Some details of the ternary system Bi$_2$O$_3$–CaO–CuO

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Before investigating the ternary system Bi$_2$O$_3$–CaO–CuO, a revision of the binary bounding system Bi$_2$O$_3$–CaO was first necessary. In the range between 20 and 70 mol % CaO the solid solutions β and α$_1''$ and the stoichiometric compounds Bi$_2$CaO$_4$, Bi$_6$Ca$_4$O$_{13}$, and Bi$_2$Ca$_2$O$_5$ were found to exist for 675 °C $\leq$ T $\leq$ 780 °C. Above 780 °C a new high temperature compound with the formula Bi$_6$Ca$_5$O$_{14}$ has been identified. The X-ray powder diffraction data, unit cell dimensions, as well as the space group, have been reported. The ternary system contains no intermediate compounds and also no solubility was found for the binary bounding phases. Below 780 °C all the Bi–Ca oxides mentioned above are in equilibrium with CuO. At 820 °C, a wide liquidus field is dominating so that these quasibinary equilibria disappear. For 780 °C < T < 820 °C the new compound Bi$_6$Ca$_5$O$_{14}$ forms an equilibrium with Ca$_2$CuO$_3$ and CuO. Other equilibria are deduced. For a fixed ternary composition the reaction path of the sintering process was investigated as a function of time and temperature.

1. Introduction

Since the discovery of superconductivity in the rare-earth-free quaternary system Bi$_2$O$_3$–CaO–SrO–CuO, at least three superconducting compounds have been identified. These compounds can be understood as a homologous series given by the formula Bi$_2$Ca$_{n-1}$Sr$_2$Cu$_n$O$_{2n+4}$ with $n = 1$ (the 2021 phase), $n = 2$ (the 2122 phase), and $n = 3$ (the 2223 phase). Several hundred papers have been published on the possibilities for their single-phase preparation. More or less empirical starting materials, starting composition, or oxygen partial pressure were varied especially to stabilize the 2223 compound. Recently, some efforts have been made to systematically study the phase relations in this quaternary system [1–4]. The calcium-free ternary bounding system Bi$_2$O$_3$–SrO–CuO was investigated by Roth et al. [5] and Ikeda et al [6] in detail. Four ternary phases were found.

Data on the other two ternary bounding systems Bi$_2$O$_3$–CaO–SrO [1] and CaO–SrO–CuO [1, 7] show that the alkaline-earth elements calcium and strontium with a difference in ionic radii of about 0.014 nm, are either completely interchangeable or form more or less extended solid solutions. This leads to the question whether intermediate phase formation in the strontium-free Bi$_2$O$_3$–CaO–CuO system is as in the calcium-free system. Present knowledge is rather sparse. According to Schulze et al. [1] as well as to Suzuki et al. [3], neither ternary phases nor binary solid solutions extend into the ternary range. At 850° C the existence of a wide liquidus field starting from the binary system Bi$_2$O$_3$–CuO at approximately 60 mol% CuO was described [1, 3]. In addition to the two three-phase equilibria between the solid phases, CaO–Ca$_2$CuO$_3$–Bi$_6$Ca$_7$O$_{16}$ and CuO–Ca$_2$CuO$_3$–Bi$_6$Ca$_7$O$_{16}$ and the two-phase equilibrium Bi$_6$Ca$_7$O$_{16}$–liquid which were experimentally confirmed by Schulze et al. [1], the other two-phase equilibria of the calcium bismuthates with the melt were only deduced.

Here we hope to contribute to the phase relations in the ternary system Bi$_2$O$_3$–CaO–CuO. The reaction path of the formation of the equilibrium phases is described, starting from the traditional materials Bi$_2$O$_3$, CaCO$_3$, and CuO. While the binary bounding systems Bi$_2$O$_3$–CuO [8, 9] and CaO–CuO [7, 10] were assumed to be known, marked discrepancies were observed for the system Bi$_2$O$_3$–CaO reported by Conflant et al. [11]. Therefore it was necessary to redetermine this system. We focused our interest on its central part.

2. Experimental procedure

In general, samples were prepared by conventional ceramic processing starting from Bi$_2$O$_3$, calcite, and CuO each of purity $\geq$ 99.0% weighted in the desired composition. The mixed and ground powders were placed in alumina crucibles and fired up to three times at temperatures ranging from 675–874 °C in air with intermediate homogenization. For the third heat treatment, the powders were pelletized. After a duration of about 20–120 h, samples were quenched by removing the crucible from the tube furnace. In order to reduce the reaction time, several calcium-rich samples were prepared using freshly decomposed CaCO$_3$.

