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Sub-solidus relations in CaO–BaO–CuO with and without carboxyl contamination

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Abstract

The sub-solidus relations in the pseudo-ternary CaO–BaO–CuO system have been investigated at temperatures between 900 and 1000°C in both oxygen and (natural) air, and a tremendous effect has been found to result from the minute amount (~ 450 ppm) of CO_2 present in the latter atmosphere. In flowing oxygen, $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$, $\text{CaBa}_7\text{Cu}_3\text{O}_{11}$ and $\text{Ba}_{1-y}\text{Ca}_y\text{CuO}_2$ ($0 \leq y \leq 0.08$) solid solutions have been identified. On the other hand, in stagnant natural air, which contains ~ 450 ppm CO_2 , there have been found oxycarbonates including $\text{CaBa}_4\text{Cu}_2\text{O}_{6+\delta}(\text{CO}_3)$, $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$, and $\text{Ca}_{1-x}\text{Ba}_8\text{Cu}_4\text{O}_{10-2x}(\text{CO}_3)_{3+x}$ ($x = 0 \sim 0.35$) solid solutions, which account for several controversial ternary “oxides” reported in the literature. The ternary phase diagrams for both atmospheres at 900°C are shown, while those at higher temperatures, up to 1000°C, are elucidated from the thermal stability studies of the detected oxides and oxycarbonates. Structural models are proposed for $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$ and $\text{Ca}_{1-x}\text{Ba}_8\text{Cu}_4\text{O}_{10-2x}(\text{CO}_3)_{3+x}$.

1. Introduction

Syntheses of Tl and Hg based high- T_c superconducting oxides, including $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$, $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$, and $\text{HgCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+2+y}$ [1–3], often adopt a two-step calcination approach to minimize the loss of either Tl or Hg via evaporation [4–8]. In such a process, a precursor powder containing stoichiometric or non-stoichiometric amounts of oxides or carbonates of Ca, Ba and Cu, is first calcined and the resulting precursor powder is then added with Tl or Hg oxide and subjected to a second calcination at somewhat lower temperatures to obtain the desired superconducting

phases. The cation composition in the precursor powder, and hence the nature of the phases resulting from the first calcination step, has been shown [4–7] to have a significant influence on the purity of the final superconducting phase, presumably because of different reaction mechanisms involved in the second calcination. To understand and to have a better control on the reaction kinetics leading to the formation of the desired superconducting oxides during the second calcination step, one requires full knowledge of the phase equilibria of CaO–BaO–CuO.

While there have been a few reports [4,9–13] on the phase behaviors of CaO–BaO–CuO, the results are rather controversial. For example, by using BaCO_3 as the Ba source and conducting calcination in air, we have previously demonstrated the success in making high-purity $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ ($n = 2\text{--}3$) oxides powder with $\text{CaBa}_2\text{CuO}_4$ (the 121 ox-

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ide) to be the precursor “compound” [4,6]. (Throughout this paper, the Ca, Ba and Cu containing compounds will be abbreviated with three digits indicating the relative cation stoichiometries in the sequence of Ca, Ba and Cu.) However, when adopting BaO_2 as the Ba source and carrying out calcination in O_2 , Kubat-Martin et al. [9] identified $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$ (143 oxide) at temperatures between 920 and 975°C but no “121 oxide”. On the other hand, Whittier and Roth [10] reported the existence of $\text{CaBa}_4\text{Cu}_2\text{O}_7$ (the 142 oxide) between 900 and 950°C, but neither the 121 nor the 143 oxide was found. Hamada et al. [11], on the other hand, reported solid solutions of $\text{Ca}(\text{Ba}_{1-x}\text{Ca}_x)_8\text{Cu}_4\text{O}_{13+z}$ (184 oxides) with $0 \leq x \leq 0.25$ and $z \sim 0.5$, which were not identified by other groups. The situation is further complicated by the recent discoveries [14,15] of a couple of Ca–Ba–Cu–O– CO_3 oxycarbonates which possess the same cation stoichiometries as those of the reported ternary oxides, such as $\text{CaBa}_4\text{Cu}_2\text{O}_{6+\delta}(\text{CO}_3)$ [15] versus $\text{CaBa}_4\text{Cu}_2\text{O}_7$ [10]. Carboxyl (CO_3^{2-}) contamination is known to be detrimental to the superconducting properties of most Ba containing high- T_c superconducting oxides. Since the second-step calcination in the syntheses of the Tl or Hg based superconducting oxides is typically carried out in a sealed container [2,3,16], carbonates are preferably to be eliminated in the precursor powder after the first-step calcination.

