | 48-O₂      | CuO + C₁₋ₓCu               |
|           |                         | 770           | 68-O₂      | CuO + C₁₋ₓCu               |
|           |                         | 780           | 30-O₂      | CuO + C₁₋ₓCu + CaOₓ        |
|           |                         | 790           | 30-O₂      | CuO + C₁₋ₓCu + CaOₓ        |
|           |                         | 800           | 36-O₂      | CuO + C₁₋ₓCu               |
|           |                         | 820           | 42-O₂      | CuO + C₁₋ₓCu               |
|           |                         | 830           | 72-O₂      | CuO + C₁₋ₓCu + C₂Cu        |
|           |                         | 840           | 36-O₂      | CuO + C₁₋ₓCu + C₂Cu        |

*CuO + CaO refers to the reaction of CuO and CaO.

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Table 1a. Experimental data for the system CaO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment$^b$ | Phys. obs.$^c$ | Results of x-ray diffraction$^d$ |
|-----------|--------------------------|-------------------|---------------|---------------------------------|
|           | CaO 1/2Bi$_2$O$_3$ CuO | temp °C           | Time h        |                                 |
| 20 nitrate| 0 80                     | 500               |               |                                 |
|           |                          | 600               |               |                                 |
|           |                          | 1007              | 1.0           | CuO + CCu$_2$ + Cu$_2$O$_4$      |
|           |                          | 1011              | 1.0           | CCu$_2$ + Cu$_2$O + CuO          |
|           |                          | 1014              | 0.16          | p.m.                             |
|           |                          | 1016              | 0.5           | p.m.                             |
|           |                          | 1020              | 0.5           | c.m.                             |
| 15 nitrate| 0 85                     | 500               |               |                                 |
|           |                          | 600               |               |                                 |
|           |                          | 1016              | 0.16          | p.m.                             |
|           |                          | 1020              | 0.33          | c.m.                             |
| 10 nitrate| 0 90                     | 500               |               |                                 |
|           |                          | 600               |               |                                 |
|           |                          | 1020              | 0.16          | p.m.                             |
| 5 nitrate | 0 95                     | 500               |               |                                 |
|           |                          | 600               |               |                                 |
|           |                          | 1016              | 0.16          | p.m.                             |
|           |                          | 1020              | 0.16          | p.m.                             |
| 10 90     | 0                         | 700               |               |                                 |
|           |                          | 750               |               |                                 |
|           |                          | 850               | 0.33          | s.m.                             |
|           |                          | 860               | 0.33          | p.m.                             |
|           |                          | 870               | 0.33          | c.m.                             |
| 20 80     | 0                         | 700               |               |                                 |
|           |                          | 750               |               |                                 |
|           |                          | 650               | 0.33          | rhomb                            |
|           |                          | 835               | 0.33          | rhomb + fcc'                     |
|           |                          | 875               | 0.33          | s.m.                             |
|           |                          | 875               | 0.33          | rhomb + fcc'                     |
|           |                          | 890               | 0.33          | c.m.                             |
|           |                          | 700→875           | at 3°/h       | rhomb + C$_3$B$_4$                |
|           |                          | 875→650           | at 3°/h       |                                 |
|           |                          | 750→870           | at 1°/h       | rhomb                            |
|           |                          | 870→845           | at 1°/h       |                                 |
### Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obs. | Results of x-ray diffraction |
|-----------|--------------------------|----------------|------------|-----------------------------|
|           | CaO 1/2Bi₂O₃ CuO        | temp °C | final | Time h |                                       |
| 23        | 77 0                      | Initial |         |       |                                       |
|           |                          |         |         |       |                                       |
|           | 700                       |         |         |       | rhomb + C₂B₃                         |
|           | 800                       |         |         |       | rhomb + C₂B₃                         |
|           | 840 0.5                   |         |         |       | fcc'                                   |
|           | 870 0.33                  |         |         |       | fcc'                                   |
|           | 880 0.33                  |         |         |       | n.m.                                   |
|           | 880 0.33                  |         |         |       | n.m.                                   |
|           | 890 0.33                  |         |         |       | c.m.                                   |
|           | 850                       |         |         |       |                                       |
|           | 750 × 2                   |         |         |       | rhomb                                 |
| 25        | 75 0                      |         |         |       |                                       |
|           | 700                       |         |         |       | rhomb + CB₂ + C₂B₁₄                   |
|           | 750                       |         |         |       | rhomb + C₂B₁₄                         |
|           | 650 16                    |         |         |       | rhomb                                 |
|           | 750 1                     |         |         |       | rhomb                                 |
|           | 780 0.5                   |         |         |       | rhomb                                 |
|           | 800 1                     |         |         |       | rhomb                                 |
|           | 950 1.2                   |         |         |       | c.m.                                   |
|           | 850                       |         |         |       |                                       |
|           | 750 × 2                   |         |         |       | rhomb                                 |
| 26        | 74 0                      |         |         |       |                                       |
|           | 700                       |         |         |       | rhomb + C₂B₃                         |
|           | 750                       |         |         |       | fcc' + rhomb                          |
|           | 820 0.33                  |         |         |       | p.m.                                   |
|           | 880 0.33                  |         |         |       | fcc' + bcc                          |
|           | 890 0.33                  |         |         |       | fcc'                                   |
| 26.32     | 73.68 0                   |         |         |       |                                       |
| #1        | (5:14)                    |         |         |       |                                       |
|           | 750                       |         |         |       |                                       |
|           | 650                       |         |         |       |                                       |
|           | 750 16                    |         |         |       |                                       |
|           | 1000 1.75                 |         |         |       |                                       |
|           | 650                       |         |         |       |                                       |
| #2        | 650 × 2                   |         |         |       |                                       |
|           | 650 × 5                   |         |         |       |                                       |
|           | 750 × 3                   |         |         |       |                                       |
|           | 650                       |         |         |       |                                       |
| #3        | 750                       |         |         |       |                                       |
|           | 750 × 2                   |         |         |       |                                       |
|           | 750 × 3                   |         |         |       |                                       |
|           | 925                       |         |         |       |                                       |
|           | 1025 0.33                 |         |         |       |                                       |
|           | 650 16                    |         |         |       |                                       |
|           | 650 336                   |         |         |       |                                       |
|           | 750 × 5                   |         |         |       |                                       |
|           | 700 100 MPa               |         |         |       |                                       |
|           | 475                       |         |         |       |                                       |
### Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obser. | Results of x-ray diffraction |
|-----------|--------------------------|----------------|--------------|----------------------------|
|           | CaO 1/2Bi₂O₃ CuO        | Initial | final | Time |                       |                           |
| 27.27     | 72.72 (3:8)              | 750     | 650   |      | rhomb + CB₂ + C₂B₃ + C₂B₁₄ |
|           |                          | 750 x 5 | 750   | 16.0 | CB₂ + C₂B₁₄ + rhomb    |
|           |                          | 850     | 750   |      | CB₂ + rhomb + C₂B₁₄    |
| 28        | 72 0                     | 700     | 860   | 0.33 | fcc'                     |
|           |                          | 750     | 870   | 0.33 | n.m.                     |
|           |                          |         | 880   | 0.33 | p.m.                     |
|           |                          |         | 900   | 0.66 | c.m.                     |
| 30        | 70 0                     | 750     | 650   |      | CB₂ + C₂B₁₄ + C₂B₃ + rhomb |
|           |                          | 750 x 5 | 750   | 1.33 | CB₂ + C₂B₁₄ + rhomb    |
|           |                          | 850     | 750   |      | CB₂ + C₂B₁₄ + rhomb    |
| 33.33     | 66.67 0                  | 800     | 0.166 | c.m. | CB₂ + C₂B₃ + CB₂ + CB₂ |
|           |                          | 750     | 16.0  |      | CB₂ + C₂B₁₄ + rhomb    |
| #1        |                          | 1000    | 65    | 96   | CB₂ + C₂B₁₄ + C₂B₃     |
|           |                          |         | 850   | 16   | fcc' + bcc₄               |
|           |                          |         |       |      | fcc' + C₂B₃               |
| #2        |                          | 700     | 65    | 96   | CB₂ + C₂B₁₄ + C₂B₃ + rhomb |
|           |                          | 750     | 850   | 16   | CB₂ + C₂B₁₄ + C₂B₃     |
|           |                          |         |       |      | fcc' + bcc₄               |
|           |                          |         |       |      | CB₂ + C₂B₃ + C₂B₃     |
| #3        |                          | 750 x 5 | 750   | 1.33 | CB₂ + rhomb + C₂B₃ +  
|           |                          |         |       |      | CB₂ + C₂B₃               |
|           |                          | 925     | 0.13  | c.m. | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 700     | 312   |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 1000    | 1.0   | c.m. | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 650     | 17    |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 650 x 4 |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 650 x 5 |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 700     |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 750 x 3 |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 750     |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 750 x 3 |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 750 x 5 |       |      | CB₂ + C₂B₃ + C₂B₃     |
|           |                          | 650     | 100 MPa |      | CB₂ + C₂B₃               |

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

| Spec. no. | Composition mole percent | Heat treatment | Phys. obs. | Results of x-ray diffraction |
|-----------|--------------------------|----------------|------------|----------------------------|
|           | CaO 1/2Bi₂O₃ CuO        | Initial        | final      |                            |
|           |                          |                | Time h     |                            |
| #5 lactate |                          | 450            |            |                            |
|           |                          | 650 × 3        |            |                            |
|           |                          | 650 × 4        |            |                            |
|           |                          | 700            |            |                            |
|           |                          | 750            |            |                            |
|           |                          |                |            |                            |
|           |                          | 35  65  0      | 750        |                            |
|           |                          | 770            | 60         |                            |
|           |                          | 780            | 0.33       |                            |
|           |                          | 790            | 0.66       |                            |
|           |                          | 820            | 0.33       |                            |
|           |                          | 830            | 0.33       |                            |
|           |                          | 830            | 8.0        |                            |
|           |                          | 840            | 0.33       |                            |
|           |                          | 840            | 13.0       |                            |
|           |                          | 850            | 0.33       |                            |
|           |                          | 850            | 1.0        |                            |
|           |                          | 920            | 0.16       | p.m.                      |
|           |                          |                |            |                            |
|           |                          | 37.5 62.5 0    | (3:5)      |                            |
|           |                          | 750            |            |                            |
|           |                          | 650            |            |                            |
|           |                          | 750 × 5        |            |                            |
| #4        |                          | 40  60  0      | (2:3)      |                            |
|           |                          | 750            |            |                            |
|           |                          | 650            |            |                            |
|           |                          | 750 × 5        |            |                            |
|           |                          | 800            |            |                            |
|           |                          | 850            |            |                            |
|           |                          | 900            | 1.0        |                            |
| #1        |                          | 750            |            |                            |
|           |                          | 650            |            |                            |
|           |                          | 750 × 5        |            |                            |
| #2        |                          | 750            |            |                            |
|           |                          | 650            |            |                            |
|           |                          | 750 × 5        |            |                            |
|           |                          | 800            |            |                            |
|           |                          | 850            |            |                            |
|           |                          | 900            | 1.0        |                            |
| #3        |                          | 700            |            |                            |
|           |                          | 700 × 5        |            |                            |
|           |                          | 850            |            |                            |
|           |                          | 900            |            |                            |
|           |                          | 750            |            |                            |
| #4        |                          | 700            |            |                            |
|           |                          | 800            |            |                            |
|           |                          | 900 × 2        |            |                            |
|           |                          | 750            |            |                            |
|           |                          |                |            |                            |
|           |                          |                |            |                            |
Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obs. | Results of x-ray diffraction |
|-----------|--------------------------|----------------|------------|-----------------------------|
|           | CaO | 1/2Bi₂O₃ | CuO | Initial temp °C | final temp °C | Time h |  |  |  |
| #5        |     |         |     |     |     |     |  |  |  |
|           | 700 |         |     |     |     |     |  |  |  |
|           | 850 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           | 825 |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
| #6        |     |         |     |     |     |     |  |  |  |
|           | 700 |         |     |     |     |     |  |  |  |
|           | 750 |         |     |     |     |     |  |  |  |
|           | 860 |         |     |     |     |     |  |  |  |
|           | 935 |         |     |     |     |     |  |  |  |
|           | 950 |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
| #1        |     |         |     |     |     |     |  |  |  |
|           | 700 |         |     |     |     |     |  |  |  |
|           | 750 |         |     |     |     |     |  |  |  |
|           | 650 |         |     |     |     |     |  |  |  |
|           | 825 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |

41.18 (7:10) 58.82 0

|           | 750 |         |     |     |     |     |  |  |  |
|           | 650 |         |     |     |     |     |  |  |  |
|           | 825 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |

42.86 (3:4) 57.14 0

|           | 700 |         |     |     |     |     |  |  |  |
|           | 750 |         |     |     |     |     |  |  |  |
|           | 850 |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |

45 55 0

|           | 700 |         |     |     |     |     |  |  |  |
|           | 750 |         |     |     |     |     |  |  |  |
|           | 650 |         |     |     |     |     |  |  |  |
|           | 850 |         |     |     |     |     |  |  |  |
|           | 870 |         |     |     |     |     |  |  |  |
|           | 890 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           | 940 |         |     |     |     |     |  |  |  |
|           | 880 |         |     |     |     |     |  |  |  |
|           | 950 | 0.33 | p.m. |     |     |     |  |  |  |
|           | 1000 | 1.75 | c.m. |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |
|           |     |         |     |     |     |     |  |  |  |

48 52 0

|           | 700 |         |     |     |     |     |  |  |  |
|           | 800 |         |     |     |     |     |  |  |  |
|           | 900 |         |     |     |     |     |  |  |  |
|           |     | 955 | 0.33 | p.m. |     |     |  |  |  |
|           |     | 960 | 0.33 |     |     |     |  |  |  |
|           |     | 940 | 0.33 |     |     |     |  |  |  |
|           |     | 970 | 0.33 |     |     |     |  |  |  |
|           |     |     |     |     |     |     |  |  |  |

50 50 0

|           | 700 |         |     |     |     |     |  |  |  |
|           | 750 |         |     |     |     |     |  |  |  |
|           | 650 |         |     |     |     |     |  |  |  |
|           | 850 |         |     |     |     |     |  |  |  |
|           | 900 | 0.33 |     |     |     |     |  |  |  |
|           |     | 940 | 1.0 |     |     |     |  |  |  |
|           |     | 940 | 2.0 |     |     |     |  |  |  |
|           |     | 820 | 15 |     |     |     |  |  |  |
|           |     | 1000 | 1.0 | c.m. |     |     |  |  |  |
|           |     |     |     |     |     |     |  |  |  |

