

On the ternary compounds of the BaO-CaO-CuO system

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Abstract. The crystal structure and the stability of the two ternary compounds $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ and $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t}$ have been investigated by means of X-ray diffraction, differential thermal analysis and thermogravimetry analysis. We find that the $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ phase has a cubic structure ($Im\bar{3}m$, $a = 8.1515(1) \text{ \AA}$ for $t = + 0.8$) for an oxygen content in the range 8.7-9.3 as reported in the literature but undergoes a transformation into a tetragonal structure ($I4/mmm$, $a = 8.1888(1) \text{ \AA}$, $c = 8.0634(1) \text{ \AA}$ for $t = - 0.3$) when the oxygen content is lowered (7.7-8.7). Both $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ and $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t}$ phases are metastable at low temperature in $p(\text{O}_2) = 1$ bar. The DTA/TGA curves indicate an equilibrium recovery between 300°C and 400°C corresponding to the decomposition into BaO_2 , CaO and $\text{Ba}_2\text{Cu}_3\text{O}_6$.

Résumé. La structure cristallographique et la stabilité des deux composés ternaires $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ et $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t}$ ont été étudiées par diffraction des rayons X, analyse thermique différentielle et analyse thermogravimétrique. Nous trouvons que la phase $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ a une structure cubique ($Im\bar{3}m$, $a = 8.1515(1) \text{ \AA}$, $t = + 0.8$) pour des contenus en oxygène élevés (8.7-9.3) comme cela est reporté dans la littérature mais subit une transition vers une structure tétragonale ($I4/mmm$, $a = 8.1888(1) \text{ \AA}$, $c = 8.0634(1) \text{ \AA}$, $t = - 0.3$) lorsque ce contenu est diminué (7.7-8.7). Ces deux composés ternaires sont métastables à basse température sous $p(\text{O}_2) = 1$ bar. Les courbes d'ATD/TG indiquent en effet un retour à l'équilibre entre 300°C et 400°C qui correspond à une décomposition en BaO_2 , CaO et $\text{Ba}_2\text{Cu}_3\text{O}_6$.

1 INTRODUCTION

The fabrication of the Tl-based high- T_c superconducting cuprates $\text{Tl}_k\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_9$ ($k = 1$ or 2) with optimised and reproducible properties requires a thorough knowledge of the complex $\text{TlO}_{1.5}$ -BaO-CaO-CuO system and of its numerous subsystems. Most of them have been studied or revisited by our group ([1] and references therein). This article is devoted to the ternary compounds of the BaO-CaO-CuO system. Previous studies [2-5] have shown the existence of two ternary phases: $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ (413) with a cubic structure ($Im\bar{3}m$, $a = 8.12 - 8.15 \text{ \AA}$) and $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t}$ (613) with a tetragonal structure ($I4/mmm$, $a = 4.055 \text{ \AA}$, $c = 21.605 \text{ \AA}$). These studies also revealed a possible substitution of Ba by Ca in BaCuO_2 up to 10 at.% and 8 three-phase fields in the 900°C isothermal section of BaO-CaO-CuO ($p(\text{O}_2) = 1$ bar) implying 413, 613, BaCuO_2 , Ca_2CuO_3 and $\text{Ba}_2\text{Cu}_3\text{O}_{3+t}$. In this article, we present original results on the crystal structure of 413 and on the stability of both 413 and 613.

2 EXPERIMENTAL

Bulk samples with composition equal or close to Ba:Ca:Cu = 4:1:3 and Ba:Ca:Cu = 6:1:3 have been prepared by solid state reaction in open system at 950°C and 900°C from BaO₂, CuO and pre-fired CaO. About 100 hours at high temperature with intermediate grindings were necessary to obtain pure 413 and 85% pure 613 in both flowing oxygen or nitrogen. Because of the existence of many oxy-carbonates with Ca, Ba and Cu as metal atoms [5,6], infrared spectroscopy was used to detect the possible presence of CO₃ groups. None of our samples was found contaminated. The powders quickly deteriorate when exposed to moisture. They are initially black but become green or dark brown and significantly increase in volume after a few minutes in ambient air with Ba(OH)₂ as one of the decomposition products. However the samples can be stored for at least a few months in a desiccating apparatus. Routine X-ray diffraction (XRD) collections for powder control after each sintering step were performed using a powder diffractometer (Co K ζ) equipped with a position sensitive detector INEL-CPS 120. The powders were placed in an evacuated chamber to avoid contact with ambient moisture. Additional X-ray data were collected for Rietveld analysis on a Philips PW1050 powder goniometer with Bragg-Brentano geometry (Cu K ζ , graphite monochromator, room temperature, 20° Ω 2 χ Ω 85°, 0.03° 2 χ step). A PE film was used to protect the powders from moisture during data collection. The crystal structures were refined using the program Fullprof [7]. Differential thermal analyses (DTA) and thermogravimetry analyses (TGA) were also conducted in both flowing oxygen and nitrogen using a SETARAM TGA 92 apparatus. The ceramic pieces, about 60 mg in weight, were analysed between 20°C and 1250°C with a heating rate of 10 K/min in Al₂O₃ crucibles.