In view of the controversies described above, we launched our own investigation of the sub-solidus phase relations of CaO–BaO–CuO. Experiments were aimed at temperatures above 900°C, where calcinations of the precursor powders have typically been carried out. As reported here, dramatic differences in the sub-solidus relations in CaO–BaO–CuO were noted between materials treated in oxygen and in (natural) air due to the presence of CO_2 in the latter atmosphere. Between 900 and 1000°C in oxygen, $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$ (143 oxide), $\text{CaBa}_7\text{Cu}_3\text{O}_{11}$ (173 oxide) and $\text{Ba}_{1-y}\text{Ca}_y\text{CuO}_2$ ($0 \leq y \leq 0.08$) (011 oxide solid solutions) have been identified to be the only stable ternary oxides. On the other hand, in air which contains ~ 450 ppm CO_2 , there were identified oxycarbonates including $\text{CaBa}_4\text{Cu}_2\text{O}_{6+\delta}(\text{CO}_3)$ (abbreviated as 142-1C), $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$ (183-4C), and $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_4\text{O}_{10-2x}(\text{CO}_3)_{3+x}$ ($x = 0 \sim 0.35$) (184-3C) solid solutions. Several of the re-

ported controversial “oxides” can, in fact, be accounted for by these oxycarbonates.

2. Experimental

The samples were synthesized by a solid-state reaction of mixtures containing BaO_2 or BaCO_3 , CaO and CuO. Calcinations were conducted by using a ZrO_2 crucible either in flowing oxygen or in stagnant (natural) air, which contains $\sim 450(\pm 30)$ ppm CO_2 . The samples were repeatedly ground and calcined with a period of 20–25 h adopted for each calcination step. At the end of each calcination, the powders were sampled to be analyzed by X-ray diffraction (XRD) for determining their phase compositions. The phases reported here were typically the results after at least 100 h of calcination. Mainly two temperature schedules, namely the high- and low-temperature schedules, have been adopted. For the low-temperature schedule, calcination has been carried out exclusively at 900°C. For the high-temperature one, calcination is first carried out at 960°C until there is no phase change according to XRD and the resulting powder is then brought to 900°C for further heat treatment. Furthermore, the identified ternary oxides and oxycarbonates have been heated at sequentially increasing temperatures up to 1000°C to determine their thermal stabilities.

Phase compositions and crystal structures were investigated by X-ray and electron diffractometries and by the Rietveld analysis using the program “RIETAN” [17,18]. The XRD data were acquired within a 2θ range from 10° to 80° with a step-scanning rate of 3 s per 0.02° 2θ increment. Since no oxygen analysis has been carried out, unless otherwise specified, the oxygen contents in the compounds are assigned by assuming divalent Ca, Ba and Cu ions.

3. Results and discussion

Fig. 1 summarizes the sub-solidus relations at 900°C in oxygen. They are established based on ~ 30 tested composition data; only those that will be discussed later are shown and numbered. Both high- and low-temperature schedules have been carried out

Fig. 1. Phase diagram of CaO–CuO–BaO at 900°C. For the pseudo-binary and ternary oxides, the cation stoichiometries are indicated by the three digits in the sequence of Ca, Ba and Cu. Only those data points that have been referred to in the text are marked and numbered. The data point marked as “*” locates the eutectic composition with the eutectic temperature of $\sim 935^\circ\text{C}$.

for each tested compositions located outside the Ca_2CuO_3 – BaCuO_2 – CuO triangle, while only the low-temperature one was carried out for those within the triangle due to powder melting. Our preliminary investigation on the liquidus relationships indicates that the lowest melting temperature is due to the ternary eutectic reaction

at $\sim 935^\circ\text{C}$ with the cation composition of Ca:Ba:Cu $\sim 1:1:3$, as indicated by the data point “*” marked in Fig. 1.

For binary compatibility, Ca_2CuO_3 (the 201 oxide) is the only binary compound detected along CuO–CaO, while no binary compound has been found along BaO–CaO (Fig. 1). The XRD data of the 201 oxide are consistent with an orthorhombic cell with the space group Immm and lattice constants $a = 12.208 \text{ \AA}$, $b = 3.768 \text{ \AA}$, and $c = 3.249 \text{ \AA}$ [19]. Along the BaO–CuO joint, BaCuO_2 (the 011 oxide) and Ba_2CuO_3 (the 021 oxide) have been identified. The XRD data of the 011 oxide are accounted for by a cubic cell with the space group of $\text{Im}3\text{m}$ and lattice constant $a = 18.285 \text{ \AA}$ [19]. The formation kinetics for the 021 oxide is much slower than that of the 011 oxide. As a result, along the course of consecutive calcinations, one observed the 011 oxide to be the major binary oxide prior to the formation of 021 oxide. (A minimum calcination time of 50 h, for

example, is needed for the 021 oxide to become the major phase at 930°C .)

Furthermore, the 021 oxide has been found to decompose, presumably by hydration, even at room temperature. A reduction by 20% in its XRD intensity, for instance, was noticed during two consecutive XRD measurements, each of which lasted for only 3 min. Thus, either a too-short calcination time or a delay in acquiring the XRD data may account for the negligence of this phase in some earlier literature [9,10,20]. Because of the lack of slow-scan XRD data, no structural refinement can be carried out for the 021 oxide. However, the fast-scan data were sufficient to confirm the existence of both orthorhombic and tetragonal phases [21], obtained respectively by furnace cooling and quenching.