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### Table 1a. Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obser. | Results of x-ray diffraction |
|-----------|---------------------------|----------------|--------------|-----------------------------|
|           | CaO | 1/2Bi₂O₃ | CuO | Initial | final | temp °C | Time h |                     |
| #2        |     |         |      |         |       |       |       |                     |
|           | CaO | 1/2Bi₂O₃ | CuO | Initial | final | Time h |       |                     |
|           |     |         |      |         |       |       |       |                     |
| #3        |     |         |      |         |       |       |       |                     |
|           |     |         |      |         |       |       |       |                     |
| #4        |     |         |      |         |       |       |       |                     |
|           |     |         |      |         |       |       |       |                     |

53.85 46.15 0 (7:6)
Table 1a. Experimental data for the system CaO-Bi$_2$O$_3$-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment$^b$ | Phys. obs.$^c$ | Results of x-ray diffraction$^d$ |
|-----------|-------------------------|-------------------|----------------|----------------------------------|
|           | CaO 1/2Bi$_2$O$_3$ CuO | temp °C | final Time h |                                |
| #1 60     | 40 0                     | 900 | 900×2 | 750×5 | CB + CaO | CB + CaO |
| #2 66.67  | 33.33 0                  | 750 | 650  | 750×5 | CB + Cu$_2$B$_2$ + CaO | CB + CaO |
|          |                         | 750×2 | 920  | 0.33  | n.m.  | CB + CaO |
|          |                         |       | 930  | 0.33  | n.m.  | C-Mon + CaO |
|          |                         |       | 940  | 0.33  | n.m.  | C-Mon + CaO |
|          |                         |       | 950  | 0.33  | n.m.  | C-Mon + CaO |
|          |                         |       | 960  | 0.33  | n.m.  | bcc + CaO |
| 71.43    | 28.57 0                  | 750×5 |       |       | CB + CaO |
| 11.11    | 44.44 44.44              | 700  | 750  | 750×5 | rhomb + CuO + B$_2$Cu | rhomb + CuO + B$_2$Cu |
| 20 40    | 40 40                    | 700  | 750  | 750×5 | CuO + rhomb + CB$_2$ | CuO + CB$_2$ + rhomb |
| 33.33    | 33.33 33.33              | 700  | 750  | 750×5 | CB + Cu$_2$B$_2$ + CuO | CB + Cu$_2$B$_2$ + CuO |
| 44.02    | 7.14 48.84 Ca$_{9}$$\text{Bi}_6$$\text{O}_{15}$ + Ca$_2$Bi$_2$O$_5$ + Cu$_7$CuO$_2$ 1:1:10 | 700 | 700×2 | 700×3 | 700×4 | C$_{12}$Cu + Cu$_2$B$_3$ + CB | C$_{12}$Cu + Cu$_2$B$_3$ + CB |
|          |                         |       |       |       |       | C$_{12}$Cu + CB + Cu$_2$B$_3$ |
|          |                         |       |       |       |       | C$_{12}$Cu + CB + Cu$_2$B$_{3r}$ |
|          |                         |       |       |       |       | C$_{12}$Cu + CB |
|          |                         |       |       |       |       | C$_{12}$Cu + CB |
| 44.44    | 22.22 33.33 Ca$_2$CuO$_3$ + Bi$_2$Cu$_2$O$_4$ 2:1 | 700 | 700×2 | 700×3 | 700×4 | C$_2$Cu + B$_2$Cu | C$_2$Cu + Cu$_2$B$_3$ + CuO |
|          |                         |       |       |       |       | C$_2$Cu + Cu$_2$B$_3$ + B$_2$Cu + CuO + CB |
|          |                         |       |       |       |       | C$_2$Cu + Cu$_2$B$_3$ + CuO + CB + B$_2$Cu$^s$ |
| 45 45    | 10                      | 700  |       |       |       | p.m.  | bcc + C-morn + CaO |
|          |                         |       | 920  | 0.33  | c.m.  | bcc + CaO + C-morn |
|          |                         |       | 940  | 0.33  | c.m.  | bcc + CaO + C-morn |

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### Table 1a. Experimental data for the system CaO−Bi₂O₃−CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment | Phys. obs. | Results of x-ray diffraction |
|-----------|--------------------------|---------------|------------|------------------------------|
|           | CaO 1/2Bi₂O₃ CuO | Initial temp °C | Time h    |                             |
| 49        | 49 2                | 700 900 0.33  | CB        |                             |
|           |                      | 750 910 0.33  | CB        |                             |
|           |                      | 915 16.0      | p.m.      |                             |
|           |                      | 930 0.33      | p.m.      | bcc + CaO                   |
| 50        | 25 25                | 700 800      | CB + CuO + CaO  |                             |
|           |                      | 750 750      | CB + CuO + CaO  |                             |
|           |                      | 750 × 5      | CB + CuO + CaO  |                             |
| 54        | 23 23                | 700 700      | CB + CaO + CuO + C₁→₄Cu |                             |
| 54.95     | 14.63 30.41          | 700 700      | C₂B₃ + C₂Cu + C₁→₄Cu |                             |
|           | Ca₂Bi₄O₁₂ + Ca₂CuO₃ + C₁→₄CuO₂ | 1:7:3 | C₂B₃ + C₂Cu + C₁→₄Cu + CB |                             |
|           |                      | 700 700      | C₂Cu + C₁→₄Cu + CB + C₂B₃ |                             |
|           |                      | 700 × 2      | C₂Cu + C₁→₄Cu + CB + C₂B₃ |                             |
|           |                      | 700 × 3      | C₂Cu + C₁→₄Cu + CB + C₂B₃ |                             |
| 56        | 24 20                | 700 700      | C₂Cu + C₂B₃  |                             |
|           | Ca₂Bi₄O₁₂ + Ca₂CuO₃ | 1:5          | C₂Cu + C₂B₃  |                             |
|           |                      | 700 700      | C₂Cu + C₂B₃  |                             |
|           |                      | 700 × 2      | C₂Cu + C₂B₃  |                             |
|           |                      | 700 × 3      | C₂Cu + C₂B₃  |                             |
|           | #1                    | 700 700      | C₂Cu + C₂B₃ + CB |                             |
|           |                      | 700 × 2      | C₂Cu + C₂B₃ + CB |                             |
|           |                      | 700 × 3      | C₂Cu + C₂B₃ + CB |                             |
|           | #2                    | 750 × 2      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 750 × 2      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 336      | C₂Cu + C₂B₃ + CuO |                             |
|           | #3                    | 700 700      | C₂Cu + C₂B₃ + CuO |                             |
|           | + C₁→₄Cuₓ           | 700 700      | C₂Cu + C₂B₃ + CuO |                             |
|           | #4                    | 700 700      | C₂Cu + C₂B₃ + CuO |                             |
|           | + C₁→₄Cu(more)      | 700 700      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 × 2      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 × 3      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 × 3      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 × 3      | C₂Cu + C₂B₃ + CuO |                             |
|           |                      | 700 × 5      | C₂Cu + C₂B₃ + CuO |                             |
| 57.14     | 9.52 33.33           | 700 700      | C₂Cu + B₂Cu  |                             |
|           | Ca₂CuO₃ + Bi₂CuO₄   | 6:1          | C₂Cu + B₂Cu  |                             |
|           |                      | 700 700      | C₂Cu + B₂Cu  |                             |
|           |                      | 700 × 2      | C₂Cu + B₂Cu  |                             |
|           |                      | 700 × 3      | C₂Cu + B₂Cu  |                             |
| 60        | 20 20                | 700 700      | CB + CaO + CuO |                             |
|           |                      | 750 750      | CB + CaO + CuO |                             |
|           |                      | 750 × 5      | CB + CaO + CuO |                             |
|           |                      | 750 × 9      | CB + CaO + CuO |                             |
Table 1a.  Experimental data for the system CaO-Bi₂O₃-CuO—Continued

| Spec. no. | Composition mole percent | Heat treatment a | Phys. obs. ° | Results of x-ray diffraction a |
|-----------|--------------------------|-----------------|--------------|------------------------------|
|           | CaO 1/2Bi₂O₃ CuO         | temp °C         |              |                              |
|           | Initial | final | Time h | CB + C₂Cu + CaO | CB + C₂Cu + CaO₂ |
| 61.29     | 19.35   | 19.35 |       | 750×2                  | 700 336    |
|           |         |       |       | CB + C₂Cu + CaO       | CB + C₂Cu + CaO₂ |
| 70        | 15      | 15    | 700   | 750×5                  | 800          |
|           |         |       |       | CaO + CB + Ca₁₋₋Cu + CuO | CaO + CB + Ca₁₋₋Cu + CuO |
|           |         |       |       | 800                     | 850          |
|           |         |       |       | CaO + CB + C₂Cu        | 900          |
|           |         |       |       | 900                     | 900          |
|           |         |       |       | 900                     | 750          |
|           |         |       |       | CaO + CB + C₂Cu        | 900          |
|           |         |       |       | 900                     | 750×7,126    |
|           |         |       |       | CaO + C₂mon + C₂Cu     |              |

* Starting materials CaCO₃, Bi₂O₃, CuO except when listed in italics. Compositions given in italics were formulated from the listed pre-reacted compounds or compositions.

* 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 for the indicated number of hours. (if hours are not specified heat treatment was overnight). O₂= heat treatment in one atmosphere of purified oxygen.

* p.m. = partially melted, c.m. = completely melted, n.m. = no melting, s.m. = slightly melted.

* Compounds are listed in order of estimated amounts, most prevalent first.

tr = trace, just barely discernable.

C₂Cu = Ca₂CuO₃
C₁₋₋Cu = Ca₁₋₋CuO₂
C₂Cu₂ = Ca₂Cu₂O₃
rhomb = rhombohedral solid solution
fcc = face centered cubic solid solution; symmetry often distorted and generally with superstructure
fcc' = very slight rhombohedral distortion of cubic symmetry, with incommensurate superstructure perpendicular to the hexagonal c * (corresponding to a', of [20]).

fcc" = metastable phase with larger rhombohedral distortion of cubic symmetry, with superstructure equal to 42 and faint incommensurate superstructure perpendicular to the hexagonal [h01] plane.

bcc = body centered cubic solid solution; symmetry often distorted and generally with superstructure.

C₂Bi₄ = Ca₂Bi₄O₆₆
CB₂ = Ca₂Bi₂O₄
C₂B₃ = Ca₂Bi₂O₁₃
CB = Ca₂Bi₂O₅ (triclinic)
C-mon = metastable C-centered monoclinic phase near Ca₆Bi₂O₁₆.5.

* Although Ca₂Bi₂O₅ has formed during first 700 °C heat treatment, further heating and grinding resulted in formation of Ca₆Bi₂O₁₆.5 which increased with the third heat treatment, indicating that the 2:3 phase was formed metastably but the 1:1 compound is the stable phase.

* Amount of 2:3 decreasing and amount of Ca₁₋₋CuO₂ may be increasing very slightly.
| Charge       | Flux        | Container          | Temperature cycle | Results                      |
|--------------|-------------|--------------------|-------------------|------------------------------|
| CaO:1/2Bi₂O₃| (KNa)Cl     | Small dia Au       | 700 °C 595 h      | biaxial xts                  |
| 1:6          | 90 wt%      | sealed             |                   |                              |
|              | 10 wt%      |                    |                   | Rhomb (Orth)                 |
| CaO:1/2Bi₂O₃| (KNa)Cl     | Small dia Au       | 700→875 °C @ 10 °C/h |                            |
| 1:4          |             | sealed             | 875→650 °C @ 3 °C/h |                              |
| CaO:1/2Bi₂O₃| (KNa)Cl     | Large dia Pt       | 750 °C→645 °C @ 1 °C/h | 645 °C 64 h                  |
| 5:14         | 80 wt%      | sealed             |                   |                              |
| CaO:1/2Bi₂O₃| (KNa)Cl     | large dia Pt       | 750 °C→645 °C @ 1 °C/h | 645 °C 64 h                  |
| 5:14         | 80 wt%      | sealed             |                   |                              |
| CaO:1/2Bi₂O₃| 10ₓLH₂O     | Small dia Au       | Hydrothermal unit  | 700 °C 100 MPa               |
|              |             | sealed             |                   |                              |
| CaO:1/2Bi₂O₃| (KNa)Cl     | Large dia Au       | 650 °C→750 °C @ 10 °C/h |                            |
| 5:14         | 20 wt%      | sealed             | 750 °C→640 @ 1 °C/h |                              |
| CaO:1/2Bi₂O₃| None        | Small dia Au       | 900 °C, 20 min. quenched (liq N₂ cooled He cup) crushed |                               |
| 5:14         |             | open               | 780 °C 67.5 h quenched (liq N₂ cooled He cup)              | fcc'                          |
| CaO:1/2Bi₂O₃| None        | Small dia Au       | 925 °C→850 °C @ 3 °C/h | Ca₅Bi₄O₂₅                   |
| 5:14         |             | sealed             | 850 °C 24 h quenched (liq N₂ cooled He cup)                  |                              |
|              |             |                    | 650 °C 2 weeks     |                              |
| CaO:1/2Bi₂O₃| None        | Small dia Au       | 925 °C→850 °C @ 3 °C/h |                            |
| 5:14         |             | sealed             |                   |                              |
| CaO:1/2Bi₂O₃| None        | Small dia Au       | 900 °C 22 h quenched (liq N₂ cooled He cup) crushed |                               |
| 3:8          |             | open               | −800 °C 3 d quenched (liq N₂ cooled He cup)                  | fcc'                          |
|              |             |                    | −760 °C 15 min pulled from furnace                          |                              |
|              |             |                    | −800 °C 1 h quenched (liq N₂ cooled He cup)                  |                              |
|              |             |                    | −760 °C 10 min quenched (liq N₂ cooled He cup)               |                              |