3 RESULTS AND DISCUSSION

3.1 Crystal structure of Ba₄CaCu₃O_z

The sample with nominal composition Ba₄CaCu₃O_z sintered in flowing oxygen (413-O₂) was found to contain only the 413 phase and its diffraction pattern was satisfactorily indexed using a cubic unit cell with $a = 8.15$ Å. Its crystal structure was refined using the published parameters [2,4] as input parameters and the final result was found very close to the starting point (Table 1). The crystal structure of 413 is derived from the perovskite-type structure: the large barium atoms occupy the twelve-fold coordinated sites while the calcium and copper atoms occupy the six-fold coordinated sites in an ordered manner which gives rise to the eight-fold superstructure ($2a, 2a, 2a$) with respect to the standard perovskite cell (Fig. 1). The calcium atoms have six neighbouring oxygen atoms located in fully occupied equivalent positions (O1 site). In contrast, the copper atoms have two oxygen neighbours in fully occupied positions (O1 site) and four others in half occupied positions (O3 site). In short, O sites located between Cu sites are only half occupied. The refined oxygen content is 8.82(18) in good agreement with the result of Kubat-Martin *et al.* [4]. Selected interatomic distances reported in Table 2.

The diffraction pattern of the Ba₄CaCu₃O_z sample sintered in flowing nitrogen (413-N₂) could not be indexed in the above mentioned cubic cell. Some reflections are split into two or three peaks whereas some others remain unchanged. This is explained by a slight tetragonal distortion. A structure model was therefore derived in space group $I4/mmm$. The structure refinement resulted in a rather good agreement between observed and calculated patterns as can be seen from Table 1 and Fig. 2. The main difference with the cubic structure lies in the reduced occupancy of some oxygen sites which is reflected in the overall oxygen content, 7.73(34), and in the cation coordination. Selected interatomic

distances and average coordination numbers are reported in Table 2. It should be mentioned that the tetragonal distortion ($a-c$)/ a strongly depends on the sintering conditions. It is all the more pronounced than the oxygen partial pressure is reduced. It may happen that, with standard quality nitrogen ($p(\text{O}_2) < 2 \cdot 10^{-6}$ atm.), the distortion be extremely small and hardly detectable. With a titanium sponge placed on the gas path in order to reduce $p(\text{O}_2)$ during sintering, the distortion is maximised. The average valence state for copper atoms deduced from the refined oxygen content (7.73 in 413-N₂ and 8.82 in 413-O₂) is 1.8 and 2.6 in 413-N₂ and 413-O₂, respectively.

Table 1. Refinement results for 413-O₂ and 413-N₂. Omitted occupancies are equal to 1.

	413-O ₂	413-N ₂
$R_{wp}(\%)$	7.04	7.70
θ^2	1.60	2.01
Main phase	Cubic 413 <i>Im-3m</i> , $Z = 2$	Tetragonal 413 <i>I4/mmm</i> , $Z = 2$
Refined Cp.	Ba ₄ CaCu ₃ O _{8.82}	Ba ₄ CaCu ₃ O _{7.73}
a (Å)	8.1515(1)	8.1888(1)
c (Å)	-	8.0634(1)
$R_{\text{Bragg}}(\%)$	2.85	3.10
Ba1	8(<i>c</i>)	8(<i>f</i>)
Ba2	-	-
Ca	2(<i>a</i>)	2(<i>a</i>)
Cu1	6(<i>b</i>)	2(<i>b</i>)
Cu2	-	4(<i>c</i>)
O1	12(<i>e</i>), $x = 0.272(5)$	8(<i>i</i>), $x = 0.288(4)$
O2	-	4(<i>e</i>), $z = 0.275(7)$, occ = 0.84(6)
O3	12(<i>d</i>), occ = 0.47(3)	4(<i>d</i>), occ = 0.13(5)
O4	-	8(<i>j</i>), $x = 0.24(2)$, occ = 0.45(3)

Table 2. Interatomic distances in the structure of 413 with the average coordination numbers (ACN).