Fig. 2. The XRD patterns of (a) $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$ (the 143 oxide); (b) furnace-cooled $\text{CaBa}_4\text{Cu}_2\text{O}_{6+\delta}(\text{CO}_3)$ (142-1C); (c) $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$ (183-4C); (d) $\text{CaBa}_8\text{Cu}_4\text{O}_{10}(\text{CO}_3)_3$ (184-3C, $x = 0$); (e) $\text{Ca}_{0.65}\text{Ba}_8\text{Cu}_4\text{O}_{9.3}(\text{CO}_3)_{3.5}$ (184-3C, $x = 0.35$).

The 011 oxide solid solutions ($\text{Ba}_{1-y}\text{Ca}_y\text{CuO}_2$) have previously been detected by Abbattista et al. [13], who assigned a maximum of $y = 0.08$. The existence of these solutions has been confirmed in this work by, for example, data point #1, which has a cation composition of $\text{Ca}:\text{Ba}:\text{Cu} = 2:1:1$. This composition falls on the line connecting CaO and BaCuO_2 ($y = 0$). As shown by XRD, this composition resulted in three phases, including the 143 oxide, CaO and the Ca rich end member of the solutions. This is in contrast to only two phases, namely CaO and 011 oxide, which would be expected if the solid solutions did not exist. The XRD patterns of the Ca substituted 011 oxide can be accounted for by the same unit cell structure as that of the unsubstituted one except for longer lattice constant a (e.g., $a = 18.338$ for maximum Ca substitution). The maximum Ca substitution in these solutions has not been rigorously searched for experimentally. However, Rietveld analysis of the XRD pattern of data #1 indicates a possible Ca substitution range between $x = 0.06$ and 0.08 .

In addition to the 011 solid solutions, there have been identified two other ternary oxides, including 143 and 173 oxides. The 143 oxide (Figs. 1 and 2a) has previously been reported by Kubat-Martin et al. [9,22] and by Abbattista et al. [13]. Based on both X-ray and neutron diffraction data [9,22], Kubat-Martin et al. proposed a cubic cell having the space group $\text{Im}3\text{m}$, while, based solely on XRD, Abbattista et al. also assumed a cubic cell but with the space group $\text{Pm}3$. Their XRD patterns were extremely similar except that Abbattista reported a few additional very weak ($I/I_0 < 0.5\%$) reflections that are neither reported by Kubat-Martin nor confirmed with certainty in this work. However, our XRD pattern simulation using the program RIETAN and based exactly on Abbattista's model (including their reported structural parameters) indicated that some reflections, such as (210, 120) and (221, 300), having theoretical intensities higher than 1%, were missing in their XRD data, while some other reflections, such as (100) and (110), having lower intensities (less than 0.5%) were reported. A similar conflict, on the other hand, did not occur for Kubat-Martin's model. Based on these considerations, Kubat-Martin's space group was adopted for indexing our XRD data, as listed in Table 1.

Table 1

The XRD data of $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$. Space group: $\text{Im}3\text{m}^a$; $a = 8.157 \text{ \AA}$

h	k	l	$d (\text{\AA})$	I/I_0
2	0	0	4.079	21
2	1	1	3.330	1
2	2	0	2.884	100
2	2	2	2.355	10
4	0	0	2.039	23
4	2	0	1.824	7
4	2	2	1.665	36
4	4	0	1.442	15
6	0	0	1.359	3
4	4	2	—	—
6	2	0	1.290	15
6	2	2	1.230	4

^a The space group follows that of Kubat-Martin et al. [22].

Noticing the presence of impurity phases, mainly the 011 oxide, Kubat-Martin et al. [22] proposed the exact chemical formula to be $\text{Ca}_{1.08}\text{Ba}_{3.92}\text{Cu}_3\text{O}_{8.85}$, of which the non-integer cation stoichiometries was accounted for by mutual substitution between Ca and Ba. Notably the 011 oxide has always been present in our calcined 143 oxide powder (Fig. 2a), but a smaller amount than that of Kubat-Martin has been obtained when a greater extent of heat treatment was employed. For example, calcination of the 143 powder at 960°C for 100 h produces a 011/143 weight ratio, as determined by Rietveld analysis, of $\sim 10/90$, as compared with $\sim 18/82$ obtained either by 24 h of calcination at the same temperature as carried out by Kubat-Martin or by 100 h calcination at 900°C in our low-temperature schedule. Thus, the cation composition of this oxide can be very close to $\text{Ca}:\text{Ba}:\text{Cu} = 1:4:3$. Indeed, in the case of our 960°C sample, XRD fitting based on Kubat-Martin's space group showed a better fitting for assuming exactly 143 stoichiometry and no Ca/Ba substitution than following Kubat-Martin's formula and substitution ratios. ($R_1 = 6.11$, $R_{\text{wp}}/R_e = 13.87/13.60$ for the former versus $R_1 = 8.23$, $R_{\text{wp}}/R_e = 14.38/13.61$ for the latter). As a final note for the 143 oxide, precaution should be taken to carry out XRD soon after the 143 oxide is formed. The 143 oxide has also been found to show signs of decomposition by hydration but apparently at a much slower rate than that of the 021 oxide described previously.