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Table 1(b). Experimental conditions for crystal growth experiments—Continued

| Charge       | Flux          | Container      | Temperature cycle                        | Results |
|--------------|---------------|----------------|------------------------------------------|---------|
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Small dia Au   | 775 °C (18h) → 645 °C @ 1 °C/h           |         |
| 33:67        |                | sealed         |                                          | CaBi₂O₄ |
| 80 wt%       | 20 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Small dia Au   | 775 °C (18h) → 645 °C @ 1 °C/h           |         |
| 33:67        |                | sealed         |                                          | CaBi₂O₄ |
| 20 wt%       | 80 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Small dia Au   | 775 °C (18h) → 645 °C @ 1 °C/h           |         |
| 33:67        |                | sealed         |                                          | CaBi₂O₄ |
| 50 wt%       | 50 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Large dia Pt   | 750 °C → 645 °C @ 1 °C/h 645 °C 64 h     |         |
| 1:2          |                | sealed         |                                          |         |
| 20 wt%       | 80 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Large dia Pt   | 750 °C → 645 °C @ 1 °C/h 645 °C 64 h     |         |
| 1:2          |                | sealed         |                                          |         |
| 20 wt%       | 80 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | None          | Small dia Au   | 925 °C → 850 °C @ 3 °C/h 850 °C 24 h quenched (liq N₂ cooled He cup) crushed |         |
| 1:2          |                | sealed         |                                          |         |
| 925 °C → 850 °C @ 3 °C/h 850 °C 24 h quenched (liq N₂ cooled He cup) crushed |         |
| Small dia Au open |  | 500 °C → 700 °C @ 3 °C/h 700 °C 168 h |         |
| CaO:1/2Bi₂O₃ | None          | Small dia Au   | 925 °C → 850 °C @ 3 °C/h 850 °C 24 h quenched (liq N₂ cooled He cup) crushed |         |
| 1:2          |                | sealed         |                                          |         |
| 925 °C → 850 °C @ 3 °C/h 850 °C 24 h quenched (liq N₂ cooled He cup) crushed |         |
| Small dia Au open |  | 500 °C → 700 °C @ 3 °C/h 700 °C 168 h |         |
| CaO:1/2Bi₂O₃ | (KNa)Cl       | Large dia Au   | 650 °C → 750 °C @ 10 °C/h                |         |
| 1:2          |                | sealed         |                                          |         |
| 80 wt%       | 20 wt%        |                |                                          |         |
| CaO:1/2Bi₂O₃ | 10 µL H₂O     | Small dia Au   | Hydrothermal unit 700 °C 100 MPa         |         |
| 1:2          |                | sealed         |                                          |         |
| CaO:1/2Bi₂O₃ | None          | Large dia Au   | 750 °C → 875 °C @ 25 °C/h 875 °C → 845 °C @ 1 °C/h |         |
| 1:2          |                | sealed         |                                          |         |
| CaO:1/2Bi₂O₃ | None          | Small dia Au   | 925 °C 10 min quenched (liq N₂ cooled He cup) crushed to a fine powder |         |
| 1:2          |                | sealed         |                                          |         |
| CaO:1/2Bi₂O₃ | None          | Small dia Au   | 500 °C → 700 °C @ 3 °C/h                 |         |
| 1:2          |                | sealed         |                                          |         |
| Charge          | Flux          | Container | Temperature cycle               | Results        |
|----------------|--------------|-----------|---------------------------------|----------------|
| CaO:1/2Bi2O3   | None         | Small dia Au sealed | 1000°C → 900°C @ 1°C/h crushed |                |
| 2:3            |              |           |                                 |                |
|                |              |           | 825°C 190 h furnace cooled       |                |
| CaO:1/2Bi2O3   | None         | Small dia Au sealed | 1000°C 1 h quenched (liq N2 cooled He cup) | Ca$_2$B$_4$O$_{13}$ |
| 2:3            |              |           | 875°C 260 h                      |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Au sealed | 840°C → 640°C @ 1°C/h           |                |
| 2:3 98 wt%      | 2 wt%        |           |                                 |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Au sealed | 840°C → 640°C @ 1°C/h           |                |
| 2:3 80 wt%      | 20 wt%       |           |                                 |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Au sealed | 840°C → 640°C @ 1°C/h           |                |
| 2:3 50 wt%      | 50 wt%       |           |                                 |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Au sealed | 840°C → 640°C @ 1°C/h           |                |
| 2:3 20 wt%      | 80 wt%       |           |                                 |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Pt sealed | 750°C → 645°C @ 1°C/h           | Ca$_2$B$_4$O$_{13}$ |
| 7:10 20 wt%     | 80 wt%       |           | 645°C 64 h                       |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Pt sealed | 750°C → 645°C @ 1°C/h           |                |
| 7:10 20 wt%     | 80 wt%       |           |                                 |                |
| CaO:1/2Bi2O3   | CaCl$_2$     | Large dia Au open | 900°C 20 h                      |                |
| 6:7 80 wt%      | 20 wt%       |           |                                 |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Small dia Au sealed | 650°C → 950°C @ 100°C/h         |                |
| 1:1 80 wt%      | 20 wt%       |           | 950°C → 990°C @ 1°C/h           |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Small dia Au sealed | 650°C → 950°C @ 100°C/h         |                |
| 1:1 50 wt%      | 50 wt%       |           | 950°C → 990°C @ 1°C/h           |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Small dia Au sealed | 650°C → 950°C @ 100°C/h         |                |
| 1:1 20 wt%      | 80 wt%       |           | 950°C → 990°C @ 1°C/h           |                |
| CaO:1/2Bi2O3   | (KNa)Cl      | Large dia Pt sealed | 750°C → 645°C @ 1°C/h           | Ca$_2$B$_4$O$_{13}$ |
| 7:6 20 wt%      | 80 wt%       |           | 645°C 64 h                       |                |

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Table 1(b). Experimental conditions for crystal growth experiments—Continued

| Charge     | Flux          | Container | Temperature cycle            | Results       |
|------------|---------------|-----------|------------------------------|---------------|
| CaO:1/2Bi2O3 | (KNa)Cl      | Large dia Pt | 750 °C→645 °C @ 1 °C/h      |               |
| 7:6        | 20 wt%        | 80 wt%    |                              |               |
| CaO:1/2Bi2O3 | (KNa)Cl      | Large dia Au sealed | 900 °C 19.5 h  |               |

3. Experimental Results and Discussion

Most of the experiments performed on the binary and ternary mixtures of CaO-Bi2O3-CuO are reported in Table 1a. Additional experiments specifically designed in an attempt to obtain crystals large enough for x-ray single crystal studies are detailed in Table 1b. Crystallographic data for various phases are reported in Table 2.

3.1 The System Bi2O3-CuO

A phase diagram for this system was already published [16], and was redrawn as Fig. 6392 in Phase Diagrams for Ceramists (PDFC) [17]. It apparently contains only one compound Bi2CuO4, (Bi2Cu). No attempt was made to reinvestigate the melting relations of this system because it does not have any great effect on the phase equilibria of the ternary system with CaO.

3.2 The System CaO-CuO

Although a revised phase diagram for this system was previously reported [7], further experimental evidence (Table 1a) was accumulated in this study and the diagram was revised again [18] as shown in Fig. 1. The CaCu2O3 compound, which was reported to be stable only above 950 °C [19], was found to be stable between 985 and 1018 °C. Previously determined temperatures, 1020 and 1013 °C [20,7] for the decomposition of CaCu2O3 (CCu2) and for eutectic melting, respectively, are within experimental error of the new values, 1018 ± 2 °C and 1012 ± 2 °C.

3.2.1 Ca2CuO3 The Ca2CuO3 (C2Cu) compound decomposes into CaO plus liquid above 1034 ± 2 °C, which is slightly above the previous estimate of 1030 °C [20,7]. The composition of the eutectic reaction is 20CaO–80CuO ± 5%, as determined from the presence or absence of the Ca2CuO3 phase in samples of varying compositions that were quenched from 1020 °C.

3.2.2 Ca1-xCuO2 Samples prepared with an original Ca:Cu ratio of 45.33:54.67 contained no detectable CaO or CuO after heating in oxygen at 700 °C, as demonstrated by x-ray diffraction (Fig. 2 and Table 3). Compositions with original Ca:Cu ratios of 45.20:54.80 and 45.45:54.54 (=5:6) yielded x-ray patterns which indicated the presence of excess CuO and excess CaO, respectively. Therefore, the Ca:Cu ratio for this compound is 0.453:0.547 or Ca1-xCuO2 with the composition Ca0.828CuO2 (x = 0.172) at 700 °C in oxygen. The single phase region for this phase probably varies with temperature and partial pressure of oxygen. The composition and structural analyses of this phase have been recently reported [15]. The x-ray powder diffraction pattern for Ca1-xCuO2 is shown in Fig. 2 and the indexed data is given in Table 3. This compound decomposes into Ca2CuO3 plus CuO above 755 °C in air and 835 °C in oxygen. In Fig. 1, the experiments conducted in air and those conducted in an oxygen atmosphere are indicated by the dashed line and the crosses, respectively. At 675 °C, Ca1-xCuO2 can be synthesized from CaCO3 plus CuO but the run product never fully equilibrates to a single- or two-phase assemblage. Rather, the metastable three-phase assemblage Ca1-xCuO2 + CaO + CuO persists: after five cycles of heating with intermittent grinding the relative proportions of phases were Ca1-xCuO2 > CaO > CuO and they remained that way for an additional overnight heat treatments. Because of its great persistence, Ca1-xCuO2 is interpreted as being an equilibrium phase, but it should be noted that reversal of its decomposition (synthesis from CuO + Ca2CuO3) was not successfully demonstrated.
### Table 2. Crystal structure data

| Chemical formula | Symmetry | Phase (°C) | a (Å)  | b (Å)  | c (Å)  | α degrees | β degrees | γ degrees |
|------------------|----------|------------|--------|--------|--------|------------|-----------|-----------|
| Ca₁₋ₓCuₓO₂, x = 0.172 | Fmmn* | T = 700°C | 2.8047² | 6.321  | 10.573 | (7)        | (2)       | (2)       |
| CaO:1/2Bi₂O₃, 1:6 | R3 | T = 750°C | 3.9448  | 27.8400 | (8)   | (8)       | (5)       |           |
|                  |         | T ≤ 735°C | 6.8188  | 3.9531  | 27.830 | (3)        | (2)       | (1)       |
| CaO:1/2Bi₂O₃, 3:8 | R3 | α' (T = 780°C) | 7.7427  | 9.465   | (9)   | (1)       | (1)       |           |
|                  |         | B2/m      | 15.5819 | 3.8077  | 10.8955 | (3)        | (1)       | (3)       |
|                  |         | α'' (T = 760°C) | 15.5819 | 3.8077  | 10.8955 | (3)        | (1)       | (3)       |
| Ca₂Bi₂O₄₆      | P1      |           | 9.934   | 15.034  | 15.008 | 82.65      | 85.27     |           |
| CaBi₂O₄        | C2/c    |           | 16.6295 | 11.5966 | 14.0055 | (8)        | (5)       | (6)       |
| Ca₂Bi₆O₁₃      | C2mm    |           | 17.3795 | 5.9419  | 7.2306 | (5)        | (2)       | (2)       |
| CaO:1/2Bi₂O₃, 9:10 | "bcc" | T = 1000°C | 4.2458  |         |        |           |           |           |
| Ca₂Bi₂O₅       | P1      |           | 10.1222 | 10.146  | 10.4833 | 116.912    | 107.135   | 92.939    |
| Caₓ₋ₓSrₓ₋ₓBi₁₊₄O₆₃, x → 6 | C-centered | monoclinic | 21.295  | 4.3863  | 12.671 | 102.74     |           |           |

* Indicates a subcell.

² Numbers in parentheses indicate uncertainties in final digits.

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**Fig. 1.** CaO-CuO phase diagram.
Table 3. X-ray powder diffraction data for the compound Cu$_{1-x}$O$_2$

| d obs (Å) | Rel f(%) | 2θ obs | 2θ calc* | hkl |
|-----------|----------|--------|----------|-----|
| 5.273     | 13       | 16.80  | 16.76    | 002 |
| 3.1554    | 21       | 28.26  | 28.21    | 002 |
| 3.0994    | 1        | 28.78* |          |     |
| 2.8914    | 6        | 30.90  | 30.91    | 1-8a,1,1-8c |
| 2.8245    | 3        | 31.65  | 31.66    | 1-8a,1,1+8c |
| 2.7106    | 100      | 33.02  | 32.99    | 022 |
| 2.6407    | 22       | 33.92  | 33.89    | 004 |
| 2.4887    | 23       | 36.06  | 36.02    | 111 |
| 2.3218    | 6        | 38.75  | 38.77    | 1-8a,1,3-8c |
| 2.2207    | 7        | 40.59  | 40.60    | 1-8a,1,3+8c |
| 2.0720    | 61       | 43.65  | 43.62    | 113 |
| 1.7666    | 4        | 51.70  | 51.72    | 1-8a,3,1-8c |
| 1.7613    | 6        | 51.87  | 51.85    | 600 |
| 1.7571    | 6        | 52.00  | 51.95    | 1-8a,1,5-8c |
| 1.7527    | 8        | 52.14  | 52.21    | 1-8a,3,1+8c |
| 1.6840    | 2        | 54.44  | 54.39    | 1-8a,1,5+8c |
| 1.6632    | 10       | 55.18  | 55.16    | 131 |
| 1.6306    | 29       | 56.38  | 56.36    | 115 |
| 1.6088    | 2        | 57.21  | 57.23    | 1-8a,3,3-8c |
| 1.5802    | 12       | 58.35  | 58.34    | 040 |
| 1.5397    | 18       | 60.04  | 60.06    | 026 |
| 1.5200    | 16       | 60.90  | 60.90    | 133 |
| 1.4811    | 1        | 62.67* |          |     |
| 1.4545    | 1        | 63.95* |          |     |
| 1.4467    | 1        | 64.34* |          |     |
| 1.4129    | 1        | 66.07* |          |     |
| 1.4025    | 6        | 66.63  | 66.64    | 200 |
| 1.3702    | 1        | 68.41  | 68.42    | 1-8a,1,7-8c |
| 1.3565    | 12       | 69.20  | 69.21    | 044 |
| 1.3471    | 2        | 69.75* |          |     |
| 1.3208    | 13       | 71.35  | 71.33    | 1-8a,1,7+8c |
| 1.3186    | 15       | 71.49  | 71.55    | 135 |
| 1.3018    | 5        | 72.56  | 72.59    | 117 |
| 1.2819    | 5        | 73.87  | 73.87    | 220 |

* Calculated on the basis of an orthorhombic subcell, Fmmm, a = 2.8047 (7), b = 6.321 (2), and c = 10.573 (2) Å.

Superstructure probably not accounted for by 8-vectors.