The melting point of several compositions was estimated by short-term heating to a maximum temperature of 960 °C.

The composition of the samples synthesized varied in the binary system Bi_2O_3–CaO between 20 and 70 mol% CaO. In the ternary system, the investigations were focused on the region between the above mentioned section of the binary system and the ternary cut Bi_2CuO_4–Ca_2CuO_3. In analogy to the calcium-free ternary system Bi_2O_3–SrO–CuO, the cation ratios Bi:Ca:Cu of 4:8:5, 2:3:2, and 2:2:1 were specially selected.

Phase identification and characterization were carried out using powder X-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM) coupled with electron probe microanalysis (EPMA) as well as thermogravimetry and differential thermal analysis (TG, DTA).

3. Results and discussion
3.1. The binary system Bi_2O_3–CaO
Fig. 1 shows the phase diagram published by Conflant et al. [11] but with $1/2$ Bi_2O_3 as the one-edge component. The dashed lines on the bismuth-rich side represent the results of Levin and Roth [12]. Obviously, there are some differences concerning the solubility of CaO in the cubic high-temperature modification of Bi_2O_3, the solid solution α_1 and the occurrence of the rhombohedral solid solution β, the so-called Aurivillius phase [13]. (According to Conflant et al. [11] there are two rhombohedral modifications of the solid solution β: β_1 and β_2). Between 25 and 30 mol% CaO, Conflant et al. found another cubic modification of the solid solution α_1, named α_1' which is not inserted into the diagram.

In the ternary phase equilibria, our interest was first aimed at the range between 20 and 70 mol% CaO including the various stoichiometric compounds.

The calcium-richest compound was found to have an average cation composition of Bi = (50.1 ± 1) at % and Ca = (49.6 ± 1) at% measured by EPMA. Therefore, its stoichiometric formula should be written as $Bi_2Ca_2O_5$. The XRD powder data are in agreement with those of Conflant et al. [11] for $Bi_6 Ca_7O_{16}$. Table I completes their d-values down to 0.1662 nm. However, there are also indications of high temperature phase in the range between $Bi_2Ca_2O_5$ and CaO. The XRD powder pattern of a sample with the starting composition Bi:Ca of 6:7

TABLE I XRD powder data for $Bi_2Ca_2O_5$. b, broad reflection

| d_{obs} (nm)	I/I_o	d_{obs}(nm)	I/I_o	d_{obs}(nm)	I/I_o
0.932	2	0.343 b	5	0.228	15
0.858	5	0.334 b	2	0.225	2
0.802	1	0.331	5	0.220 b	2
0.787	10	0.329	5	0.205	15
0.718 b	5	0.323	2	0.1983	10
0.686	1	0.318	5	0.1963	5
0.682	7	0.308	40	0.1922	5
0.501 b	5	0.298	100	0.1905 b	2
0.471	2	0.287	30	0.1806	5
0.461	20	0.282	35	0.1788	5
0.437 b	2	0.277	5	0.1769	10
0.422	5	0.271	2	0.1726	5
0.415	15	0.264	2	0.1696	5
0.395	10	0.254 b	10	0.1683	5
0.390	5	0.240 b	2	0.1662	15
0.381	10	0.236	2		
0.367 b	2	0.229	10		
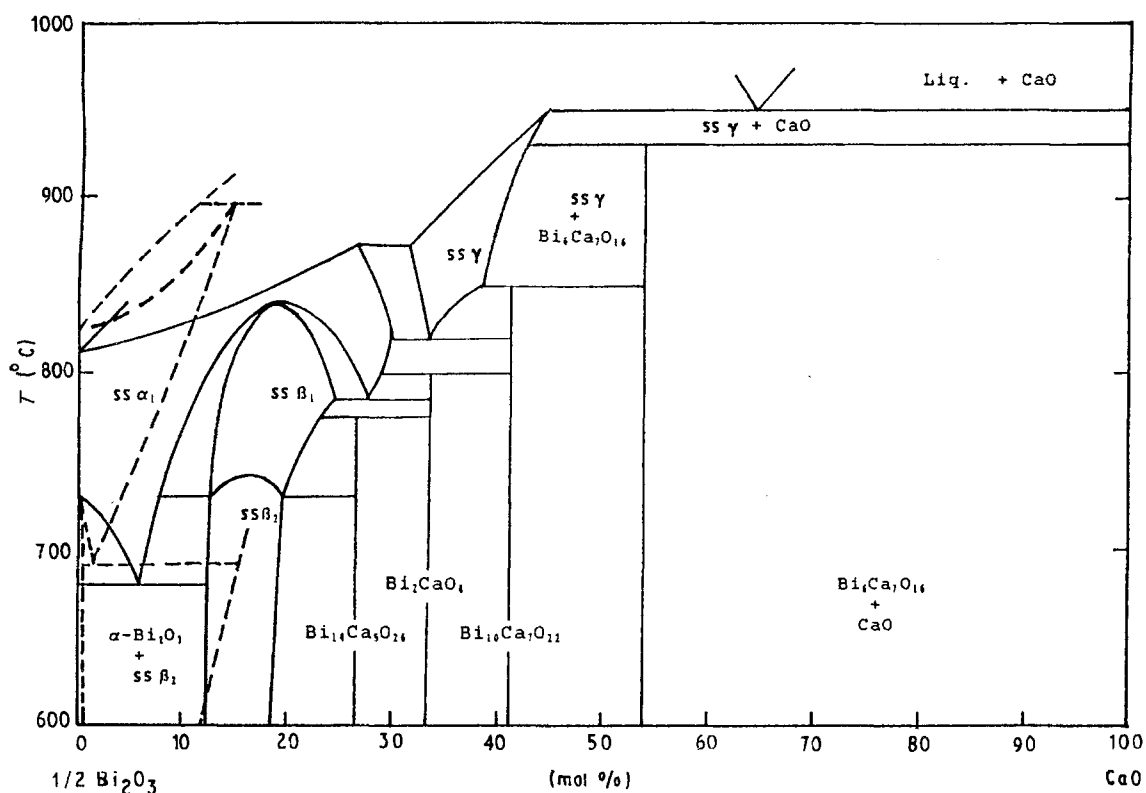
Figure 1 Phase diagram of the Bi_2O_3–CaO system published by Conflant et al. [11] with (---) inserted Bi_2O_3-rich part published by Levin and Roth [12]. The diagrams are modified with respect to the edge component chosen to be $1/2$ Bi_2O_3