Table 2
The XRD data of $\text{CaBa}_7\text{Cu}_3\text{O}_{11}$ ^a

d (Å)	I/I_0
3.979	18
3.623	9
3.533	4
2.963	100
2.862	53
2.532	3
2.464	5
2.246	16
2.174	14
2.074	5
2.024	21
1.971	3
1.804	3
1.776	12
1.767	9
1.731	21
1.671	35
1.564	2

^a To minimize decomposition by hydration, the XRD data were taken at a scanning rate of $4^\circ 2\theta/\text{min}$.

Abbattista et al. [13] once reported the XRD data of $\text{CaBa}_6\text{Cu}_3\text{O}_{10.5}$ (163 oxide; which has mistakenly assigned to be $\text{CaBa}_6\text{CuO}_{10.5}$ in the PDF file #42-523). Our experimental results, however, indicated that the correct cation ratios should be $\text{Ca}:\text{Ba}:\text{Cu} = 1:7:3$ (Fig. 1). Table 2 lists the XRD data of the 173 oxide, which are consistent with those reported by Abbattista et al. [13] for the 163 oxide except for small variations in intensity and the absence of a couple of very weak ($<0.4\%$) reflections. Calcination of the powder with $\text{Ca}:\text{Ba}:\text{Cu} = 1:6:3$ has been found to result in a mixture of 143 and 173 oxides, while that with $\text{Ca}:\text{Ba}:\text{Cu} = 1:7:3$ gave only the 173 oxide. In addition, this newly assigned composition has been confirmed by several other tested compositions. For example, the data #2 shown in Fig. 1 has a cation ratio of $\text{Ca}:\text{Ba}:\text{Cu} = 1:2:1$, which falls on the line connecting CaO and the 1-6-3 composition in the phase diagram. The calcined powder with this composition gave three phases, including CaO , 143 and 173 oxides, rather than two oxides if the 163 oxide compound existed. Furthermore, as discussed later, the complete decomposition of an oxycarbonate having the cation composition of $\text{Ca}:\text{Ba}:\text{Cu} = 1:8:4$ into oxides resulted in 143 and

174 oxides, while the 143 oxide would not be produced if the 163 oxide existed.

It is noted that the reaction kinetics for forming the 173 oxide is very slow. Calcination, for instance, at 900°C for 100 h gave no sign of this compound. Thus, the 173 oxide has been detected only via the high-temperature (960°C) schedule. Exposing the already formed 173 oxide to 900°C with prolonged heating does not cause any phase change. These results indicate that the 173 oxide is indeed a stable phase at 900°C in oxygen. The slow synthesis rate of 173 oxide may be the main reason why it has not been detected in some previous studies [9,12]. When exposed in air at room temperature, the 173 oxide was found to be unstable and to decompose by hydration. As a result, only fast-scan XRD data are available (Table 2) and a structural refinement cannot be carried out with certainty based on these data.

Fig. 3 summarizes the sub-solidus relations established by calcinations at 900°C in stagnant (natural) air, which contains $\sim 450 (\pm 30)$ ppm of CO_2 . They were established based on ~ 50 tested composition data, part of which were shown. BaCO_3 , rather than Ba oxide, is used to denote one of the corner elemental compounds. This is because, for prolonged calcinations in such an air environment, any unreacted Ba eventually exists in the carbonate form, as shown by XRD. In contrast, BaO becomes dominant in oxygen irrespective of whether BaO_2 or BaCO_3 is used as the Ba source. The key to such a difference is the presence of ~ 450 ppm CO_2 in our natural air environment. BaCO_3 is stable up to $910\text{--}915^\circ\text{C}$ at this CO_2 level [23].

The lowest melting temperature, $\sim 890^\circ\text{C}$, occurs at the same eutectic composition ($\text{Ca}:\text{Ba}:\text{Cu} = \sim 1:1:3$; marked by the data point “*” in Fig. 3) as that detected in oxygen. Calcinations of powders with overall cation compositions falling within the $\text{Ca}_2\text{CuO}_3\text{--BaCuO}_2\text{--CuO}$ triangle (the hatched area in Fig. 3) always resulted in powder melting. This is true irrespective of whether elemental oxides or carbonates or binary oxides, namely 201 and 011 oxides, were used as reactants. Furthermore, as described later, the majority of the oxycarbonate compounds have a stability temperature lower than 920°C . Therefore, only the low-temperature schedule has been adopted for establishing the phase relations shown in Fig. 3.

Fig. 3. Phase diagram of CaO–CuO–BaCO₃ at 900°C. For the pseudo-binary and ternary oxides and oxycarbonates, the cation stoichiometries are indicated by the first three digits in the sequence of Ca, Ba and Cu, while the carboxyl stoichiometry in an oxycarbonate is indicated by the fourth digit. Only part of the data points are marked. The data point marked “*” locates the eutectic composition with the eutectic temperature of ~890°C.