413-O ₂	413-N ₂
Ba-O1 2.89(2)x6	Ba-O1 2.89(2)x4
Ba-O2 2.882(0)x6x0.47	Ba-O2 2.903(4)x2x0.84
ACN(Ba) = 8.82	Ba-O3 2.895(0)x2x0.13
Ca-O1 2.21(3)x6	Ba-O4 2.873(0)x4x0.45
ACN(Ca) = 6	ACN(Ba) = 6.84
Cu-O1 1.86(3)x2	Ca-O1 2.36(3)x4
Cu-O2 2.038(0)x4x0.47	Ca-O2 2.22(6)x2x0.84
ACN(Cu) = 3.88	ACN(Ca) = 5.68
	Cu1-O2 1.81(6)x2x0.84
	Cu1-O4 2.047(0)x4x0.45
	ACN(Cu1) = 3.48
	Cu2-O1 1.737(0)x2
	Cu2-O3 2.016(0)x2x0.13
	Cu2-O4 2.047(0)x2x0.45
	ACN(Cu2) = 3.16

3.2 Phase stability

Differential thermal analyses combined with thermogravimetry analyses were performed on 413 and 613 ceramic pieces in both flowing oxygen and nitrogen. Fig. 3 shows the resulting curves for the tetragonal 413 phase in $p(\text{O}_2) = 1$ bar. Between 300°C and 400°C, one can clearly see two exothermic peaks in the DTA curve associated with significant weight gains due to oxygen uptake. Such thermal

events are usually attributed to equilibrium recoveries which means that the 413 phase is not stable at low temperature under $p(\text{O}_2) = 1$ bar. The first peak with an onset at 300°C is associated to the transformation from tetragonal 413 to cubic 413 as demonstrated by high temperature XRD experiments not shown here. The second peak with a larger weight gain and also a larger heat flow is due to the decomposition of 413 according to the following reaction:



The equilibrium below 700°C involves therefore BaO_2 , CaO and $\text{Ba}_2\text{Cu}_3\text{O}_6$ and not the 413 phase. This is confirmed by the long annealing of a 413 sample at 600°C in flowing oxygen. The BaO_2 - BaO - CaO - CuO quaternary system (Fig. 4) has to be considered here because of the reversible reaction $\text{BaO}_{2-x} \rightleftharpoons \text{BaO}_{1+y} + [1-(x+y)]/2 \text{ O}_2$ in oxygen. If we make the assumption that the overall oxygen content is O_8 just before melting (Cu atoms in oxidation state +2), then its value after the second exothermic peak is O_{11} which is consistent with the reaction given above. The values computed before and just after the first exothermic peak indicate that the tetragonal form of the 413 phase can accommodate up to 8.7 O atoms while the oxygen content for the cubic form is in the range 8.7 – 9.3. It is deduced that the oxidation state of copper covers the range 1.8-2.9.

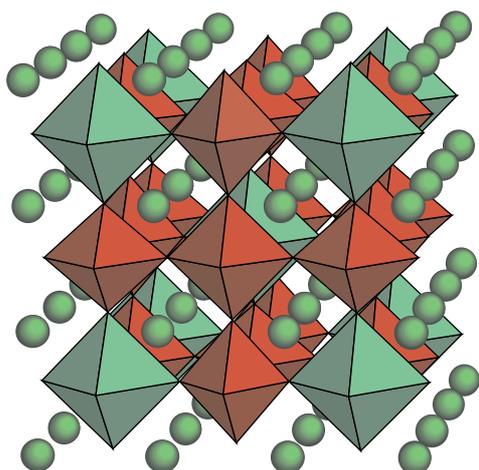


Figure 1. Schematic representation of the structure of cubic 413. CuO_6 octahedrons: dark grey. CaO_6 octahedrons: light grey.