annealed at temperatures around 835 °C showed some additional peaks, (among others a relatively strong one at 0.416 nm) which do not correspond with any of the known phases.

According to Parise et al. [14] the compound $Bi_{10}Ca_7O_{22}$ of Conflant et al. was found to have a cation ratio Bi:Ca of 3:2. The average composition determined by EPMA amounted to Bi = (60.5 ± 1) at % and Ca = (39.5 ± 1) at % and so the formula must be $Bi_6Ca_4O_{13}$. Using the single crystal data of Parise et al. [14] (C2mm: a = 1.7399 (5) nm, b = 0.5944 (2) nm, c = 0.7232 (2) nm) the XRD powder pattern could be indexed completely.

Moreover, a new high-temperature compound was observed, the average composition of which was determined to be Bi = (55.1 ± 1) at % and Ca = (44.9 ± 1) at %. The formula could be written as $Bi_{22}Ca_{18}O_{51}$. On comparing all the EPMA values, a systematic slight bismuth-excess is obvious and therefore the formula should be $Bi_6Ca_5O_{14}$. At temperatures above 780 °C, $Bi_6Ca_5O_{14}$ forms equilibria with both $Bi_2Ca_2O_5$ as well as $Bi_6Ca_4O_{13}$. Starting from a sample composition Bi:Ca of 6:7, at 956 °C $Bi_6Ca_5O_{14}$ was found to be in coexistence with a calcium-rich melt. It should be mentioned that this compound is also formed during the synthesis of the quaternary samples starting from a composition Bi:Ca:Sr:Cu of 2:1.5:1.5:2 as soon as parts of the sample began to melt. By EPMA the composition was determined to be about Bi = 55 at %, Ca = 35 at %, and Sr = 10 at % i.e. calcium was partly substituted by strontium. By choosing this cation ratio we could prepare single crystals for structural investigations [15]. The space group is C2/m with the unit cell dimensions a = 2.1515 (12) nm, b = 0.4363 (2) nm, c = 1.2771 (5) nm, and β =, 102.78 (4) °. The XRD powder data are given in Table II.

The preparation of the stoichiometric bismuth-richer compounds Bi_2CaO_4 and $Bi_{14}Ca_5O_{26}$ was not so successful, especially because the temperature had to be lowered to about 700 °C. $Bi_{14}Ca_5O_{26}$ could not be found at all and it was impossible to obtain single-phase material of Bi_2CaO_4. The XRD powder pattern always showed precipitations of $Bi_6Ca_4O_{13}$ and of Conflant's rhombohedral α_1'' solid solution which should only be formed during very slow cooling of the α_1' solid solution.