The binary compatibility relationships in air are similar to those in oxygen except that the 021 oxide is absent. A small region of partial melting took place near Ba:Cu = 2:1. For the ternary relations, none of the ternary oxides, namely the 143 and 173 oxides, detected in oxygen is formed in air. Rather, there have been identified oxycarbonates at compositions of Ca:Ba:Cu = 1:4:2, 1:8:3, and 1-x:8:4 with $0 \leq x \leq 0.35$. The FTIR spectra (curves 1–3 in Fig. 4) of these materials showed strong absorptions due to the internal vibration modes, $\nu_1 \sim \nu_4$, of CO₃, which are, as expected, absent in the spectra of the 143 and 173 oxides. The relative intensities and line profiles (asymmetry) of these absorptions are typical of those of oxycarbonates [24] but distinct from those of BaCO₃ (curve 4). Notably, the ν_3 mode of CO₃ in an oxycarbonate shifts toward lower frequency and also becomes either split or asymmetric as compared with that in BaCO₃. Chemical analysis (Elemental Analyzer, Perkin Elmer 2400) gave carbon contents of 1.31, 2.67, 1.91 and 2.18 wt.% for the 1:4:2, 1:8:3, 1:8:4 and 0.65:8:4 oxycarbonates, respectively, which corresponds to the compositions of CaBa₄Cu₂O₆(CO₃) (142-1C), CaBa₈Cu₃O₈(CO₃)₄ (183-4C) and Ca_{1-x}Ba₈Cu₄O_{10-2x}(CO₃)_{3+x}, where $x = 0$ and 0.35 within the instrument's accuracy (± 0.2 wt.%). It was noticed that all these compositions can be expressed in terms of the perovskite-related formula ABO_x with A = Ca, Cu and/or CO₃ and B = Ba.

Table 3

The XRD data of furnace-cooled CaBa₄Cu₂O_{6+δ}(CO₃). Space group ^a: P4/mmm; $a = b = 5.804$ Å, $c = 8.055$ Å

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀
0	0	1	8.055	4	2	0	4	1.654	18
1	0	1	4.709	2	3	1	3	1.515	2
1	1	0	4.104	20	1	1	5	1.499	1
0	0	2	4.027	10	4	0	0	1.451	8
2	0	0	2.902	53	2	2	4	1.437	15
1	1	2	2.875	100	3	3	0	1.368	1
2	0	2	2.354	26	4	0	2	1.365	3
1	1	3	2.247	3	3	1	4	1.357	5
2	2	0	2.052	29	4	2	0	1.298	8
0	0	4	2.014	12	3	3	2	1.295	9
3	1	0	1.836	6	1	1	6	1.276	8
2	2	2	1.828	5	4	2	2	1.235	6
1	1	4	1.808	6	2	0	6	1.218	2
3	1	2	1.670	40					

^a The space group follows that of Kikuchi et al. [15].

The 142-1C oxycarbonate gives XRD data that are consistent with those reported by Kikuchi et al. [15]. Table 3 and Fig. 2(b) show the XRD data of the furnace-cooled 142-1C sample. These data are accounted for by a tetragonal cell with the space group of $P4/mmm$ [15] and lattice constants $a = 5.804$ Å and $c = 8.033$ Å. It was also noticed that the lattice constants were significantly affected by the cooling rate. For instance, the sample quenched from 900°C in air shows a shorter a (5.780 Å) but a longer c (8.084 Å) than the furnace-cooled sample. Similar

results were also noted by Kikuchi et al. and were identified to be caused by different oxygen contents, which is generally greater than 6 O atom/formula unit. On the other hand, care should also be taken to avoid prolonged oxygenation of 142-1C at lower temperatures. For instance, our attempts to oxygenate 142-1C at 700°C in the same air environment for 20 h has been found to cause decomposition, which results in a mixture containing $BaCO_3$, 011 and a third compound of which the composition remains to be identified.

Table 4

The XRD data and refined structural parameters of $CaBa_8Cu_3O_8(CO_3)_4$. Space group: $P4/mmm$; $a = b = 8.154$ Å, $c = 7.931$ Å^a

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀
0	0	1	7.931	11	0	0	5	1.586	1
2	0	0	4.077	28	4	2	3	1.501	4
0	0	2	3.966	13	2	0	5	1.478	1
2	2	0	2.883	57	4	4	0	1.441	8
2	0	2	2.843	100	4	0	4	1.421	11
2	2	2	2.332	32	2	2	5	1.390	2
2	0	3	2.218	9	6	0	0	1.359	2
4	0	0	2.038	28	4	4	2	1.355	3
0	0	4	1.983	10	4	2	4	1.342	6
4	0	1	1.974	2	6	2	0	1.289	8
2	2	3	1.948	1	6	0	2	1.286	8
4	2	0	1.823	9	2	0	6	1.257	6
4	0	2	1.813	9	4	0	5	1.252	2
2	0	4	1.783	9	6	2	2	1.226	7
4	2	2	1.657	37	2	2	6	1.202	2
2	2	4	1.634	13	–	–	–	–	–