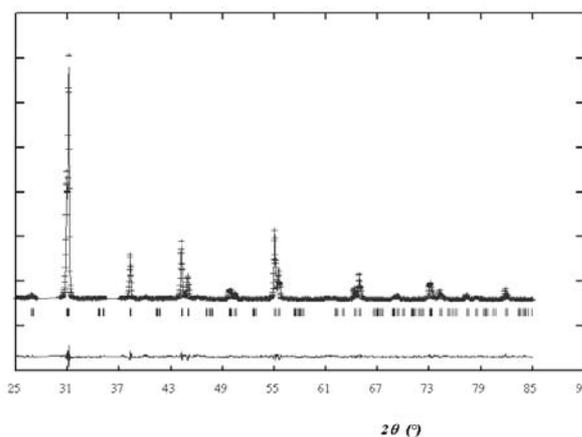


Figure 2. Observed, calculated and difference patterns for 413- N_2 . Regions with peaks due to PE (see text) were excluded from the refinement.

The small oxygen losses between 420°C and 700°C are attributed to a gradual decrease of the oxygen content in BaO_2 and/or $\text{Ba}_2\text{Cu}_3\text{O}_6$. Above 700°C , BaO_2 is not stable anymore in $p(\text{O}_2) = 1$ bar and the endothermic peak associated with large oxygen losses is attributed to the formation of cubic 413 from BaO_{2-x} , CaO and $\text{Ba}_2\text{Cu}_3\text{O}_{5+t}$. The reaction temperature is 717°C . The second endothermic peak at 778°C corresponds to the transformation from cubic to tetragonal 413. Finally melting occurs at 1157°C and is congruent in nature. In summary, tetragonal 413 is stable between 1157°C and 778°C and cubic 413 between 778°C and 717°C , temperature of its eutectoid decomposition. However the 413 phase can be easily obtained at room temperature as a metastable phase in $p(\text{O}_2) = 1$ bar. The equilibrium with the oxygen gas is not reached when the ceramics are well-sintered so that only the structure transformations occur. For the same reason, the equilibrium recovery leading to the phase decomposition may not occur during a DTA/TGA experiment. This is illustrated in Fig. 5 for a sample

initially prepared in nitrogen. The same phenomenon was observed for $\text{Ba}_2\text{CuO}_{3+t}$ [9]. In an inert atmosphere, DTA/TGA show that the tetragonal form of 413 is stable from RT up to 1090°C.

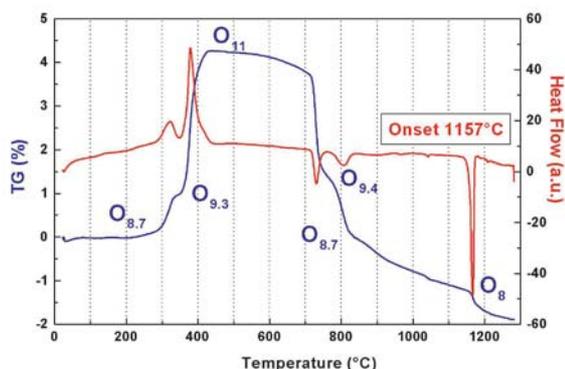
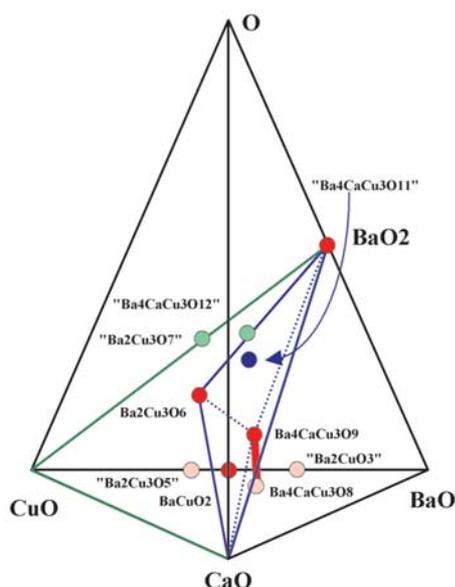
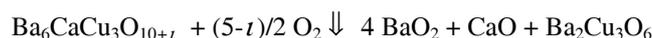


Figure 3. DTA/TGA of a tetragonal 413 ceramic. The overall oxygen content is computed assuming that copper ions are in +2 oxidation state just before melting at 1157°C.

Figure 4. Composition pyramid showing the three phase field ($\text{BaO}_2\text{-CaO-Ba}_2\text{Cu}_3\text{O}_6$) involved in the low temperature decomposition of 413 in $p(\text{O}_2) = 1$ bar (equilibrium recovery). The fixed oxygen partial pressure imposes a three solid phase equilibrium which is effectively observed.