At a composition Bi:Ca of 4:1 the solid solution β was formed together with a small amount of α_1''. Although the results concerning the reaction path will be discussed below it should be mentioned here that probably a metastable phase was also observed, the composition of which lies in the range 64–66 at % Bi and 36–34 at % Ca. Independent of the sample composition after a first heat treatment at about 700 °C for 24–66 h, in addition to $CaCO_3$ and one or two other binary compounds, this phase, called X-phase, was one of the dominating components as the XRD powder pattern showed. Some characteristic peaks are listed in Table III. During subsequent firings this phase was always destroyed.

TABLE II XRD powder data for the new high-temperature phase $Bi_6Ca_{5-x}Sr_xO_{14}$ with x = 1

d_{obs}(nm)	d_{cal}(nm)	I/I_o	hkl	
1.236	1.245	9	001	/ 00$\bar{1}$
1.045	1.049	3	200	
0.904	0.907	17	20$\bar{1}$	
0.725	0.727	2	201	
0.595	0.597	2	20$\bar{2}$	
0.525	0.525	11	400	
0.489	0.490	20	202	
0.454	0.454	84	40$\bar{2}$	
0.3666	0.3668	3	31$\bar{1}$	
0.3596	0.3598	12	203	
0.3496	0.3497	3	600	
0.3441	0.3440	16	311	
0.3381	0.3386	16	60$\bar{2}$	
0.3117	0.3114	10	004	/ 00$\bar{4}$
0.3045	0.3047	53	11$\bar{3}$	
0.3024	0.3025	100	60$\bar{3}$	/ 510
0.2952	0.2953	39	403	
0.2905	0.2909	12	51$\bar{2}$	
0.2818	0.2820	15	204	
0.2686	0.2689	8	80$\bar{1}$	
0.2631	0.2633	2	60$\bar{4}$	
0.2553	0.2554	9	20$\bar{5}$	
0.2489	0.2491	25	005	/ 00$\bar{5}$
0.2460	0.2459	3	801	
0.2182	0.2182	9	020	
0.2128	0.2128	48	20$\bar{6}$	
0.2099	0.2098	9	$\bar{1}$000	
0.2095	0.2095	9	91$\bar{1}$	/ 40$\bar{6}$
0.2079	0.2079	3	405	
0.1963	0.1963	3	315	
0.1952	0.1952	6	$\bar{1}$00$\bar{4}$	
0.1940	0.1940	3	71$\bar{5}$	

3.2. The ternary system Bi_2O_3–CaO–CuO

In accordance with Schulze et al. [1] and Suzuki et al. [3] we also found no ternary compound in the Bi_2O_3–CaO–CuO system, and for the binary compounds, no solubility could be detected with respect to the opposite component. Instead of this, at temperatures between 675 and 780 °C, CuO appears to form equilibria with all the Bi–Ca oxides. Figs 2 and 3 document, for example, its coexistence with the calcium-richest compound $Bi_2Ca_2O_5$ on the one side, and with the bismuth-richest separate solid solution β on the other.

In the reaction path, very fine precipitations of CuO (≤ 5μm) within the $Bi_2Ca_2O_5$ grains and the larger

TABLE III Some characteristic XRD powder data for the metastable X-phase. The peak intensity is only estimated: vst, very strong; st, strong; m, medium; w, weak

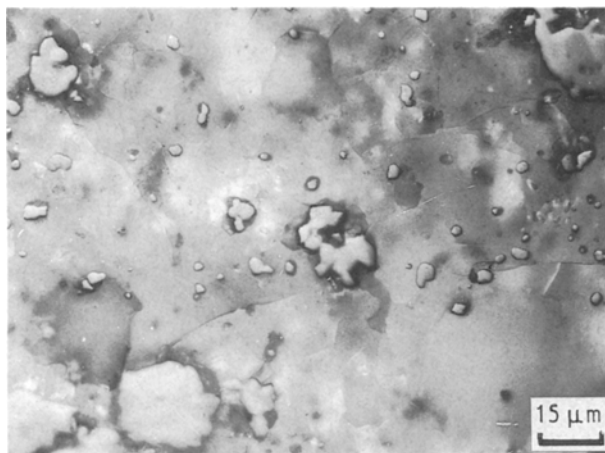| d_{obs} (nm)	I_{est}
1.27	vst
0.58	w
0.384	vst
0.365	m
0.349	m
0.290	st
0.217	m
0.202	st