		<i>X</i>	<i>Y</i>	<i>Z</i>	Occupancy ^b
Ba	8r	0.25	0.25	0.235	1.0
Cu(1)	1a	0.0	0.0	0.0	1.0
Cu(2)	2f	0.5	0.0	0.0	1.0
Ca	1c	0.5	0.5	0.0	1.0
C(1)	1d	0.5	0.5	0.5	1.0
C(2)	1b	0.0	0.0	0.5	1.0
C(3)	2e	0.5	0.0	0.5	1.0
O(1)	4l	0.238	0.0	0.0	1.0
O(2)	4n	0.239	0.5	0.0	1.0
O(3)	8s	0.076	0.0	0.365	0.25
O(4)	8t	0.424	0.5	0.365	0.25
O(5)	8t	0.076	0.5	0.365	0.25
O(6)	8s	0.424	0.0	0.365	0.25
O(7)	4m	0.151	0.0	0.5	0.25
O(8)	4o	0.348	0.5	0.5	0.25
O(9)	4o	0.151	0.5	0.5	0.25
O(10)	4m	0.348	0.0	0.5	0.25

^a $R_{wp} = 13.2$, $R_p = 9.8$, $R_c = 6.4$, $R_1 = 3.9$, $R_F = 3.0$.

^b The structural model is shown in Fig. 5.

Greaves et al. [14] once reported $\text{CaBa}_4\text{Cu}_{2.24}\text{O}_{6.96}(\text{CO}_3)_{0.5}$, which contains slightly more Cu but less CO_3 than the 142-1C compound. However, it was found that prolonged calcination of the powders having Greave's cation composition resulted in the formation of 142-1C, 011 and CaO. The 142-1C oxycarbonate along with a small amount of CaO accounts for the XRD data that we have previously mistakenly assigned to be “ $\text{CaBa}_2\text{CuO}_4$ ” [4]. The 142-1C oxycarbonate is also believed to be the “142 oxide” that was suggested by Whitler and Roth [10] but not detected by other groups. In their study, Whitler and Roth carried out calcination at tempera-

tures between 900 and 950°C in air. Thus, their samples also likely suffered carboxyl contamination as encountered in this work.

For the other oxycarbonates, namely 183-4C and $(1-x)84 - (3+x)\text{C}$, there has been no reported oxycarbonate carrying similar cation compositions. Comparisons between the XRD patterns of quenched and furnace-cooled samples of these oxycarbonates showed negligible changes in d spacings, suggesting insignificant oxygen loss. The XRD data of the 183-4C can be fitted by a tetragonal cell with lattice constants $a = 8.154 \text{ \AA}$ and $c = 7.931 \text{ \AA}$ (Fig. 2(c) and Table 4). Single-crystal electron-diffraction pat-

Table 5

The XRD data and refined structural parameters of $\text{CaBa}_8\text{Cu}_4\text{O}_{10}(\text{CO}_3)_3$. Space group: $P4/\text{mmm}$; $a = b = 8.117 \text{ \AA}$, $c = 8.121 \text{ \AA}$ ^a

h	k	l	$d (\text{\AA})$	I/I_0	h	k	l	$d (\text{\AA})$	I/I_0
0	0	1	8.122	6	2	2	4	1.658	15
0	0	2	4.061	10	4	2	2	1.657	37
2	0	0	4.058	23	4	2	3	1.508	1
2	0	2	2.871	100	4	0	4	1.435	14
2	2	0	2.870	48	4	4	0	1.435	7
2	2	2	2.343	30	4	2	4	1.353	6
2	0	3	2.252	3	4	4	2	1.353	3
0	0	4	2.030	12	6	0	0	1.353	1
4	0	0	2.029	27	2	0	6	1.284	7
2	2	3	1.969	1	6	0	2	1.284	8
4	0	1	1.969	1	6	2	0	1.283	7
2	0	4	1.816	7	4	0	5	1.268	1
4	0	2	1.815	5	2	2	6	1.224	2
4	2	0	1.815	6	6	2	2	1.224	6
			X	Y				Z	Occupancy ^b
Ba			8r	0.25				0.239	1.0
Cu(1)			1a	0.0				0.0	1.0
Cu(2)			2f	0.0				0.0	1.0
Cu(3)			1d	0.5				0.5	1.0
Ca			1b	0.0				0.5	1.0
C(1)			1c	0.5				0.0	1.0
C(2)			2e	0.5				0.5	1.0
O(1)			4l	0.239				0.0	1.0
O(2)			4n	0.5				0.0	0.75
O(3)			2g	0.0				0.258	1.0
O(4)			4o	0.268				0.5	0.25
O(5)			8t	0.432				0.117	0.25
O(6)			8t	0.068				0.382	0.25
O(7)			8s	0.0				0.382	0.25
O(8)			4n	0.365				0.0	0.25
O(9)			4o	0.135				0.5	0.25
O(10)			4m	0.0				0.5	0.25

^a $R_{\text{wp}} = 11.4$, $R_p = 8.3$, $R_e = 6.3$, $R_1 = 7.8$, $R_F = 5.0$.