3.2.3 Cu$_2$O in the Binary System Cu$_2$O, which is known to be stable in air only above 1026 °C, was found in this system above 1012 °C. Therefore, Cu$^+$ and Cu$^{2+}$ must have coexisted in the samples that were quenched in air from temperatures between 1012 and 1026 °C. The Cu$_2$O observed in samples that were quenched from below 1026 °C is probably formed during solidification of the liquid phase; i.e., an oxygen deficiency in the liquid may result in the solidification of Cu$_2$O as well as CuO.

3.3 The System CaO-Bi$_2$O$_3$

The phase equilibria diagram for the system CaO-Bi$_2$O$_3$ was reported in [21] and redrawn as Fig. 6380 in PDFC [17]. It is reproduced here as Fig. 3 with the scale changed to 1/2Bi$_2$O$_3$-CaO instead of Bi$_2$O$_3$-CaO, to maintain consistency with the other phase diagrams in this report. An interpretation of the experimental results recorded in Table 1 was published in [19] and it is shown in Fig. 4 (cf. Fig. 3). The major differences between our new diagram and the one presented in [21] are: 1) the composition of “Ca$_7$Bi$_{10}$O$_{22}$” [21,22] is revised to Ca$_2$Bi$_6$O$_{13}$ (2:3) and its crystal structure is reported in [23]; 2) the composition of “Ca$_7$Bi$_6$O$_{16}$” [21,22] is now reported as Ca$_2$Bi$_6$O$_3$, and its crystal structure is given in [24]; 3) a metastable phase ~Ca$_5$Bi$_6$O$_{16.5}$ was formed at about 925 °C on the CaO-rich side of Ca$_2$Bi$_6$O$_3$, but at about 885 °C on the CaO-poor side; 4) melting relations have been determined in the region of 20-50 mol % CaO.

3.3.1. Rhombohedral Solid Solution (Sillen Phase-Rhomb) The rhombohedral solid solution was first reported by Sillen [25]. Phase relations in the CaO-rich region of the Sillen phase field were previously [20] represented as exhibiting a congruent transition to the fcc solid solution, and the present experiments indicate such a point at (~ 22 mol % CaO, ~ 835 °C). Conflant et al. [21] reported a phase transition from one rhombohedral phase to another at about 735–740 °C. Differential thermal analysis of a 1:6 ratio CaO:1/2Bi$_2$O$_3$ specimen confirms the presence of a reversible transition at about 735 °C. Samples quenched from ~750 °C are clearly rhombohedral as previously reported [21,22], but x-ray patterns (Figs. 5a, 5b; Tables 4, 5, 6) from samples that were quenched from ≤ 735 °C exhibit peak splitting and faint superstructure reflections (Fig. 5b). The diffraction patterns for both the high and low temperature forms are much sharper if the specimens are not ground after quenching. Apparently, it is easy to induce mechanical deformation in these samples by grinding. The peak splitting can be indexed with an orthorhombic cell a = 6.8188(3), b = 3.9531(2), and c = 10.573(2) Å, which is most easily observed in the rhombohedral (0,2,13) and (3,0,9) reflections corresponding to (2,2,13) + (4,0,13) and (3,3,9) + (6,0,9), respectively, in the orthorhombic indexing (Figs. 5a, 5b, and Tables 5, 6). Dimensionally the unit cell is orthorhombic, but the symmetry cannot be higher than monoclinic because it is the derivative of a rhombohedral (rather than hexagonal) high symmetry phase. Single crystals prepared at 700 °C with a salt eutectic flux (Table 1b) give a biaxial interference figure, in polarized light, parallel to the pseudo-rhombohedral c axis.
Fig. 2. Ca$_{1-x}$CuO$_2$ x-ray diffraction powder pattern (CaO:CuO 45.328:54.672).

Fig. 3. CaO-$1/2$Bi$_2$O$_3$ phase diagram as changed from PDFC 6380-Conflant et al.
Fig. 4. CaO-$\frac{1}{2}$Bi$_2$O$_3$—present phase diagram.

Fig. 5a. X-ray powder diffraction pattern CaO:$\frac{1}{2}$Bi$_2$O$_3$ 1:6 quenched from 740 °C.
Fig. 5b. X-ray powder diffraction pattern of CaO:1/2Bi₂O₃ 1:6 quenched from 740°C (rhombohedral indexing) and 725°C (orthorhombic indexing).

Table 4. X-ray powder diffraction data for the high temperature rhombohedral (Sillen phase) indexing of CaO:1/2Bi₂O₃ 1:6

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc | hkl  |
|-----------|----------|--------|---------|------|
| 9.254     | 4        | 9.55   | 9.52    | 003  |
| 4.633     | 8        | 19.14  | 19.11   | 006  |
| 3.3897    | 23       | 26.27  | 26.26   | 101  |
| 3.166     | 31       | 26.86  | 26.85   | 012  |
| 3.0922    | 93       | 28.85  | 28.84   | 009  |
| 3.0651    | 100      | 29.11  | 29.09   | 014  |
| 2.9099    | 56       | 30.70  | 30.68   | 015  |
| 2.5896    | 16       | 34.61  | 34.58   | 017  |
| 2.4372    | 17       | 36.85  | 36.84   | 018  |
|           | 2        | 39.90p |         |      |
| 2.1578    | 10       | 41.83  | 41.82   | 1,0,10 |
|           | 2        | 43.67p |         |      |
| 2.0326    | 17       | 44.54  | 44.52   | 0,1,11 |
| 1.9726    | 57       | 45.97  | 45.98   | 110  |
| 1.9263    | 1        | 47.09  | 47.07   | 113  |
| 1.8554    | 12       | 49.06  | 49.04   | 0,0,15|
| 1.8149    | 57       | 50.23  | 50.22   | 116  |
|           |          |        | 50.24   | 1,0,13|
| 1.7188    | 24       | 53.25  | 53.26   | 0,1,14|
| 1.7043    | 8        | 53.74  | 53.72   | 021  |
| 1.6953    | 10       | 54.05  | 54.05   | 202  |
| 1.6629    | 72       | 55.19  | 55.19   | 119  |
| 1.6333    | 16       | 56.28  | 56.29   | 205  |
| 1.5694    | 6        | 58.79  | 58.79   | 027  |
| 1.5500    | 10       | 59.60  | 59.58   | 1,0,16|
| 1.5467    | 18       | 59.74  | 59.74   | 0,0,18|
| 1.5334    | 6        | 60.31  | 60.31   | 208  |
| 1.4770    | 12       | 62.87  | 62.88   | 0,1,17|
| 1.4561    | 2        | 63.88  | 63.89   | 0,2,10|
| 1.4157    | 6        | 65.93  | 65.92   | 2,0,11|

Table 4. X-ray powder diffraction data for the high temperature rhombohedral (Sillen phase) indexing of CaO:1/2Bi₂O₃ 1:6—Continued

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc | hkl  |
|-----------|----------|--------|---------|------|
| 1.3516    | 7        | 69.49  | 69.49   | 1,1,15|
| 1.3555    | 12       | 70.45  | 70.46   | 0,2,13|
| 1.2956    | 8        | 72.96  | 72.95   | 2,0,14|
| 1.2891    | 10       | 73.39  | 73.39   | 0,1,20|
| 1.2856    | 11       | 73.62  | 73.61   | 122  |
| 1.2693    | 15       | 74.73  | 74.71   | 214  |
| 1.2579    | 13       | 75.52  | 75.53   | 125  |
| 1.2280    | 4        | 77.70  | 77.69   | 217  |
| 1.2171    | 21       | 78.53  | 78.53   | 1,1,18|
| 1.2105    | 5        | 79.04  | 79.03   | 128  |
| 1.1868    | 14       | 80.94  | 80.95   | 1,0,22|
| 1.1823    | 9        | 81.31  | 81.33   | 2,0,17|
| 1.1712    | 2        | 82.25  | 82.24   | 2,1,10|
| 1.1598    | 3        | 83.24  | 83.22   | 0,0,24|
| 1.1503    | 5        | 84.08  | 84.09   | 1,2,11|
| 1.1407    | 8        | 84.95  | 84.93   | 0,1,23|
| 1.1386    | 12       | 85.15  | 85.13   | 300  |
| 1.1122    | 1        | 87.67  | 87.68   | 0,2,19|
| 1.1059    | 13       | 88.30  | 88.30   | 306  |
|           |          |        | 88.31   | 2,1,13|
| 1.0828    | 7        | 90.70  | 90.68   | 1,2,14|
| 1.0790    | 2        | 91.11  | 91.10   | 2,0,20|
| 1.0686    | 10       | 92.25  | 92.24   | 309  |
| 1.0587    | 2        | 93.37  | 93.36   | 1,0,25|
| 1.0368    | 2        | 95.97  | 95.95   | 2,1,16|
| 1.0309    | 7        | 96.70  | 96.67   | 0,0,27|
| 1.0217    | 8        | 97.86  | 97.86   | 0,1,26|
| 1.0169    | 8        | 98.49  | 98.50   | 0,2,22|
| 1.0141    | 9        | 98.86  | 98.87   | 1,2,17|

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Table 4. X-ray powder diffraction data for the high temperature rhombohedral (Sillen phase) indexing of CaO:1/2Bi2O3 1:6—Continued

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl   |
|-----------|----------|--------|---------|------|
| 0.9999    | 3        | 100.77 | 100.78  | 1,1,24 |
| 0.9876    | 3        | 102.52 | 102.52  | 2,0,23 |
| 0.9863    | 4        | 102.70 | 102.72  | 220  |
| 0.9707    | 1        | 103.04 | 105.05  | 3,0,15 |
| 0.9469    | 8        | 108.88 | 108.87  | 1,31  |
| 0.9454    | 4        | 109.14 | 109.15  | 312  |
| 0.9394    | 8        | 110.16 | 110.13  | 229  |
| 0.9341    | 4        | 111.10 | 111.11  | 315  |
| 0.9330    | 3        | 111.31 | 111.33  | 0,2,25|
| 0.9243    | 2        | 112.90 | 112.91  | 0,1,29|
| 0.9218    | 3        | 113.36 | 113.38  | 137  |
| 0.9171    | 7        | 114.27 | 114.28  | 3,0,18|
| 0.9141    | 10       | 114.84 | 114.83  | 318  |
| 0.9076    | 3        | 116.14 | 116.15  | 2,2,12|
| 0.9072    | 3        | 116.22 | 116.22  | 2,0,26|
| 0.9038    | 7        | 116.92 | 116.93  | 1,2,22|
| 0.8970    | 1        | 118.35 | 118.36  | 1,3,10|
| 0.8875    | 2        | 120.45 | 120.47  | 3,1,11|
| 0.8832    | 3        | 121.45 | 121.45  | 1,2,25|
| 0.8686    | 6        | 124.95 | 124.97  | 1,0,31|
| 0.8665    | 7        | 125.50 | 125.49  | 1,3,13|
| 0.8554    | 4        | 128.46 | 128.46  | 3,1,14|

*Calculated on the basis of a rhombohedral unit cell, R33, a = 3.9448(8) Å, c = 27.8400(8) Å.

Table 5. X-ray powder diffraction data for the low temperature orthorhombic indexing of CaO:1/2Bi2O3 1:6—Continued

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl   |
|-----------|----------|--------|---------|------|
| 1.7188    | 22       | 53.25  | 53.26   | 1,1,14|
| 1.7174    | 15       | 53.30  | 53.30   | 2,0,14|
| 1.7070    | 6        | 53.65  | 53.66   | 221  |
| 1.7011    | 5        | 53.85  | 53.84   | 401  |
| 1.6976    | 6        | 53.97  | 53.98   | 222  |
| 1.6924    | 5        | 54.15  | 54.16   | 402  |
| 1.6660    | 34       | 55.08  | 55.10   | 029  |
| 1.6618    | 54       | 55.23  | 55.23   | 319  |
| 1.6607    | 47       | 55.27  | 55.28   | 224  |
| 1.6563    | 28       | 55.43  | 55.45   | 404  |
| 1.6343    | 10       | 56.24  | 56.23   | 225  |
| 1.6298    | 9        | 56.41  | 56.41   | 405  |

*Apparently due to an unidentified structure.
Table 5. X-ray powder diffraction data for the low temperature orthorhombic indexing of CaO:1/2Bi_2O_3 1:6—Continued

| d obs (Å) | Rel I (%) | 2 θ obs | 2 θ calc* | hkl |
|-----------|-----------|---------|-----------|-----|
| 1.1039    | 6         | 88.50   | 88.51     | 606 |
| 1.0842    | 3         | 90.55   | 90.53     | 1,3,14 |
| 1.0827    | 4         | 90.71   | 90.71     | 4,2,14 |
| 1.0818    | 4         | 90.80   | 90.82     | 5,1,14 |
| 1.0793    | 3         | 91.07   | 91.07     | 2,2,20 |
| 1.0780    | 3         | 91.22   | 91.22     | 4,0,20 |
| 1.0694    | 5         | 92.16   | 92.14     | 3,3 |
| 1.0666    | 6         | 92.47   | 92.46     | 609 |
| 1.0586    | 2         | 93.38   | 93.39     | 1,1,25 |
| 1.0356    | 2         | 96.11   | 96.10     | 5,1,16 |
| 1.0306    | 5         | 96.74   | 96.72     | 0,0,27 |
| 1.0216    | 5         | 97.88   | 97.89     | 1,1,26 |
| 1.0170    | 6         | 98.48   | 98.48     | 2,2,22 |
| 1.0157    | 6         | 98.65   | 98.62     | 4,0,22 |

*Calculated on the basis of an orthorhombic unit cell, Cmmm, a = 6.8188(3), b = 3.9531(2), and c = 27.830(1) Å.

^ Apparently due to an unidentified structure.