Figure 2 Optical micrograph of a 2:2:1 sample quenched from 775 °C (oil immersion, without polars). Light grey, partly dissolved CuO grains are embedded in the $Bi_2Ca_2O_5$ matrix brightened by inner yellowish reflections.
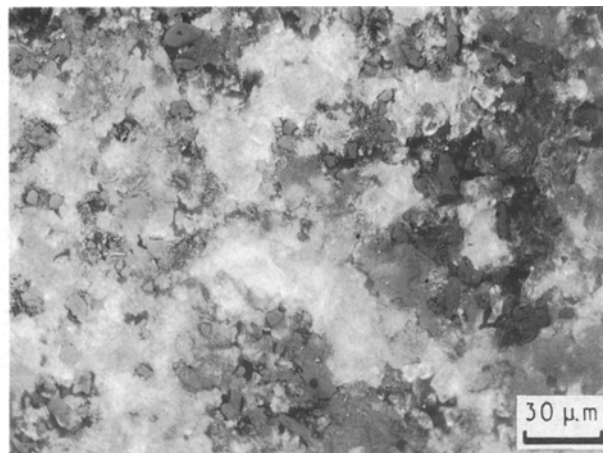

Figure 4 Optical micrograph of a 15:3:2 sample quenched from 705 °C (oil immersion, without polars). Dark grey, nearly iso-morphic grains of Bi_2CuO_4 are embedded in the β-phase brightened by inner yellowish reflections

Figure 3 Optical micrograph of a 3:1:2 sample quenched from 820 °C (slightly uncrossed polars). The quasi-eutectic microstructure is formed by the β-phase which includes fine directed CuO precipitations and larger, partly dissolved CuO grains.

partly dissolved CuO grains demonstrate the partici-pation of some of the weighted CuO in the synthesis process. The average composition of β in equilibrium with CuO was determined to be Bi = (74.5 ± 1) at % and Ca = (25.5 ± 1) at %. Fig. 4 illustrates the coexistence of β, the average composition of which was determined to be Bi = (81.6 ± 1) at % and Ca = (18.4 ± 1) at % with $Bi_2\,CuO_4$ the only com-pound of the Bi_2O_3–CuO system.

The three-phase equilibrium between $Bi_2Ca_2O_5/$ ($Bi_6Ca_7O_{16}$), Ca_2CuO_3 and .CuO described by Schulze *et al.* [1] for a temperature of 850 °C could not be verified. At 820 °C samples with a composition Bi:Ca:Cu of 2:2:1, 2:3:2, or 1:3:2 always showed melted parts. The liquidus field must have already crossed the $Bi_2Ca_2\,O_5/(Bi_6Ca_7O_{16})$, –CuO tie line as indicated by Suzuki *et al.* [3]. However, not $Bi_2Ca_2O_5/\,(Bi_6Ca_7O_{16})$, but the high-temperature compound $Bi_6Ca_5O_{14}$ was the crystallizing Bi–Ca oxide at the sample compositions mentioned above. Fig. 5 shows the XRD powder pattern of a 2:3:2

sample annealed at 850 °C for 17 h. In addition to $Bi_6Ca_5O_{14}$ the reflections of Ca_2CuO_3 and CuO are present. Fig. 6 shows an image of the microstructure of the 2:3:2 sample. Longish grains of Ca_2CuO_3 and more isometric grains of CuO are embedded in the $Bi_6Ca_5O_{14}$ matrix. Additional very fine dendritic precipitations of CuO are visible within parts of the $Bi_6Ca_5O_{14}$ matrix referring to an eutectic solidi-fication (Fig 7). From these observations we con-cluded that a three-phase equilibrium Ca_2CuO_3 –CuO–$Bi_6Ca_5O_{14}$ exists for 780 °C < T < 820° C, changing to liquid–Ca_2CuO_3–CuO and liquid –Ca_2CuO_3– $Bi_6Ca_5O_{14}$ as soon as the melt crosses the tie line $Bi_6Ca_5O_{14}$–CuO. At lower tem-peratures, the three-phase equilibria $Bi_2Ca_2O_5$ /($Bi_6Ca_7O_{16}$) –Ca_2CuO_3– CaO and $Bi_2Ca_2O_5/$ ($Bi_6Ca_7O_{16}$) –Ca_2CuO_3–CuO could not be con-firmed. Samples where the processing temperature never exceeded 805 °C always consisted of $Bi_2Ca_2O_5$, CuO, and CaO and/or $Ca(OH)_2$. ($Ca(OH)_2$ was con-sidered to be the reaction product of CaO and the ambient atmosphere.) However, it seems to be a kin-etic problem. Thermal investigations showed Ca_2CuO_3 will be formed only at temperatures above 800 °C. Therefore, the coexistence between $Bi_2Ca_2O_5$, CuO, and CaO should be a metastable one.

