

THE FORMATION OF THE $\text{Ba}(\text{CuO}_x)_{1-y}(\text{CO}_3)_y$ A new phase in the Ba–Cu–C–O system: thermal analysis results

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Abstract

Carbocuprate compounds are generally described as multiple perovskites with CO_3^{2-} and Cu–O alternating layers containing Ba and/or Sr; they have gained an unexpected importance in the high temperature superconductivity field, because many compounds with transition temperature above 100 K belong to this class of materials.

We have started a systematic study on phase formation and stabilisation in the Ba–Cu–C–O system in the temperature range 20–600°C, by using thermal analysis techniques. Starting from a BaCO_3 – BaO_2 –CuO mixture (3:1:1 mol), a new phase isomorphic with BaCO_3 formed after heat treatment above 390°C in air. TG, DSC, EGA and high temperature XRD were employed to follow the complex interaction of the reactants with the atmosphere and the formation of the new phase.

Keywords: Ba–Cu–C–O system, carbocuprate compounds, isomorphic BaCO_3 new phase

Introduction

Since the discovery of copper oxycarbonates with layered perovskite structure [1] and, very soon after, of high T_c superconductivity in many of these compounds [2], a lot of studies have been devoted to this new class of materials.

One of the most striking findings is related to the observation that, in some barium based copper oxycarbonates, copper and carbon (i.e., cuprate CuO_x and carbonate CO_3 groups respectively), show the tendency to occupy the same crystallographic sites. This unexpected behaviour has been found both in layered perovskite materials like $\text{Ba}_4\text{CuNa}(\text{CO}_3)_2\text{O}_4$ [3] or $\text{Ba}_2\text{Cu}_{1.25}(\text{CO}_3)_{0.75}\text{O}_{2+8}$ [4], and in non-perovskite materials, like the well-known $\text{BaCuO}_{2+\delta}$ compounds where it has been shown that carbonate groups substitute up to 10% of the copper ions [5]. The structural affinity of cuprate and carbonate groups in barium compounds has induced to a deeper consideration of many unclear phenomena that had occurred over the course of the past studies. In particular we have ob-

served by High Temperature XRD (HTXRD) that compounds like $\text{BaCu}_{1.25}(\text{CO}_3)_{0.75}\text{O}_{2+\delta}$ are metastable and decompose at about 400°C . The decomposition products exhibit a XRD pattern that is almost identical to that of BaCO_3 and shows no traces of copper-containing crystalline phases. Moreover, its colour varies from brownish dark grey to black. Techniques sensible to locally ordered structures, like IR absorption, Raman spectroscopy or High Resolution Electron Microscopy, reveal that this material has an extremely peculiar structure: a) the unit cell size and average symmetry are identical to those exhibited by BaCO_3 ; b) the barium atoms are arranged exactly in the same way as in BaCO_3 ; c) the grains have a microdomain structure with typical fully ordered dimension of 100\AA ; d) copper substitutes a large fraction of carbonate anions.

A more detailed description of the new phase is being reported elsewhere [6]. Figure 1 shows a TEM high resolution image of a typical 'black BaCO_3 ' grain. The domain structure is evident. Some of the domains show an alterna-