Table 6. X-ray powder diffraction data for the high temperature rhombohedral (Sillen phase) indexing versus the orthorhombic indexing of CaO:1/2Bi_2O_3 1:6

| 2 θ obs | Rhombohedral | Orthorhombic |
|---------|--------------|--------------|
| hkl     | hkl          | 2 θ obs      |
|         | a            | b            |                |
| 9.55    | 003          | 003          | 9.52          |
| 19.14   | 006          | 006          | 19.11         |
| 26.27   | 101          | 111          | 26.25         |
| 26.86   | 012          | 112          | 26.84         |
| 28.85   | 009          | 009          | 28.86         |
| 29.11   | 104          | 114          | 29.06         |
| 30.70   | 015          | 115          | 30.67         |
| 34.61   | 107          | 117          | 34.59         |
| 36.85   | 018          | 118          | 36.82         |
|         | 208          |              | 36.87         |
| 39.90   | 003          | 003          | 38.29         |
| 41.83   | 10,10        | 1,1,10       | 38.90         |
| 43.67   | 01,11        | 1,1,11       | 40.76         |
| 44.54   | 01,11        | 2,0,10       | 41.86         |
| 45.97   | 10,10        | 2,0,10       | 43.01         |
| 47.09   | 110          | 021          | 45.97         |
| 49.06   | 00,15        | 00,15        | 47.17         |
| 50.23   | 116          | 1,1,13       | 50.22         |
|         | 1,0,13       | 316          | 50.25         |
| 53.25   | 01,14        | 1,1,14       | 52.07         |
|         | 2,0,14       | 53.25        | 52.90         |

^ Calculated on the basis of an orthorhombic unit cell, Cmmm, a = 6.8188(3), b = 3.9531(2), and c = 27.830(1) Å.

^ Apparently due to an unidentified structure.
patterns from quenched "fee" samples that contain CaO, is labeled "fcc" because neither the data presented here nor that in [20] provides a sound basis for drawing definitive phase boundaries. The minimum shown in Fig. 4 at ~773 °C for the CaO-rich end of this solid solution is in relatively good agreement with the value of 785 °C which can be interpreted from [21] (Fig. 3). When a single-phase specimen of composition near this minimum (5:14-3:8, CaO:1/2Bi203) is quenched after 10 min annealing at ~760 °C (~13 °C below the equilibrium minimum), the rhombohedral splitting of cubic maxima was greatly enhanced; this is the α" phase of [21] (Fig. 6; Table 8). As with the rhombohedral Sillen-type phases, these rhombohedral distorted fcc phases are highly susceptible to mechanical damage during routine grinding, therefore the line splitting of α" can only be seen if the quenched specimen is not ground. X-ray analysis of this sample yielded α" = 7.616, c/α" = 9.6477, a/α" = 1.2668, whereas hexagonal indexing of a truly cubic pattern would give c/a = 1.2247; [1,1,1]c = [0,0,0,3]H and [2,2,0]c = [2,2,4,0]H. Thus, the rhombohedral distorted phase that was quenched from the stable "fcc" region (α") had a c/a ratio that was slightly smaller than the cubic value, but the metastable lower-temperature phase (α") that was quenched from below the "fcc" region had a c/a ratio that was considerably larger than the cubic value. Single crystal x-ray precession patterns from the α" phase (Fig. 7) can be indexed with either a monoclinic or a rhombohedral cell with a = 4a_{sub} as shown in Table 8.

3.3.3. The "Body-Centered-Cubic" Solid Solution ("bcc") The phase referred to as body-centered-cubic ("bcc") solid solution was reported as a high temperature phase in [21]. In the present study this phase was found to extend from about 35 to 45 mol % CaO. The exact boundaries of the two-phase "fcc-bcc" region were not determined because the compositions of coexisting phases were not consistently reproduced. Just as with the "fcc" phase the "bcc" phase also exhibits line splitting and superstructure. Distortions from cubic symmetry (Fig. 8, Table 9), seem to be greatest in samples that are quenched from the region near the decomposition point of the 2:3 phase, (Fig. 9, Table 10). Single crystal x-ray diffraction precession data (Fig. 10) confirm the distortion recorded in Fig. 9 and Table 10 and indicate the nature of the superstructure.
CaO-rich phase boundaries of the “bcc” field have not been precisely determined in part because of complications arising from the presence in many experiments of a metastable phase (see “C-mon” below). This bcc-type phase was found to be stable down to a minimum temperature of 825±5°C (Fig. 4) which is in good agreement with the value of 819 °C interpreted from [20] (see Fig. 3).

Table 7. X-ray powder diffraction data for the α’ phase (CaO:1/2Bi₂O₃ mol ratio 3:8, 780 °C quench, sample not ground)—Continued

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl |
|-----------|----------|--------|----------|-----|
|           |          |        |          |     |
| 8.990     | 2        | 9.83   |          |     |
| 4.669     | 4        | 18.99  |          |     |
| 3.5296    | 7        | 25.21  |          |     |
| 3.5050    | 6        | 25.39  |          |     |
| 3.1565    | 100      | 28.25  | 28.26    | 003 |
| 2.9946    | 2        | 29.81  |          |     |
| 2.9492    | 1        | 30.28  |          |     |
| 2.7339    | 58       | 32.73  | 32.71    | 202 |
| 2.3510    | 4        | 38.25  |          |     |
| 2.0031    | 5        | 45.22  |          |     |
| 1.9517    | 3        | 46.49  |          |     |
| 1.9341    | 54       | 46.94  | 46.96    | 024 |
| 1.8882    | 2        | 48.15  |          |     |
| 1.8801    | 5        | 48.37  |          |     |
| 1.7875    | 1        | 51.05  |          |     |
| 1.7752    | 2        | 51.43  |          |     |
| 1.6940    | 1        | 54.09  |          |     |

*Calculated on the basis of a rhombohedral unit cell, R3, a = 7.7427(9) and c = 9.465(1) Å.
Fig. 7. X-ray precession photograph of the fcc $\alpha_1^*$ phase (Mo radiation).

Table 8. X-ray powder diffraction data for the $\alpha_1^*$ phase (CaO:1/2Bi$_2$O$_3$ mol ratio 3:8, 760 °C quench, not ground)

| $d$ obs (Å) | Rel I (%) | $2\theta$ obs | $2\theta$ calc$^*$ | $hkl^*$ | $2\theta$ calc$^b$ | $hkl^b$ |
|------------|-----------|----------------|---------------------|--------|-----------------|--------|
| 8.812      | <2        | 10.03          | 10.05               | 300    | 10.05           | 101    |
| 4.631      | 1         | 19.15          | 19.16               | 051    | 19.16           | 301    |
|            | <1        | 21.41          | 23                  | 23     | 23              |        |
| 3.5618     | 15        | 24.98          | 24.99               | 050    | 24.99           | 103    |
| 3.5120     | 11        | 25.34          | 25.35               | 071    | 25.35           | 111    |
| 3.2156     | 27        | 27.72          | 27.72               | 003    | 27.72           | 402    |
| 3.1208     | 100       | 28.58          | 28.58               | 081    | 28.58           | 402    |
| 2.931      | 2         | 29.38          | 23                  | 23     | 23              |        |
| 3.0225     | 7         | 29.53          | 29.55               | 030    | 29.55           | 303    |
|            | 30.80°    |                |                     |        |                 |        |
|            | <1        | 31.09°         |                     |        |                 |        |
|            | 1         | 32.27°         |                     |        |                 |        |
| 2.7226     | 55        | 32.87          | 32.87               | 082    | 32.87           | 004    |
|            | <1        | 34.39°         |                     |        |                 |        |
|            | <1        | 34.57°         |                     |        |                 |        |
| 2.5817     | <1        | 34.72          | 34.73               | 031    | 34.73           | 113    |
| 2.3417     | 4         | 34.81          | 34.81               | 032    | 34.81           | 511    |
| 2.3265     | 3         | 38.67          | 38.65               | 01,1,1 | 38.66           | 503    |
| 2.3231     | 3         | 38.73          | 38.73               | 050    | 38.74           | 313    |
| 2.1934     | 2         | 41.12          | 41.12               | 054    | 41.12           | 701    |
| 2.1707     | <1        | 41.57          | 41.56               | 244    |                 |        |
| 2.1485     | 1         | 42.02          | 42.00               | 244    | 42.04           | 105    |
| 2.0322     | 8         | 44.55          | 44.57               | 074    | 44.56           | 513    |
| 1.9866     | 4         | 45.63          | 45.64               | 13,0,1 | 45.65           | 305    |
| 1.9466     | 28        | 46.62          | 46.62               | 084    | 46.62           | 800    |
| 1.9039     | 34        | 47.73          | 47.73               | 880    | 47.73           | 020    |
Table 8. X-ray powder diffraction data for the α" phase (CaO:1/2Bi₂O₃ mol ratio 3:8, 760 °C quench, not ground)—Continued

| d (Å) | Rel I (%) | 2θ obs (°) | 2θ calc* (°) | hkl* | 2θ calc* (°) | hkl* |
|-------|-----------|------------|---------------|------|---------------|------|
| 8.812 | <2        | 10.03      | 10.05         | 300  | 10.05         | 101  |
| 4.631 | 1         | 19.15      | 19.16         | 051  | 19.16         | 301  |
| 1.9866| <1        | 21.41      | 2.3           |      | 2.3           |      |
| 1.9466| 4         | 45.63      | 45.64         | 13.0,1| 45.65         | 305  |
| 1.9039| 28        | 46.62      | 46.62         | 084  | 46.62         | 800  |
| 1.8828| 34        | 47.73      | 47.73         | 800  | 47.73         | 020  |
| 1.8382| 9         | 48.30      | 48.29         | 853  | 48.30         | 115  |
| 1.8125| 3         | 50.89      | 50.90         | 384  | 50.90         | 315  |
| 1.7929| 1         | 51.87      | 51.88         | 15.3,1| 51.89         | 315  |
| 1.7613| <1        | 53.29      | 53.29         | 075  | 53.29         | 713  |
| 1.7176| 4         | 53.86      | 53.86         | 0,11,4| 53.87         | 901  |
| 1.7088| 1         | 54.63      | 54.62         | 3,13,2| 54.62         | 123  |
| 1.6652| 12        | 55.11      | 55.10         | 805  | 55.10         | 406  |
| 1.6384| 34        | 56.09      | 56.09         | 883  | 56.09         | 422  |
| 1.6253| 20        | 56.58      | 56.58         | 16,0,1| 56.58         | 406  |
| 1.6102| 4         | 57.16      | 57.14         | 15.5 | 57.14         | 323  |
| 1.6079| 4         | 57.25      | 57.25         | 006  | 57.25         | 804  |
| 1.5821| 4         | 58.27      | 58.29         | 306  | 58.28         | 705  |
| 1.5650| 4         | 59.97      | 59.94         | 835  | 59.95         | 911  |
| 1.5602| 13        | 59.17      | 59.17         | 0,16,2| 59.17         | 024  |
| 1.5526| 4         | 59.49      | 59.48         | 13.0,4| 59.48         | 107  |
| 1.5490| 2         | 59.64      | 59.63         | 295  | 59.63         | 307  |
| 1.5033| 1         | 61.65      | 61.64         | 11.0,5| 61.64         | 307  |
| <1    |           | 62.58*     |               |      |               |      |
| 1.4738| <1        | 63.02      | 63.03         | 16,3,1| 63.03         | 523  |
| 1.4382| 1         | 64.77      | 64.78         | 13,3,4| 64.78         | 117  |
| 1.4303| 1         | 65.17      | 65.18         | 16,1,3| 65.18         | 913  |
| 1.4218| 1         | 65.61      | 65.63         | 8,13,1| 65.63         | 715  |
| 1.3773| 3         | 68.01      | 68.01         | 13,8,2| 68.01         | 317  |
| 1.3743| 3         | 68.18      | 68.18         | 19.0,1| 68.18         | 325  |
| 1.3614| 6         | 68.92      | 68.93         | 16,0,4| 68.93         | 008  |
| 1.3338| 1         | 70.55      | 70.56         | 18,0,3| 70.57         | 11,0,3| 820  |
| 1.3221| 4         | 71.27      | 71.27         | 856  | 71.27         | 57  |
| 1.3127| 2         | 71.86      | 71.86         | 3,13,5| 71.86         | 527  |
| 1.2942| 2         | 73.05      | 73.04         | 707  | 73.03         | 707  |
| 1.2717| 2         | 74.56      | 74.55         | 11,1,3| 74.56         | 12,0,2| 816  |
| 1.2687| 2         | 74.77      | 74.79         | 16,3,4| 74.80         | 921  |
| 1.2536| 4         | 75.83      | 75.83         | 0,16,5| 75.84         | 12,0,2|
| 1.2360| 4         | 77.10      | 77.09         | 8,16,1| 77.09         | 426  |
| 1.2285| 4         | 77.66      | 77.66         | 886  | 77.66         | 824  |
| 1.2256| 4         | 77.88      | 77.89         | 387  | 77.88         | 717  |
| 1.2168| 3         | 78.55      | 78.56         | 11,5,6| 78.56         | 923  |
| 1.2065| 8         | 79.35      | 79.33         | 16,8,2| 79.34         | 824  |
| 1.2011| 2         | 79.78      | 79.78         | 10,15,1| 79.79         | 10,0,6| 208  |
Table 8. X-ray powder diffraction data for the α<sup>+</sup> phase (CaO:1/2Bi₂O₃ mol ratio 3:8, 760 °C quench, not ground)—Continued