3.3. Remarks on the reaction path
The investigations concerning the reaction path are a consequence of the difficulties in reaching equilibrium conditions especially at temperatures below 800 °C. The standard starting composition choosen for these experiments was Bi_2O_3:2$CaCO_3$:CuO and the reac-tion temperature, 705 °C, so that at the very end the samples had to reach the quasibinary equilibrium $Bi_2Ca_2O_5$–CuO.

As previously expected, Bi_2O_3 was the most active component in this process while the decomposition of $CaCO_3$ determined the rate of the reaction. Although the emission of CO_2 always started at 635 °C the
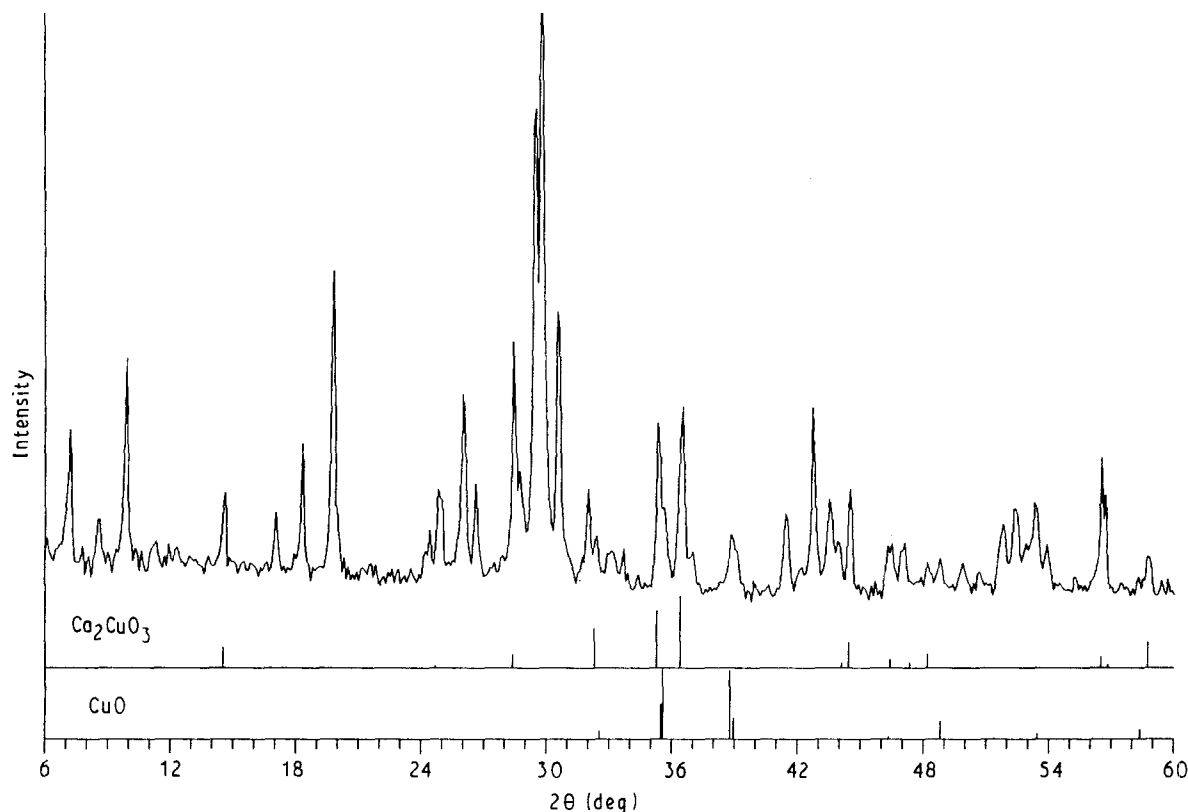
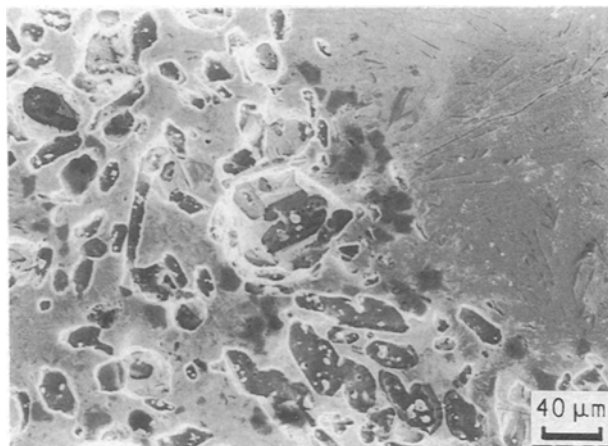*Figure 5* XRD powder pattern of a $2:3:2$ sample quenched from $850\,^\circ$C.