The behaviour of 613 is very similar to that of 413. In flowing oxygen (Fig. 6), an equilibrium recovery also occurs at about 400°C. It corresponds to the decomposition:



which is consistent with a maximum O content of 15 at 450°C. Above 700°C, several endothermic reactions indicate changes in equilibrium domains. In particular, the first one with an onset at 710°C is believed to correspond to the formation of the 613 phase. The nature of the three others, with onsets at 823°C, 996°C and 1072°C, respectively, is not fully understood but the possible temperature range for the sintering of 613 indicates that the peak at 996°C could be associated with the reaction $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t} \downarrow 2 \text{BaO}_{1+y} + \text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$, so that the 823°C event would correspond to some structure transformation of 613. Finally the 1155°C event corresponds to complete melting. It is therefore believed that, in $p(\text{O}_2) = 1$ bar, the 613 phase is stable between 996°C, temperature of its peritectoid formation, and 710°C, temperature of its eutectoid decomposition. Under flowing nitrogen, the 613 phase is stable below 920°C-930°C, temperature of the decomposition into 413 and BaO_{1+y} .

These results illustrate the importance of the reversible reaction $\text{BaO}_{2-x} \leftarrow \text{BaO}_{1+y} + [1-(x+y)]/2 \text{O}_2$ in the stability of Ba-containing oxides in the presence of oxygen. In the complex $\text{TlO}_{1.5}\text{-BaO-CaO-CuO}$ system, all phases in which barium is the main metallic element, are not equilibrium phases below 700°C in $p(\text{O}_2) = 1$ bar: $\text{Tl}_2\text{Ba}_4\text{O}_7$ [9], $\text{Ba}_2\text{CuO}_{3+t}$, $\text{Ba}_4\text{CaCu}_3\text{O}_{8+t}$ and $\text{Ba}_6\text{CaCu}_3\text{O}_{10+t}$. The reaction mentioned above should therefore be considered in the study of higher order systems as it may influence the equilibrium states and the local oxygen content of the phases under investigation [1].

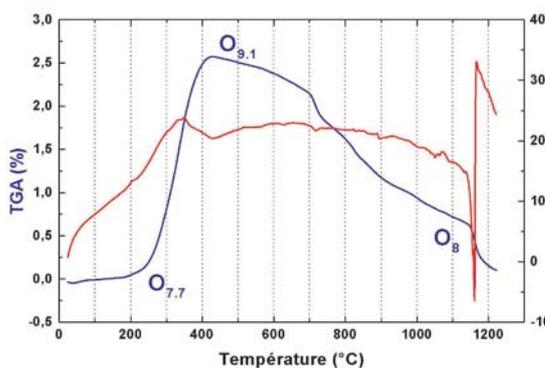


Figure 5. DTA/TGA curves of a well-sintered tetragonal ceramic in O_2 . The transformation to the cubic form of 413 is observed but not the low temperature decomposition into BaO_2 , CaO and $Ba_2Cu_3O_6$.

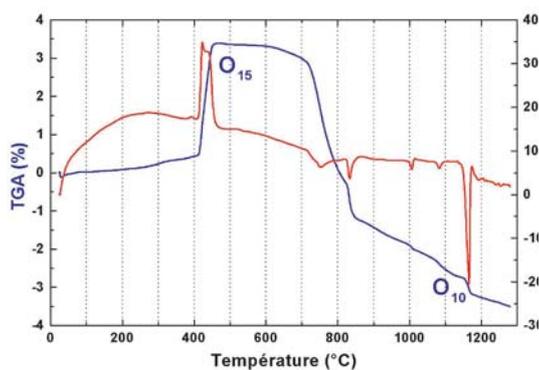


Figure 6. DTA/TGA of curves of a 613 ceramic in O_2 . The equilibrium recovery associated with large weight gains corresponds to the decomposition into BaO_2 , CaO and $Ba_2Cu_3O_6$.

4 CONCLUSION

The study of the two ternary compounds $Ba_4CaCu_3O_{8+l}$ (413) and $Ba_6CaCu_3O_{10+l}$ have shown that (i) 413 has two different crystal structures depending on the oxygen content, (ii) the average valence for copper atoms varies from 1.8 to 2.9 and (iii) both phases are metastable below $700^\circ C$ in $p(O_2) = 1$ bar. They undergo an eutectoid decomposition at this temperature because of the great stability of the BaO_2 phase: $413/613 \Downarrow BaO_2 + CaO + Ba_2Cu_3O_6$.

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