| d<sub>obs</sub> (Å) | Rel I (%) | 2θ<sub>obs</sub> | 2θ<sub>calc</sub> | hkl<sup>*</sup> | 2θ<sub>calc</sub>| hkl<sup>b</sup> |
|----------------------|-----------|----------------|----------------|------------|----------------|------------|
| 1.1798               | 1         | 81.52          | 81.51          | 3,16,5     | 81.51          | 327        |
| 1.1703               | 1         | 82.33          | 82.34          | 21,0,3     | 82.34          | 309        |
| 1.1526               | 2         | 83.87          | 83.88          | 13,8,5     | 83.87          | 119        |
| 1.1489               | 2         | 84.21          | 84.23          | 078        | 84.23          | 111,5      |
| 1.1402               | 1         | 85.00          | 84.99          | 18,6,3     | 85.00          | 234        |
|                      |           |                | 85.00          | 13,0,7     | 85.00          | 509        |
|                      |           |                |                |            | 85.00          | 630        |
|                      |           |                |                |            | 85.00          | 13,1       |
| 1.1331               | 2         | 85.66          | 85.67          | 16,1,6     | 85.66          | 319        |
| 1.1272               | 1         | 86.22          | 86.23          | 019,5      | 86.24          | 11,2       |
| 1.1226               | 1         | 86.66          | 86.69          | 11,13,4    | 86.69          | 533        |
| 1.1074               | 5         | 88.15          | 88.16          | 8,16,4     | 88.16          | 028        |
|                      |           |                |                |            | 88.16          | 434        |
|                      |           |                |                |            | 88.16          | 12,1,4     |
| 1.0990               | 4         | 88.96          | 88.97          | 24,0,0     | 88.98          | 808        |
| 1.0922               | 2         | 89.70          | 89.69          | 16,10,3    | 89.69          | 228        |
|                      |           |                | 89.70          | 13,3,7     | 89.69          | 519        |
|                      |           |                |                |            | 89.69          | 10,2,4     |
|                      |           |                |                |            | 89.70          | 11,2,3     |
| 1.0786               | 1         | 91.35          | 91.31          | 5,19,4     | 91.38          | 335        |
| 1.0641               | 1         | 92.75          | 92.76          | 309        | 92.75          | 11,0,7     |
|                      |           |                |                |            | 92.75          | 13,0,5     |
| 1.0575               | 1         | 93.51          | 93.51          | 16,0,7     | 93.50          | 4,0,10     |
|                      |           |                |                |            | 93.51          | 12,2,2     |
| 1.0468               | 3         | 94.76          | 94.74          | 16,8,5     | 94.74          | 382        |
|                      |           |                |                |            | 94.74          | 12,2,2     |
| 1.0402               | 4         | 95.55          | 95.56          | 24,0,3     | 95.56          | 40,10      |
|                      |           |                | 95.57          | 7,12,7     | 95.56          | 12,0,6     |
| 1.0343               | 1         | 96.28          | 96.27          | 2,12,8     |              |            |
| 1.0212               | <1        | 97.93          | 97.93          | 4,15,7     |              |            |
| 1.0203               | <1        | 98.05          | 98.06          | 639        |              |            |
| 1.0115               | 1         | 99.20          | 99.22          | 21,8,1     | 99.22          | 719        |
| 1.0002               | 1         | 100.73         | 100.72         | 3,13,8     | 100.72         | 15,1,1     |
| 0.9968               | 1         | 101.21         | 101.19         | 16,13,3    | 101.19         | 329        |
|                      |           |                |                |            | 101.20         | 11,2,5     |
| 0.9946               | 1         | 101.52         | 101.50         | 8,13,7     | 101.50         | 15,1,1     |
| 0.9898               | 1         | 102.20         | 102.20         | 26,1,1     | 102.18         | 15,0,3     |
| 0.9781               | 1         | 103.92         | 103.90         | 19,0,7     | 103.90         | 529        |
| 0.9733               | 2         | 104.64         | 104.64         | 859        | 104.64         | 15,1,3     |
| 0.9622               | 1         | 106.37         | 106.37         | 0,2,10     | 106.36         | 14,0,6     |
| 0.9520               | 2         | 108.03         | 108.02         | 16,16,0    | 108.03         | 828        |
|                      |           |                |                |            | 108.04         | 040        |
| 0.9432               | 1         | 109.51         | 109.52         | 5,25,1     | 109.54         | 16,1,0     |
| 0.9371               | 1         | 110.57         | 110.58         | 21,8,4     | 110.58         | 3,1,11     |
| 0.9332               | 1         | 111.26         | 111.27         | 26,2,3     | 111.29         | 935        |
| 0.9289               | 1         | 112.05         | 112.05         | 11,5,9     | 112.05         | 11,2,7     |
| 0.9258               | 1         | 112.61         | 112.60         | 0,25,5     | 112.62         | 15,0,5     |
| 0.9242               | 1         | 112.91         | 112.91         | 27,10      | 112.92         | 2,3        |
|                      |           |                | 112.92         | 22,4,5     |              |            |
| 0.9127               | 2         | 115.13         | 115.11         | 3,20,7     | 115.11         | 12,2,6     |
| 0.9104               | 5         | 115.58         | 115.56         | 0,19,8     | 115.57         | 15,2,1     |
|                      |           |                | 115.57         | 17,0,1     |              |            |
| 0.9074               | 3         | 116.19         | 116.17         | 24,0,6     | 116.18         | 12,3,0     |
|                      |           |                | 116.21         | 9,13,8     | 116.18         | 16,0,4     |
Table 8. X-ray powder diffraction data for the $\alpha_1$ phase (CaO:1/2Bi$_2$O$_3$ mol ratio 3:8, 760 °C quench, not ground)—Continued

| $d$ (Å) | Rel I (%) | $2\theta$ obs (°) | $2\theta$ calc$^a$ (°) | $hkl^a$ | $2\theta$ calc$^b$ (°) | $hkl^b$ |
|---------|-----------|-------------------|-----------------------|--------|-----------------------|--------|
| 0.8984  | 2         | 118.05            | 118.06                | 20.4,7 | 118.07                | 12.3,2 |
| 0.8939  | 1         | 119.02            | 119.00                | 29.0,2 | 119.01                | 7.0,11 |
| 0.8780  | 1         | 122.64            | 122.66                | 29.2,0 | 122.67                | 7.0,11 |
| 0.8755  | 1         | 123.25            | 123.23                | 5,24,5 | 123.23                | 12.11  |
| 0.8738  | 1         | 123.66            | 123.66                | 13,11,8| 123.66                | 11.3,5 |
| 0.8732  | 1         | 123.80            | 123.81                | 21,13,2| 123.79                | 139    |
|         |           |                   |                       | 123.80 | 741                   |        |
| 0.8710  | 1         | 124.35            | 124.37                | 5,18,8 | 124.35                |        |
| 0.8665  | 1         | 125.49            | 125.49                | 27.6,0 | 125.49                |        |

$^a$ Calculated on the basis of a rhombohedral unit cell, $R_3$, $a = 30.4640(5)$ and $c = 9.6477(2)$ Å.
$^b$ Calculated on the basis of a monoclinic unit cell, $B2/m$, $a = 15.5819(3)$, $b = 3.8077(1)$, $c = 10.8955(3)$ Å, and $\beta = 91.829(2)^\circ$.
$^c$ Apparently due to an unidentified superstructure.
$^d$ Not indexable by the monoclinic cell.

Fig. 8. X-ray powder diffraction pattern for the bcc phase.
Table 9. X-ray powder diffraction data for the body centered cubic phase (CaO:1/2Bi2O3 mol ratio 9:10, 1000 °C quench)

| d (Å)     | Rel (%) | 2θ obs | 2θ calc | hkl |
|-----------|---------|--------|---------|-----|
| 3.0006    | 100     | 29.75  | 29.73   | 110 |
| 2.1239    | 34      | 42.53  | 42.52   | 200 |
| 1.7330    | 51      | 52.78  | 52.77   | 211 |
| 1.5011    | 14      | 61.75  | 61.75   | 220 |
| 1.4340    | 12      | 70.00  | 70.02   | 310 |
| 1.2255    | 3       | 77.89  | 77.88   | 222 |
| 1.1346    | 10      | 85.52  | 85.51   | 321 |
| 1.0617    | 1       | 93.03  | 93.06   | 400 |
| 1.0008    | 3       | 100.65 | 100.66  | 330 |
| 0.9494    | 2       | 108.45 | 108.46  | 420 |
| 0.9052    | 1       | 116.64 | 116.63  | 332 |
| 0.8667    | 1       | 125.43 | 125.45  | 422 |
| 0.8926    | 2       | 135.39 | 135.37  | 510 |

* Calculated on the basis of a body centered cubic cell with a = 4.2458(1) Å.

Table 10. X-ray powder diffraction data for the distorted body centered cubic phase with line splitting and superstructure (CaO:1/2Bi2O3 mol ratio 2:3, 860 °C)—Continued

| d (Å)     | Rel (%) | 2θ obs | 2θ calc | hkl |
|-----------|---------|--------|---------|-----|
| 2.1233    | 23      | 42.54  | 42.52   | 200 |
| 2.0531    | 2       | 44.07  |         |     |
| 2.0187    | 1       | 44.86  |         |     |
| 1.9815    | 2       | 45.75  |         |     |
| 1.9746    | 2       | 45.92  |         |     |
| 1.9270    | 1       | 47.12  |         |     |
| 1.8977    | 1       | 48.11  |         |     |
| 1.8440    | 2       | 49.38  |         |     |
| 1.8253    | 1       | 49.92  |         |     |
| 1.8111    | 1       | 50.34  |         |     |
| 1.7908    | 1       | 50.95  |         |     |
| 1.7720    | 4       | 51.53  |         |     |
| 1.7524    | 7       | 52.15  |         |     |
| 1.7335    | 49      | 52.76  | 52.77   | 211 |
| 1.6990    | 3       | 53.92  |         |     |
| 1.6871    | 2       | 54.33  |         |     |
| 1.6673    | 3       | 55.03  |         |     |
| 1.6626    | 3       | 55.20  |         |     |
| 1.6502    | 1       | 55.65  |         |     |
| 1.6252    | 1       | 56.28  |         |     |
| 1.6078    | 1       | 57.25  |         |     |
| 1.5278    | 1       | 60.55  |         |     |
| 1.5111    | 3       | 61.29  |         |     |
| 1.5025    | 9       | 61.68  | 61.75   | 220 |
| 1.4951    | 3       | 62.02  |         |     |
| 1.3651    | 2       | 68.70  |         |     |
| 1.3532    | 1       | 69.39  |         |     |
| 1.3481    | 10      | 69.69  | 70.02   | 310 |
| 1.3356    | 2       | 70.44  |         |     |
| 1.3235    | 1       | 71.18  |         |     |

* Calculated on the basis of a body centered cubic cell with a = 4.2458 (1) Å.

3.3.4. “Ca₅Bi₄O₉₆” (Ca₅Bi₄:5:14) A compound with the composition Ca₅Bi₄O₉₆ was previously reported [21,22] as stable up to at least 650 °C. We have no contrary evidence and indeed an apparently single phase x-ray diffraction pattern can be obtained for the 5:14 ratio (26.32% CaO; Fig. 11, Table 11) by annealing a quenched liquid of this composition overnight at 650 °C. The exact composition should be regarded as provisional, however, pending a crystal structure determination. The x-ray pattern in Table 11 corresponds well with that published in [22] except for a small but consistent shift in observed d amounting to ~ 1/4° 2θ for CuKα radiation. Apparently the earlier work had an unrecognized deviation in calibration of the diffraction data. The diffraction pattern has not yet been indexed even with the aid of some single crystal data (Fig. 12). The complexity of the pattern and consideration of the single crystal data suggests triclinic symmetry.
Fig. 9. X-ray powder diffraction pattern for the distorted bcc phase with line splitting and superstructure (CaO:1/2Bi₂O₃ 2:3 860 °C).

Fig. 10. X-ray precession photograph of the bcc distorted phase (Mo radiation).
At 732±7 °C the 5:14 phase decomposes to a mixture of the rhombohedral phase plus CaBi$_2$O$_4$ (1:2). This equilibrium was demonstrated by both the breakdown of single phase material after heating above this range, and by nucleation of 5:14 in a two phase mixture of rhombohedral + 1:2 below it. This is considerably lower than the value of 772 °C which may be interpreted from [21] (Fig. 3).

3.3.5. CaBi$_2$O$_4$ (CB$_{-}$1:2) The compound CaBi$_2$O$_4$ was synthesized at 650 °C [22] and reported as stable up to about 800 °C [21] where it was shown (Fig. 3) to decompose to fcc plus 2:3. Apparently inconsistent data in our own work required us to determine the decomposition temperature by simultaneous quenching of single phase 1:2, originally prepared by annealing at 650 °C, and reheating a sample of quenched liquid from which fcc plus 2:3 was synthesized. These experiments suggest that the 1:2 phase is not stable above 778±5 °C. This may be compared with the value of 799 °C which can be interpreted from [21] (Fig. 3).

The 1:2 phase often occurs along with other phases in samples that are air quenched from temperatures greater than about 800 °C. The x-ray powder diffraction pattern of the 1:2 phase Fig. 13, Table 12, corresponds well with that reported in [22] except for the observed shift in 2θ mentioned in section 3.3.4. Several attempts were made to synthesize single crystals of the 1:2 phase (see Table 1b), but the only procedure that succeeded was to anneal single phase 1:2 + a 50/50 NaCl/KCl flux (50/50 flux/charge) at 775 °C and then cool at 1 °C/h to 645 °C. The single crystal x-ray diffraction precession data are shown in Fig. 14. The x-ray powder diffraction pattern was indexed on the C-centered monoclinic cell C2/c obtained from the single-crystal precession data. The lattice parameters refined by least-squares analysis with the aid of calculated structure factors and the calculated powder pattern based on single crystal structure determination are $a = 16.6295(8)$, $b = 11.5966(5)$, $c = 14.0055(6)$ Å, and $\beta = 134.036(3)^\circ$. 
Fig. 12. X-ray precession photographs of Ca$_3$Bi$_4$O$_{28}$ (Mo radiation) (a) ($h0l$) unfiltered $\mu = 10^\circ$, (b) ($h0l$) Zr filter (c) alternate plane, unfiltered.
Fig. 13. X-ray powder diffraction pattern of the CaBi$_2$O$_4$ compound.

Fig. 14. X-ray precession photographs of CaBi$_2$O$_4$ (Mo radiation) (a) (h0l), (b) (h1l).
### Table 11. X-ray powder diffraction data for the compound Ca₅Bi₄O₄₁

| d(obs) (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl |
|------------|----------|--------|----------|-----|
| 2.9053     |          |        |          |     |
| 3.0539     |          |        |          |     |
| 3.0744     |          |        |          |     |
| 3.2877     |          |        |          |     |
| 2.8212     |          |        |          |     |
| 2.8422     |          |        |          |     |
| 2.9285     |          |        |          |     |
| 2.9323     |          |        |          |     |
| 3.4308     |          |        |          |     |
| 3.4903     |          |        |          |     |
| 3.5534     |          |        |          |     |
| 3.6525     |          |        |          |     |
| 3.5756     |          |        |          |     |
| 3.6383     |          |        |          |     |
| 3.6752     |          |        |          |     |
| 3.6838     |          |        |          |     |
| 4.0756     |          |        |          |     |
| 3.9277     |          |        |          |     |
| 3.8620     |          |        |          |     |
| 3.7652     |          |        |          |     |
| 3.6336     |          |        |          |     |
| 3.3178     |          |        |          |     |
| 3.2997     |          |        |          |     |
| 3.2877     |          |        |          |     |
| 3.2293     |          |        |          |     |
| 3.1347     |          |        |          |     |
| 3.1272     |          |        |          |     |
| 3.1112     |          |        |          |     |
| 3.0744     |          |        |          |     |
| 3.0539     |          |        |          |     |
| 3.0195     |          |        |          |     |
| 2.9743     |          |        |          |     |
| 2.9361     |          |        |          |     |
| 2.9323     |          |        |          |     |
| 2.9285     |          |        |          |     |
| 2.9053     |          |        |          |     |
| 2.8662     |          |        |          |     |
| 2.8422     |          |        |          |     |
| 2.8212     |          |        |          |     |
| 2.7997     |          |        |          |     |
| 2.7777     |          |        |          |     |
| 2.7718     |          |        |          |     |
| 2.7250     |          |        |          |     |

*Calculated on the basis of a triclinic cell, α = 9.934(1),
 b = 15.034(2), c = 15.008(2) Å, α = 82.65(1), β = 85.27(1), and
 γ = 77.17(1)*.