Figure 6 SEM image of $2:3:2$ sample quenched from $850\,^\circ$C. Longish grains of Ca_2CuO_3 and more isometric grains of CuO are embedded in the $Bi_6Ca_5O_{14}$ matrix.

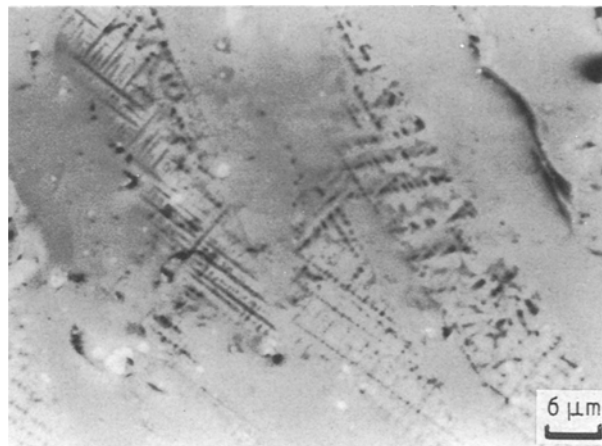*Figure 7* SEM image of the same sample seen in Fig. 6. Very fine dendritic CuO precipitations are visible within the $Bi_6Ca_5O_{14}$ matrix, indicating eutectic solidification.

reaction really came into action above $780\,^\circ$C. Using thermogravimetry at $800\,^\circ$C, only one-fifth of the total amount of CO_2 was found to have escaped. So, after 24 h at $705\,^\circ$C the calcium supply was still limited. Only very bismuth-rich Bi–Ca oxides were formed as the β-phase and the above-described metastable X-phase. The remaining Bi_2O_3 reacted with CuO forming Bi_2CuO_4. After a further 21 h, nothing else had happened. Perhaps the $CaCO_3$ content had decreased slightly. After another 117 h, $CaCO_3$ was decomposed to a large extent. Bi_2CuO_4 could react with CaO to form $Bi_6Ca_4O_{13}$ whereby CuO remained as very fine precipitations in this matrix, as mentioned above.

Corresponding to the XRD pattern, $Bi_6Ca_4O_{13}$ and CuO were the main phases but the X-phase and β could still be detected. Even after in total 430 h the equilibrium state was not reached, and $Bi_2Ca_2O_5$, CuO and $Bi_6Ca_4O_{13}$ still remained the main phases. Because of the starting composition also some $CaCO_3$ had to be present. (All strong peaks of $CaCO_3$ and CaO coincide with those of $Bi_6Ca_4O_{13}$ in the XRD powder pattern). Fig. 8 shows schematically the final reaction path at $705\,^\circ$C. Surprisingly, the other binary bismuth-rich Bi–Ca oxides as Bi_2CuO_4 and the a_1''-solid solution were never found here. Deleting CuO and the copper-containing compound
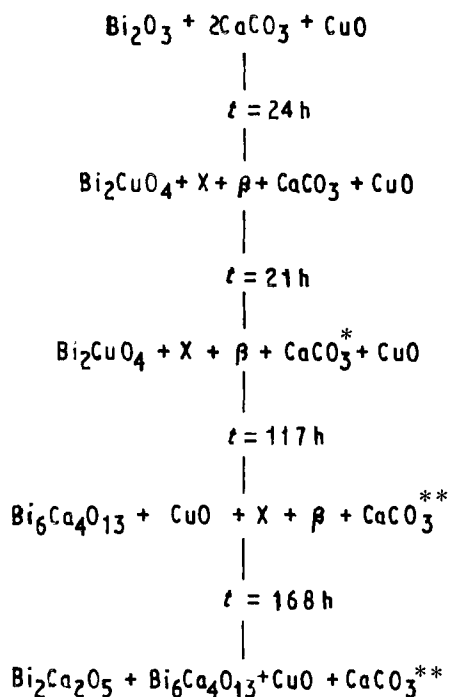
115