^b The structural model is shown in Fig. 6.

terms taken from individual crystallites by using TEM showed 2mm symmetry along both the [110] and the [111] orientation. These results narrow the possible space groups down to one, namely P4/mmm. A structural model that is analogous to the well-established $\text{Sr}_2\text{CuO}_2(\text{CO}_3)$ [24] structure with Sr being replaced by Ba and 25% of Cu within the basal plane orderly replaced by Ca is proposed. Accordingly, as shown in Fig. 5, the cell contains an infinite layer of CO_3 groups separating two layers of Ba ions. The

carbonate group is assumed to have a flag-like configuration and to possess four equal-probability sub-set orientations with the flag-tip pointing to the four equivalent [100] directions. For each orientation, the C atom lies on the $z = \frac{1}{2}$ plane, which also contains one of the oxygen atoms of the carbonate group. The remaining two oxygen atoms, which are located on either side of the plane, point toward either Ca or Cu within the adjacent layers to form apical bonds of distorted CaO_6 and CuO_6 octahedra. Structure re-

Table 6

The XRD data and refined structural parameters of $\text{Ca}_{0.65}\text{Ba}_8\text{Cu}_4\text{O}_{9.3}(\text{CO}_3)_{3.35}$. Space group: P4/mmm; $a = b = 8.081 \text{ \AA}$, $c = 8.012 \text{ \AA}$ ^a

<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀	<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> ₀
0	0	1	8.012	10	0	0	5	1.602	1
2	0	0	4.040	25	4	2	3	1.497	4
0	0	2	4.006	14	2	0	5	1.489	2
2	2	0	2.857	59	4	4	0	1.429	9
2	0	2	2.845	100	4	0	4	1.422	13
2	2	2	2.326	34	2	2	5	1.398	2
2	0	3	2.228	9	6	0	0	1.347	2
4	0	0	2.020	28	4	4	2	1.345	3
0	0	4	2.003	11	4	2	4	1.342	5
4	0	1	1.959	2	6	2	0	1.278	8
2	2	3	1.951	2	6	0	2	1.276	8
4	2	0	1.807	8	2	0	6	1.268	6
4	0	2	1.804	8	4	0	5	1.255	2
2	0	4	1.794	7	6	2	2	1.217	6
4	2	2	1.647	38	2	2	6	1.210	2
2	2	4	1.640	15	–	–	–	–	–
			X	Y				Z	Occupancy ^b
Ba			8r	0.25				0.232	1.0
Cu(1)			1a	0.0				0.0	1.0
Cu(2)			2f	0.5				0.0	1.0
Cu(3)			1d	0.5				0.5	1.0
Ca/C			1b	0.0				0.5	0.65/0.35
C(1)			1c	0.5				0.0	1.0
C(2)			2e	0.5				0.5	1.0
O(1)			4l	0.254				0.0	1.0
O(2)			4n	0.261				0.0	0.75
O(3)			2g	0.0				0.258	0.65
O(4)			4o	0.268				0.5	0.25
O(5)			8t	0.417				0.143	0.25
O(6)			8t	0.083				0.357	0.25
O(7)			8s	0.0				0.357	0.25
O(8)			4n	0.335				0.0	0.25
O(9)			4o	0.166				0.5	0.25
O(10)			4m	0.0				0.5	0.25
O(11)			8s	0.083				0.357	0.0875
O(12)			4m	0.166				0.5	0.0875

^a $R_{\text{wp}} = 14.5$, $R_p = 10.8$, $R_e = 6.4$, $R_1 = 5.4$, $R_F = 3.0$.

^b The structural model is shown in Fig. 6.

Fig. 4. FTIR spectra of oxycarbonates, showing ν_1 – ν_4 modes of the carboxyl ion. Curve (1) is for 184-3C; (2) for 183-4C; (3) for 142-1C; and (4) for BaCO_3 .

finement has been carried out for the positions of Ba and oxygen and the results are summarized in Table 4.

The XRD data of 184-3C, as shown in Fig. 2(d) and Table 5, can be indexed within instrument's resolution either with a cubic cell having $a = 8.115$ Å or with a tetragonal cell having $a = 8.117$ Å and

Fig. 5. Structural model of $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$ (183-4C). Only one of the four configurations of each CO_3 flag is shown for clarity.

Fig. 6. Structural model of $\text{CaBa}_8\text{Cu}_4\text{O}_{10}(\text{CO}_3)_3$ (184-3C, $x = 0$). Only one of the four configurations of each CO_3 flag is shown for clarity.

$c = 8.121$ Å. However, as Ca is increasingly substituted by CO_3 , i.e., as x increases in the $(1-x):8:4:3+x$ formula, the tetragonal cell becomes increasingly apparent (Fig. 2(e) and Table 6). Thus, the tetragonal cell is adopted for indexing the XRD data of the solid solutions (Tables 5 and 6). Electron-diffraction patterns along $[110]$ and $[111]$ again confirmed the space group to be $P4/mmm$. A structural model that gives fairly good fitting of these data is shown in Fig. 6 and the associated structure parameters are summarized in Table 5. In this model, CO_3 flags are located at the six face-center positions and all have the four-fold symmetry axis parallel to the c -axis. The Ca atoms are placed in alternating sequence with carbonate groups within the $z = \frac{1}{2}$ plane so as to avoid direct connection between carbonates when part of Ca is substituted by carbonate group in the $x > 0$ phases. At the center of the cell, we assume there to be a distorted CuO_4 square so that the total oxygen content corresponds to the case of divalent copper. The assumption of a distorted CuO_6 octahedron at this position gives an average valence of copper of 3.0, which will be too high. Alternative models assuming either complete replacement between Cu(1) and Ca or partial mutual substitution of Ca/Cu and of Ca/Ba systematically result in worse fitting.