### Table 12. X-ray powder diffraction data for the compound CaO:1/2Bi₂O₃ (36:67)

| d(obs) (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl | |F| calc |
|------------|----------|--------|----------|-----|---|-------|
| 8.847      | 4        | 9.99   | 9.98     | 111 | 35 |
| 8.324      | 2        | 10.62  | 10.62    | 110 | 27 |
| 5.977      | 7        | 14.81  | 14.81    | 200 | 79 |
| 5.805      | 5        | 15.26  | 15.27    | 202 | 50 |
| 5.018      | 5        | 17.66  | 17.64    | 102 | 46 |
| 4.957      | 7        | 17.88  | 17.85    | 132 | 14 |
| 4.7413     | 6        | 18.70  | 18.70    | 222 | 56 |
| 4.4316     | 10       | 20.02  | 20.03    | 222 | 57 |
| 3.8179     | 20       | 23.23  | 23.27    | 133 | 78 |
| 3.8018     | 31       | 23.38  | 23.38    | 222 | 47 |
| 3.7700     | 11       | 23.58  | 23.59    | 310 | 79 |
| 3.6808     | 10       | 24.16  | 24.18    | 130 | 30 |
| 3.6029     | 2        | 24.69  | 24.68    | 112 | 31 |
| 3.4308     | 10       | 25.95  | 25.95    | 404 | 79 |
| 3.3546     | 9        | 26.55  | 26.53    | 422 | 58 |
| 3.3385     | 14       | 26.68  | 26.67    | 314 | 81 |
| 3.3312     | 15       | 26.74  | 26.77    | 132 | 78 |
| 3.3190     | 7        | 26.84  | 26.83    | 221 | 14 |
| 3.2723     | 42       | 27.23  | 27.27    | 204 | 24 |
| 3.2574     | 8        | 27.53  | 27.52    | 131 | 77 |
| 3.1941     | 22       | 27.91  | 27.89    | 513 | 117 |
| 3.1631     | 100      | 28.19  | 28.21    | 332 | 276 |
The diffraction pattern of this phase is shown in Fig. 15 and is in good agreement with [21]. The x-ray powder diffraction temperature (Table 1 and Fig. 4) of 855 ±5 °C (40 mol % CaO) rather than 7:10, but the decomposition temperature (Table 1 and Fig. 4) of 855 ±5 °C is in good agreement with [21]. The x-ray powder diffraction pattern of this phase is shown in Fig. 15 and recorded in Table 13. These results agree well with those in [22] (except for the shift in 2θ previously mentioned). Single crystals of Ca₃Bi₆O₁₃ were grown both by utilizing a 50/50 NaCl/KCl flux and by reannealing a quenched liquid. The compound is orthorhombic a = 17.8865(6), b = 5.9419(2), c = 7.2306(2) Å, with a C-centered space group, as determined from single crystal x-ray precession photographs (Fig. 16) and x-ray diffraction data refined by least squares. A complete crystal structure determination [23] including single crystal x-ray analysis, neutron diffraction Rietveld analyses, and measurements of second harmonic generation, proved that the true space group is the non-centrosymmetric C2mm. The crystal structure was reported in [23] from data collected on crystals prepared in this study.

A complete discussion of the indexing of this phase with comparison to the calculated powder pattern is given in [27]. The crystal structure determination [23] reveals that Bi^{3+} occurs in two coordination types with 2/3 of the Bi^{3+} ions five-coordinate and 1/3 of the Bi^{3+} ions only three-coordinate, by oxygen. Determinations of the crystal structures of more of these phases will perhaps result in a better understanding of the role played by Bi^{3+} coordination in 3- and 4-component superconductors.

### 3.3.7. Ca₃Bi₆O₁₃ (C₂B₁₁-1:1) The compound “Ca₃Bi₆O₁₃”, (53.846 mol % CaO) was reported in [22] and [21], and the phase diagram in [21] (re-drawn as Fig. 3) can be interpreted as indicating that it decomposes at about 929 °C. Experiments performed in the present work (Table 1) combined with a structure determination performed on crystals prepared in this study [24] indicate that the composition of this phase is really 1:1 (50 mol % CaO) rather than 7:6. The x-ray powder diffraction pattern of the phase shown in Fig. 17 and Table 14 agrees well with that reported in [22] (except for the shift in 2θ noted above). Single crystal x-ray diffraction precession photographs (Fig. 18) indicate that the 1:1 compound is triclinic, and powder x-ray diffraction data [27] yield least squared values of a = 10.1222(7), b = 10.146(6), c = 10.4833(7) Å, and β = 117.3795(5)°. The indexing of this pattern out to high angles in 2θ could only be accomplished with the aid of calculated structure factors and the calculated powder pattern based on the single crystal structure determination reported in [24]. The structure determination reveals a unique Bi^{3+} coordination of U-shaped Bi₂O₃ units with one five-fold coordinated Bi^{3+} bridging two four-fold “saw-horse” shaped polyhedra [24].

### Table 12. X-ray powder diffraction data for the compound Ca₃Bi₆O₁₃ (CaO:1/2Bi₂O₃ 33:67) - Continued

| d obs (Å) | Rel I (%) | 2θ obs | 2θ calc | hkl | | | | | | |
|-----------|-----------|--------|---------|-----|---|---|---|---|---|
| 1.4386    | 4         | 62.56  | 62.58   | 404 | 153 | | | | |
| 1.4793    | 8         | 62.76  | 62.76   | 629 | 89  | | | | |
| 1.4753    | 8         | 62.95  | 62.97   | 622 | 93  | | | | |
| 1.4715    | 5         | 63.13  | 63.12   | 519 | 65  | | | | |
| 1.4692    | 4         | 63.24  | 63.24   | 572 | 66  | | | | |
| 1.4649    | 4         | 63.45  | 63.46   | 574 | 78  | | | | |
| 1.4606    | 4         | 63.66  | 63.65   | 247 | 51  | | | | |
| 1.4520    | 6         | 64.08  | 64.06   | 460 | 110 | | | | |
| 1.4414    | 3         | 64.61  | 64.60   | 739 | 42  | | | | |
| 1.4474    | 5         | 64.81  | 64.83   | 841 | 78  | | | | |
| 1.4366    | 6         | 65.95  | 64.94   | 881 | 116 | | | | |
| 1.4299    | 8         | 65.19  | 65.18   | 102 | 103 | | | | |
| 1.4295    | 8         | 65.21  | 65.24   | 357 | 101 | | | | |
| 1.4216    | 3         | 65.62  | 65.61   | 954 | 80  | | | | |
| 1.4170    | 6         | 65.86  | 65.88   | 136 | 130 | | | | |
| 1.4090    | 1         | 66.28  | 66.28   | 426 | 28  | | | | |
| 1.4027    | 1         | 66.62  | 66.61   | 10,2 | 37  | | | | |
| 1.4080    | 2         | 66.72  | 66.71   | 11,1,9 | 67  | | | | |
| 1.3984    | 2         | 66.85  | 66.86   | 462 | 58  | | | | |
| 1.3977    | 3         | 66.89  | 66.91   | 267 | 57  | | | | |
| 1.3942    | 3         | 67.08  | 67.07   | 525 | 56  | | | | |
| 1.3923    | 3         | 67.18  | 67.21   | 866 | 91  | | | | |
| 1.3820    | 1         | 67.75  | 67.72   | 283 | 49  | | | | |
| 1.3802    | 1         | 67.85  | 67.85   | 11,3,5 | 42  | | | | |
| 1.3750    | 5         | 68.14  | 68.13   | 750 | 84  | | | | |
| 1.3736    | 6         | 68.22  | 68.23   | 558 | 73  | | | | |
| 1.3672    | 2         | 68.67  | 68.67   | 372 | 63  | | | | |
| 1.3631    | 2         | 68.82  | 68.80   | 10,2,3 | 63  | | | | |
| 1.3614    | 3         | 68.92  | 68.92   | 467 | 43  | | | | |
| 1.3610    | 3         | 68.94  | 68.95   | 391 | 37  | | | | |
| 1.3540    | 5         | 69.35  | 69.34   | 354 | 82  | | | | |
| 1.3465    | 4         | 69.79  | 69.79   | 481 | 69  | | | | |
| 1.3457    | 5         | 69.84  | 69.83   | 867 | 68  | | | | |

*Calculated on the basis of a monoclinic unit cell, space group C2/c, a = 16.6295(8), b = 11.5986(3), c = 14.0055(6) Å, and β = 116.036(3)°.
Fig. 15. X-ray powder diffraction pattern of the Ca₄Bi₄O₁₃ compound.

Fig. 16. X-ray precession photographs of Ca₄Bi₄O₁₃ (Mo radiation), (a) \( (hkl) \), (b) \( (0kl) \).
### Table 13. X-ray powder diffraction data for the compound Ca$_2$Bi$_3$O$_7$

| d obs (Å) | Rel I (%) | 2θ obs | 2θ calc | hkl | | Fcalc |
|-----------|-----------|--------|---------|-----|-----|
| 8.708     | 13        | 10.15  | 10.17   | 200 | 250 |
| 5.629     | 4         | 15.73  | 15.75   | 110 | 136 |
| 4.434     | 1         | 20.01  | 19.99   | 111 | 45  |
| 4.346     | 5         | 20.42  | 20.42   | 400 | 217 |
| 4.145     | 47        | 21.42  | 21.40   | 310 | 571 |
| 3.614     | 52        | 24.61  | 24.60   | 002 | 138 |
| 3.338     | 52        | 26.68  | 26.69   | 202 | 118 |
| 3.0386    | 100       | 29.37  | 29.35   | 112 | 748 |
| 2.9987    | 68        | 29.77  | 29.75   | 510 | 893 |
| 2.9694    | 31        | 30.07  | 30.05   | 020 | 829 |
| 2.8117    | 8         | 31.80  | 31.81   | 220 | 306 |
| 2.7794    | 44        | 32.18  | 32.18   | 402 | 766 |
| 2.7230    | 2         | 32.84  | 32.84   | 312 | 93  |
| 2.6192    | 2         | 36.62  | 36.61   | 430 | 187 |
| 2.4107    | 1         | 37.27  | 37.28   | 003 | 103 |
| 2.3225    | 1         | 38.74  | 38.74   | 203 | 116 |
| 2.3088    | 3         | 38.98  | 38.98   | 512 | 158 |
| 2.2918    | 3         | 39.28  | 39.90   | 710 | 135 |
| 2.2609    | 12        | 39.84  | 39.85   | 602 | 501 |
| 2.2187    | 3         | 40.63  | 40.62   | 222 | 165 |
| 2.1717    | 13        | 41.55  | 41.54   | 800 | 667 |
| 2.0847    | 1         | 43.37  | 43.39   | 313 | 85  |
| 2.0815    | 1         | 43.44  | 43.46   | 801 | 35  |
| 2.0733    | 1         | 43.62  | 43.61   | 620 | 64  |
| 2.0291    | 53        | 44.62  | 44.61   | 422 | 846 |
| 1.9686    | 1         | 46.07  | 46.09   | 130 | 159 |
| 1.9357    | 4         | 46.90  | 46.92   | 712 | 227 |
| 1.8744    | 7         | 48.53  | 48.54   | 330 | 437 |
| 1.8625    | 1         | 48.86  | 48.87   | 802 | 182 |
| 1.8368    | 2         | 49.59  | 49.60   | 910 | 189 |
| 1.8288    | 1         | 49.82  | 49.79   | 223 | 81  |
| 1.8078    | 14        | 50.44  | 50.44   | 004 | 917 |
| 1.7991    | 12        | 50.70  | 50.71   | 622 | 466 |
| 1.7699    | 2         | 51.60  | 51.60   | 204 | 195 |
| 1.7357    | 11        | 52.11  | 52.11   | 820 | 602 |
| 1.7376    | 9         | 52.62  | 52.62   | 10,0 | 679 |
| 1.7285    | 23        | 52.93  | 52.93   | 132 | 607 |
| 1.7206    | 18        | 53.19  | 53.18   | 114 | 141 |
| 1.6688    | 1         | 54.98  | 54.97   | 404 | 197 |
| 1.6640    | 2         | 55.15  | 55.16   | 332 | 149 |
| 1.6574    | 10        | 55.39  | 55.40   | 314 | 423 |
| 1.6278    | 31        | 56.13  | 56.13   | 912 | 804 |
| 1.5782    | 1         | 58.43  | 58.45   | 822 | 170 |
| 1.5670    | 1         | 58.89  | 58.92   | 10,0 | 93 |
| 1.5533    | 2         | 59.46  | 59.44   | 532 | 183 |
| 1.5486    | 21        | 59.66  | 59.67   | 514 | 696 |
| 1.5446    | 10        | 59.83  | 59.84   | 634 | 675 |
| 1.5265    | 1         | 60.61  | 60.59   | 11,10 | 141 |
| 1.5206    | 3         | 60.87  | 60.88   | 224 | 232 |
| 1.5004    | 7         | 61.78  | 61.79   | 10,0 | 599 |
| 1.4857    | 5         | 62.46  | 62.47   | 404 | 682 |
| 1.4645    | 2         | 63.47  | 63.48   | 240 | 332 |
| 1.4532    | 1         | 63.92  | 63.93   | 424 | 185 |
| 1.4350    | 1         | 64.37  | 64.37   | 005 | 112 |
| 1.4262    | 1         | 65.38  | 65.37   | 205 | 120 |
| 1.4233    | 3         | 65.53  | 65.53   | 732 | 321 |
| 1.4064    | 2         | 66.42  | 66.41   | 11,12 | 221 |
| 1.4060    | 2         | 66.44  | 66.46   | 440 | 235 |
| 1.3896    | 6         | 67.33  | 67.33   | 804 | 528 |
| 1.3831    | 1         | 67.69  | 67.61   | 930 | 197 |
| 1.3738    | 1         | 68.21  | 68.20   | 042 | 210 |

* Calculated on the basis of an orthorhombic unit cell, space group C2mm, a = 17.3975(5), b = 5.9419(2), and c = 7.2306(2) Å.
Fig. 17. X-ray powder diffraction pattern of the Ca$_2$Bi$_2$O$_5$ compound.