$$Bi_2O_3 + 2CaCO_3 + CuO$$

$$\downarrow \; t = 24\,h$$

$$Bi_2CuO_4 + X + \beta + CaCO_3 + CuO$$

$$\downarrow \; t = 21\,h$$

$$Bi_2CuO_4 + X + \beta + CaCO_3^* + CuO$$

$$\downarrow \; t = 117\,h$$

$$Bi_6Ca_4O_{13} + CuO + X + \beta + CaCO_3^{**}$$

$$\downarrow \; t = 168\,h$$

$$Bi_2Ca_2O_5 + Bi_6Ca_4O_{13} + CuO + CaCO_3^{**}$$

Figure 8 Schematic representation of the reaction path at 705 °C starting from a composition $Bi_2O_3:2CaCO_3:CuO$.
The sequence of the phases detected represents their amount qualitatively. * The $CaCO_3$ content has decreased with respect to the former heat treatment. ** Using XRD, small amounts of $CaCO_3$ could not be detected.

Bi_2CuO_4, the reaction path for a starting composition $Bi_2O_3:2CaCO_3$ was the same as illustrated in Fig. 8.

To analyse the dependence on the temperature at a given reaction time the same starting composition was used. At 705 °C after 24 h, Bi_2CuO_4, X, β, $CaCO_3$, and CuO were the components found. At 726 °C $Bi_6Ca_4O_{13}$ was already one of the main phases in addition to X, β, CuO, and $CaCO_3$. On the other hand, only traces of Bi_2CuO_4 could be found. At 745 °C as well as at 764 °C after 20 h, $Bi_6Ca_4O_{13}$, CuO, and a small amount of $CaCO_3$ were present. With the formation of $Bi_6Ca_5O_{14}$, the range for the quasibinary equilibrium $Bi_2Ca_2O_5$–CuO was exceeded at 782 °C and the three-phase equilibrium $Bi_6Ca_5O_{14}$–CuO–Ca_2CuO_3 must have been reached. However, the duration of heat treatment was not sufficient to form this equilibrium state. In addition to $Bi_6Ca_5O_{14}$, $Bi_6Ca_4O_{13}$, and CuO were found and also some $CaCO_3$ or CaO was expected to be present. At 800 °C after only 2 h, the sample was melted to a large extent. The XRD powder pattern of this sample when quenched showed $Bi_6Ca_5O_{14}$, CuO, $Bi_6Ca_4O_{13}$, $Bi_2Ca_2O_5$, and also Ca_2CuO_3.

4. Conclusions

The binary system Bi_2O_3–CaO was redetermined in the range between 20 and 70 mol% CaO. At temperatures ranging from 675–780 °C, in addition to the solid solutions β and a_1'' the stoichiometric compounds Bi_2CaO_4, $Bi_6Ca_4O_{13}$, and $Bi_2Ca_2O_5$, were found to exist. At temperatures above 780 °C, a new high-temperature compound with the stoichiometric formula $Bi_6Ca_5O_{14}$, could be identified. This compound was also found to exist when substituting about 22% of the calcium by strontium. In contrast to the calcium-free system, the system Bi_2O_3–CaO–CuO forms no ternary compounds and the phases of the bounding binaries show no remarkable solubility extending into the ternary range. Below 780 °C, all the Bi–Ca oxides found in the range 20–70 mol% CaO were in equilibrium with CuO. The new high-temperature compound $Bi_6Ca_5O_{14}$, was observed only in samples quenched from temperatures above 780 °C. Therefore, an equilibrium $Bi_6Ca_5O_{14}$–Ca_2CuO_3–CuO was concluded. At 820 °C the three-phase equilibrium liquid–CuO–Ca_2CuO_3 was confirmed experimentally. From its existence the following other equilibria can be deduced: liquid–$Bi_6Ca_5O_{14}$–CuO, $Bi_6Ca_5O_{14}$–Ca_2CuO_3–$Bi_2Ca_2O_5$, and, if there is no further calcium-rich high-temperature phase, also the equilibrium $Bi_2Ca_2O_5$–Ca_2CuO_3–CaO. In the sample preparation, obviously the temperature and time have a large influence on the formation of the phase equilibrium. For temperatures below 800 °C, a predecomposition of $CaCO_3$ is advisable to increase the reaction rate and to lower the necessary time of heat treatment. A short-term melting of the sample seems to be suitable for homogenization, and can become the initial step for kinetically inhibited reactions.

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