The XRD data of the $x > 0$ phases can also be accounted for with good fitting by the same structure model assuming random substitution of Ca by car-

bonate group. For instance, Table 6 lists the refined structural parameters of the $x = 0.35$ phase. With increasing CO_3 substitution for Ca, the lattice constants a and c decreases. This is expected from the model.

The 184-3C phase has the same cation composition as the end member ($y = 0$) of the solid solution $\text{Ca}(\text{Ba}_{1-y}\text{Ca}_y)_8\text{Cu}_4\text{O}_{13+z}$ proposed by Hamada et al. [11], who carried out calcination in air with BaCO_3 , CaCO_3 , CuO as precursor. However, our attempts to vary the Ba and Ca contents based on Hamada's formula with $y < 0.1$ resulted in mixtures containing either 142-1C, 184-3C, and 011 in air or 143, 173 and 021 in oxygen.

The thermal stabilities of these ternary oxycarbonates were investigated by heating them at increasing temperatures from 900 to 1000°C with an increment of 20°C and a treatment period of ~ 20 h at every selected temperature. The 142-1C oxycarbonate was found to have the highest thermal stability and remains stable at 1000°C in air. The 183-4C oxycarbonate decomposes at 920°C, resulting in 184-3C as the major product. For the solid solutions $(1-x)84-(3+x)\text{C}$ ($x = 0-0.35$), all the phases with $x > 0$ decompose between 920 and 940°C to give the $x = 0$ phase as the major product. The decomposition of the $x = 0$ phase in air commenced at 940°C and became extensive at 960°C, resulting in the 143 and 173 oxides and a small extent of powder melting. These results again confirm the existence of the 173 oxide, rather than the 163 oxide. That is, if 163 oxide existed, the decomposition products would not contain 143 oxide.

Comparisons among the decomposition temperatures of these oxycarbonates established a trend suggesting that the oxycarbonate is less stable as the carboxyl content increases. For instance, the decomposition temperature decreased from above 1000°C for the lowest carboxyl content of $3.7 \times 10^{-3} \text{ \AA}^{-3}$ in 142-1C to below 920°C for the highest one of $7.5 \times 10^{-3} \text{ \AA}^{-3}$ in 183-4C. An increase in temperature under a fixed CO_2 partial pressure results in a decrease in the chemical potential of CO_2 . Thus, the trend can be simply interpreted in terms of an oxycarbonate with a higher carboxyl content requiring a higher CO_2 chemical potential to stabilize it. Consequently, at CO_2 chemical potentials higher than that in this work, one expects the decomposition tempera-

tures of these oxycarbonates to increase and anticipates the possibility of the existence of an additional oxycarbonate having a higher carboxyl content than the 183-4C phase.

The appearance of the 173 and 143 oxides as the major products from the decomposition of 184-3C phase in air suggested that these oxides are stable at $950(\pm 10)^\circ\text{C}$ in air. This is confirmed in separate experiments by forming 143 and 173 powders under these conditions. Furthermore, BaCO_3 also becomes unstable above 920°C. Thus, one can envision that, as temperature increases, and hence the CO_2 chemical potential falls between that in air and essentially zero in flowing oxygen, the phase diagrams in air and oxygen established at 900°C (Figs. 1 and 3) begin to merge. At $\sim 950^\circ\text{C}$ in air, there exist only three ternary solids, namely the 143 and 173 oxides and the 142-1C oxycarbonate.

4. Conclusion

In an attempt to resolve the sub-solidus relations in CaO-BaO-CuO , we noticed a tremendous impact from the minute amount of CO_2 present in the natural air. The sub-solidus relations were established at temperatures between 900 and 1000°C in both oxygen and air. In oxygen, there are identified pseudo-ternary oxides including $\text{CaBa}_4\text{Cu}_3\text{O}_{8+x}$, $\text{CaBa}_7\text{Cu}_3\text{O}_{11}$ and $\text{Ba}_{1-y}\text{Ca}_y\text{CuO}_2$ solid solutions. In contrast, in air, which contains ~ 450 ppm of CO_2 , there are identified several oxycarbonates, including $\text{CaBa}_4\text{Cu}_2\text{O}_{6+\delta}(\text{CO}_3)$, $\text{CaBa}_8\text{Cu}_3\text{O}_8(\text{CO}_3)_4$, and $\text{Ca}_{1-x}\text{Ba}_x\text{Cu}_4\text{O}_{10-2x}(\text{CO}_3)_{3+x}$ solid solutions, of which some bear the same cation compositions as the ternary "oxides" reported in the literature. Studies on the thermal stabilities of these oxycarbonates indicate the strong dependence of the sub-solidus relations on the chemical potential of CO_2 , suggesting the need for a better controlled and characterized environment when one is dealing with material processing involved in this pseudo-ternary system.

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