Fig. 18. X-ray precession photographs of Ca$_2$Bi$_2$O$_5$ (Mo radiation) (a) ($hk'l$), (b) ($h0l$).
## Table 14. X-ray powder diffraction data for the compound Ca₃Bi₂O₇

| d obs (Å) | $\theta$ | $\theta$ obs | 2 $\theta$ | $\theta$ calc | hkl | $|F|$ calc | $|F|$ calc |
|-----------|----------|--------------|------------|--------------|-----|------------|------------|
| 9.461     | 4        | 9.34         | 9.36       | 100          | 59  |            |            |
| 8.717     | 7        | 10.14        | 10.12      | 100          | 56  |            |            |
| 8.001     | 11       | 11.05        | 11.07      | 101          | 109 |            |            |
| 7.303     | 4        | 12.11        | 12.14      | 110          | 66  |            |            |
| 6.916     | 6        | 12.79        | 12.81      | 111          | 70  |            |            |
| 5.069     | 4        | 17.48        | 17.49      | 112          | 40  |            |            |
| 5.013     | 2        | 17.68        | 17.69      | 101          | 71  |            |            |
| 4.965     | 1        | 17.85        | 17.87      | 201          | 31  |            |            |
| 4.721     | 4        | 18.78        | 18.78      | 200          | 98  |            |            |
| 4.648     | 16       | 19.08        | 19.09      | 102          | 191 |            |            |
| 4.421     | 6        | 23.47        | 23.49      | 202          | 91  |            |            |
| 4.352     | 3        | 20.39        | 20.41      | 202          | 79  |            |            |
| 4.237     | 8        | 20.95        | 20.97      | 211          | 141 |            |            |
| 4.182     | 19       | 21.23        | 21.23      | 122          | 206 |            |            |
| 3.9940    | 10       | 22.24        | 22.24      | 202          | 146 |            |            |
| 3.9746    | 7        | 22.35        | 23.33      | 112          | 104 |            |            |
| 3.9209    | 7        | 22.66        | 22.65      | 211          | 130 |            |            |
| 3.8341    | 11       | 23.18        | 23.19      | 210          | 169 |            |            |
| 3.7480    | 1        | 23.72        | 23.69      | 122          | 38  |            |            |
| 3.7065    | 4        | 23.99        | 24.00      | 120          | 103 |            |            |
| 3.5243    | 3        | 25.25        | 25.23      | 221          | 81  |            |            |
| 3.5120    | 3        | 25.34        | 25.33      | 202          | 82  |            |            |
| 3.4957    | 6        | 25.46        | 25.48      | 121          | 127 |            |            |
| 3.4530    | 2        | 25.78        | 25.79      | 222          | 65  |            |            |
| 3.3834    | 2        | 26.32        | 26.31      | 221          | 37  |            |            |
| 3.3696    | 3        | 26.43        | 26.43      | 301          | 98  |            |            |
| 3.3571    | 3        | 26.53        | 26.52      | 123          | 76  |            |            |
| 3.3361    | 14       | 26.70        | 26.69      | 201          | 197 |            |            |
| 3.3226    | 8        | 26.81        | 26.80      | 212          | 88  |            |            |
| 3.3045    | 11       | 26.96        | 26.96      | 032          | 192 |            |            |
| 3.2806    | 6        | 27.16        | 27.13      | 013          | 135 |            |            |
| 3.2501    | 5        | 27.42        | 27.41      | 131          | 133 |            |            |
| 3.2179    | 4        | 27.70        | 27.70      | 221          | 117 |            |            |
| 3.1456    | 8        | 28.35        | 28.33      | 300          | 127 |            |            |
| 3.1059    | 54       | 28.72        | 28.74      | 311          | 471 |            |            |
| 3.0600    | 3        | 29.12        | 29.15      | 223          | 97  |            |            |
| 3.0006    | 100      | 29.75        | 29.73      | 203          | 427 |            |            |
| 2.9938    | 57       | 29.82        | 29.82      | 22           | 469 |            |            |
| 2.9099    | 5        | 30.70        | 30.69      | 003          | 132 |            |            |
| 2.8989    | 9        | 30.82        | 30.82      | 033          | 111 |            |            |
| 2.8897    | 36       | 30.92        | 30.93      | 123          | 83  |            |            |
| 2.8361    | 36       | 31.52        | 31.49      | 312          | 228 |            |            |
| 2.7828    | 7        | 32.14        | 32.13      | 230          | 172 |            |            |
| 2.7519    | 2        | 32.51        | 32.50      | 202          | 81  |            |            |
| 2.7234    | 5        | 32.86        | 32.84      | 321          | 155 |            |            |
| 2.6620    | 3        | 33.64        | 33.65      | 303          | 101 |            |            |
| 2.5510    | 12       | 35.15        | 35.14      | 114          | 259 |            |            |

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Table 14. X-ray powder diffraction data for the compound
Ca$_{4}$Bi$_{6}$O$_{13}$—Continued

| $d$ obs (Å) | Rel I (%) | 2 $\theta$ obs | 2 $\theta$ calc* | $h$ $k$ $l$ | $|F|$ calc |
|-------------|-----------|----------------|-----------------|-----------|-----------|
| 1.7660      | 6         | 51.72          | 51.73           | 352       | 280       |
| 1.7569      | 3         | 52.01          | 52.01           | 333       | 176       |
| 1.7459      | 3         | 52.36          | 52.36           | 521       | 156       |
| 1.7418      | 2         | 52.49          | 52.47           | 443       | 107       |
| 1.7388      | 4         | 52.59          | 52.58           | 555       | 100       |
| 1.7349      | 8         | 52.72          | 52.73           | 142       | 261       |
| 1.7306      | 3         | 52.86          | 52.88           | 405       | 127       |
| 1.7267      | 7         | 52.99          | 53.01           | 444       | 300       |
| 1.7200      | 4         | 53.21          | 53.23           | 254       | 177       |

1.7135 4 53.43 53.45 255 223
1.7017 12 53.83 53.84 421 377
1.6883 9 54.29 54.27 336 250
1.6846 4 54.42 54.40 215 108
1.6738 7 54.80 54.78 163 269
1.6682 16 55.00 54.98 155 305
1.6443 15 55.14 55.13 433 183
1.6396 3 55.31 55.32 223 128
1.6350 5 55.55 55.53 600 260
1.6503 5 55.65 55.63 115 217
1.6370 4 56.14 56.14 116 105
1.6357 5 56.19 56.18 151 231
1.6248 1 56.60 56.58 262 110
1.6201 2 56.78 56.77 164 106
1.6172 2 56.89 56.89 105 161
1.6092 7 57.20 57.21 442 213
1.5997 4 57.57 57.56 452 242
1.5919 2 57.88 57.87 535 154
1.5884 2 58.02 58.00 611 150
1.5846 2 58.17 58.16 261 152
1.5797 2 58.37 58.35 133 266
1.5694 1 58.79 58.81 136 129
1.5672 2 58.88 58.88 165 145
1.5621 1 59.09 59.11 255 133
1.5523 6 59.50 59.51 622 300
1.5453 2 59.80 59.82 124 159

* Calculated on the basis of a triclinic unit cell, space group $P\overline{1}$, $a = 10.1222(7)$ Å, $b = 10.1466(6)$ Å, $c = 10.4833(7)$ Å, $\alpha = 116.912(5)$, $\beta = 107.135(6)$, and $\gamma = 92.939(6)^*$. 

b Calculated $|F|$ greater than 100 but cannot be distinguished from nearby peaks.

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3.3.8 "C-mon" Metastable Phase $\sim$Ca$_{4}$Sr$_{4}$Bi$_{6}$O$_{13}$ (x $\rightarrow$ 6) When the 1:1 phase is heated between 885 and 925 °C for 20 min to 3 h a metastable C-centered monoclinic phase is formed which may be nearly single phase $[a = 21.295(4)$ Å, $b = 4.3863(8)$ Å, $c = 12.671(2)$ Å, and $\beta = 102.74(1)^\circ]$. After overnight heat treatments, however, this phase decomposes to a "bce" plus CaO assemblage. Comparison of the X-ray powder diffraction patterns (Fig. 19, Table 15) for this phase and for Ca$_{4}$Sr$_{4}$Bi$_{6}$O$_{13}$ (x $\rightarrow$ 8) indicates that it is the metastable end member extension of the stable ternary solid solution.

3.4 The System CaO-Bi$_{2}$O$_{3}$-CuO

Ternary phase relations of the system CaO-1/2Bi$_{2}$O$_{3}$-CuO have been studied at temperatures between 700 and 900 °C. No ternary compounds were discovered, but new data on the CaO-1/2Bi$_{2}$O$_{3}$ and CaO-CuO binaries have been incorporated. The ternary phase relations at 700-750 and 750-800 °C are shown in Figs. 20 and 21 respectively. There remains some uncertainty about the equilibrium phase relations involving Ca$_{1-x}$Cu$_{2}$O$_{2}$.

To verify that the three-phase equilibria inferred from synthesis runs (products of a synthesis from CaCO$_{3}$, Bi$_{2}$O$_{3}$, and CuO) reflected equilibrium phase assemblages, various three phase mixtures of pre-made binary compounds were reacted isothermally. For example, such experiments demonstrate that a mechanical mixture of Ca$_{3}$Bi$_{13}$O$_{16}$ $+$ 7Ca$_{2}$CuO$ _{3}$ $+$ 3Ca$_{53}$Cu$_{3}$Cu$_{54}$O$_{10}$ (bulk composition 51.80: 9.84: 38.36) is metastable with respect to a mixture of Ca$_{2}$Bi$_{2}$O$_{3}$ $+$ Ca$_{2}$CuO$_{3}$ $+$ Ca$_{53}$Cu$_{3}$Cu$_{54}$O$_{10}$ at 700 °C. Because the nucleation (or increase in volume fraction) of Ca$_{1-x}$Cu$_{2}$O$_{2}$ from binary compounds was never demonstrated at 700 °C (see Sec. 3.2.2) the possibilities of three phase equilibria including Ca$_{2}$CuO$_{3}$ (and/or Ca$_{1-x}$Cu$_{2}$O$_{2}$) plus Bi$_{2}$Ca$_{1}$O$_{4}$ cannot be ruled out. For example, the mechanical mixture 5Ca$_{2}$CuO$_{3}$ $+$ Ca$_{2}$Bi$_{2}$O$_{3}$ which has a bulk composition of 56:24:20 shows no convincing evidence of Ca$_{1-x}$Cu$_{2}$O$_{2}$ even after six heating/grinding treatments at 700 °C.
Fig. 19. X-ray powder diffraction pattern comparing the "C-mon" metastable phase –Ca_{6+5}Sr_{6-7}Bi_{14}O_{33} x→6 to the ternary x→0.

### Table 15. X-ray powder diffraction data for the "C-mon" Metastable Phase

| d obs (Å) | Rel I(%) | 2θ obs | 2θ calc* | hkl |
|-----------|----------|---------|-----------|-----|
| 12.405    | 2        | 7.12    | 7.15      | 001 |
| 10.419    | 3        | 8.48    | 8.51      | 200 |
| 9.009     | 6        | 9.81    | 9.83      | 201 |
| 7.219     | 1        | 12.25   | 12.27     | 402 |
| 5.221     | 4        | 16.97   | 16.99     | 401 |
| 4.865     | 11       | 18.22   | 18.24     | 401 |
| 4.489     | 27       | 19.76   | 19.74     | 401 |
| 4.447     | 4        | 19.95   | 19.94     | 401 |
|           | 1        | 20.62b  |           |     |
| 4.109     | 2        | 21.61   | 21.59     | 111 |
| 3.7049    | 4        | 24.00   | 24.00     | 310 |
|           | 5        | 24.07b  |           |     |
| 3.6718    | 8        | 24.22   | 24.23     | 311 |
| 3.6044    | 11       | 24.68   | 24.69     | 402 |
|           |          |         |           |     |
| 3.5730    | 6        | 24.90   | 24.93     | 203 |
| 3.4491    | 22       | 25.81   | 25.79     | 112 |
| 3.4360    | 23       | 25.91   | 25.88     | 311 |
| 3.3583    | 11       | 26.52   | 26.53     | 312 |
| 3.3521    | 11       | 26.57   | 26.57     | 602 |
| 3.1576    | 2        | 28.24   | 28.24     | 601 |
| 3.1565    | 2        | 28.25   | 28.24     | 204 |
| 3.0922    | 3        | 28.85   | 28.87     | 004 |
| 3.0457    | 74       | 29.30   | 29.31     | 511 |
| 3.0406    | 88       | 29.35   | 29.34     | 113 |
| 3.0265    | 97       | 29.49   | 29.51     | 312 |
| 3.0056    | 100      | 29.70   | 29.59     | 510 |
|           |          |         |           | 603 |
| 2.9267    | 69       | 30.52   | 30.50     | 403 |
| 2.8299    | 2        | 31.59   | 31.61     | 511 |

*Calculated on the basis of a monoclinic unit cell, C2/m, a = 21.295(4), b = 4.3863(8), c = 12.671(2) Å, and β = 102.74(1)°.
Fig. 20. CaO-Bi₂O₃-CuO 700–750 °C phase diagram.
Fig. 21. CaO-Bi₂O₃-CuO 750–800 °C phase diagram.
4. Summary

A new phase diagram is presented for the system CaO-CuO with the composition of the phase Ca_{1-x}CuO_{2} corresponding to a Ca:Cu ratio of 45.33: 54.67. This compound decomposes at \(-755{^\circ}C\) in air and \(835{^\circ}C\) in O\(_2\). The phases previously reported as "Ca_{v}Bi_{io}O_{zo}" and "Ca_{v}Bi_{io}O_{is}" \([21,22]\) are really Ca_{4}Bi_{6}O_{13} and Ca_{2}Bi_{2}O_{5} respectively. X-ray powder and single crystal data are reported for almost all of the binary phases encountered. No ternary phases were found in the system CaO-1/2Bi_{2}O_{3}-CuO. Above \(775{^\circ}C\) CuO is in equilibrium with all of the binary CaO-Bi_{2}O_{3} phases, and this is probably true below \(775{^\circ}C\) as well.

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