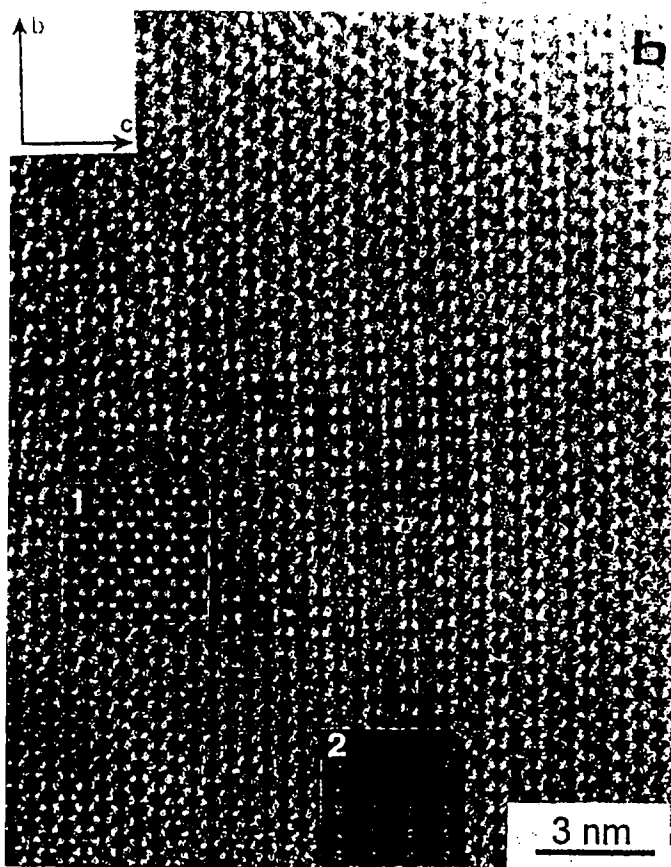


Fig. 1 TEM high resolution image of barium carbonate (1) and cuproaragonite (2)

tion of bright and dark rows, indicating a variation of the electronic density along the columns perpendicular to the plane of the image (the crystallographic plane a, b of the BaCO₃ structure). This is a univoque sign of CuO_x substituting for CO₃ columns. From the same image it can be deduced that the order parameter is smaller than the length of the domains, as it seems that the density of copper-rich columns is almost random.

With such a disordered microstructure, very little information can be extracted from the standard structural techniques based on diffraction. As a matter of fact, all the attempts to refine the "black BaCO₃" structure resulted in no difference with respect to pure BaCO₃. As the copper sublattice is ordered only over the range of very few unit cells, it simply does not contribute to the coherent scattering of X-rays or neutrons but mostly to the incoherent background radiation. On the other hand neither optical techniques nor TEM analysis can solve the problem of whether the new phase (corresponding to the general formula: Ba(CuO_x)_{1-y}(CO₃)_y ($0 < y < 0.6$), named barium-cuprocarbonate) forms at the surface of the BaCO₃ grains or in the bulk of the material. In this frame we have started a systematic study on phase formation and stabilisation in the Ba-Cu-C-O system in the temperature range 20–600°C, by using thermal analysis techniques.

Experimental

The present results have been obtained using BaCO₃ (99.98%), CuO (99.99%) and BaO₂ (95–97%) powders. The low degree of purity of the barium peroxide is mainly due to the unavoidable presence of decomposition products of the unstable barium oxide fraction, that is in equilibrium with the peroxide during its synthesis. In particular, we have estimated a 2% content of BaCO₃ (by absorption of evolved CO₂ on ascarite) and the rest of impurities are unidentified hydrate compounds (Ba(OH)₂+nH₂O).

Pure reagents and their binary and ternary mixtures with different molar ratios have been analysed by TG, DSC and EGA (Evolved Gas Analysis) and powder HTXRD in air (static or flowing) and in the temperature range 20–600°C.

All the thermal treatments related to TG, DSC and EGA experiments have been performed placing about 100 mg of sample in pure alumina crucibles. TG and DSC measurements were carried out using Perkin-Elmer series 7 TG/DSC automatic system.

EGA measurements were obtained during the TG experiments sampling the atmosphere, just above the sample with respect to the gas flow direction, through a stainless steel capillary (Balzers gas inlet system GES-010) connected to a vacuum system; the sampled gas was pumped down to the working pressure ($\ll 10^{-4}$ mbar) of a 100 a.m.u. quadrupole gas analyser (Inficon Trans- pector C100F).

XRD analysis at various temperature (HTXRD), was used to study the structure of the developed phases and establish their stability field as a function of temperature. The HTXRD Θ - 2Θ patterns have been collected using a Rigaku III D-max powder diffractometer, equipped with a high temperature attachment, using $\text{CuK}\alpha$ radiation produced at 40 kV, 40 mA; the Ni-Al furnace shields acted as $\text{CuK}\beta$ filter. The samples have been placed in a platinum sample holder kept in vertical position in static or flowing dried natural air. After a short transient due to the heating stage, the temperature control during isothermal measurements was better than $\pm 2^\circ\text{C}$. In order to reduce the scanning time and better follow the kinetics of the transformations, the scans have been limited to the interval $20^\circ < 2\Theta < 40^\circ$ where the main reflections of the involved phases are found.

Results and discussion

In order to understand the chemical reactions that develop in the Ba-Cu-C-O system, a series of DSC/TG was carried out in dry air, on a series of pure chemical compounds and mixtures. Among the different mixtures tested, in the present paper we show only the results for the compositions that have demonstrated the most significant thermal effects. The DSC results are reported in Fig. 2. As significant weight changes were not observed, TG curves are not pre-

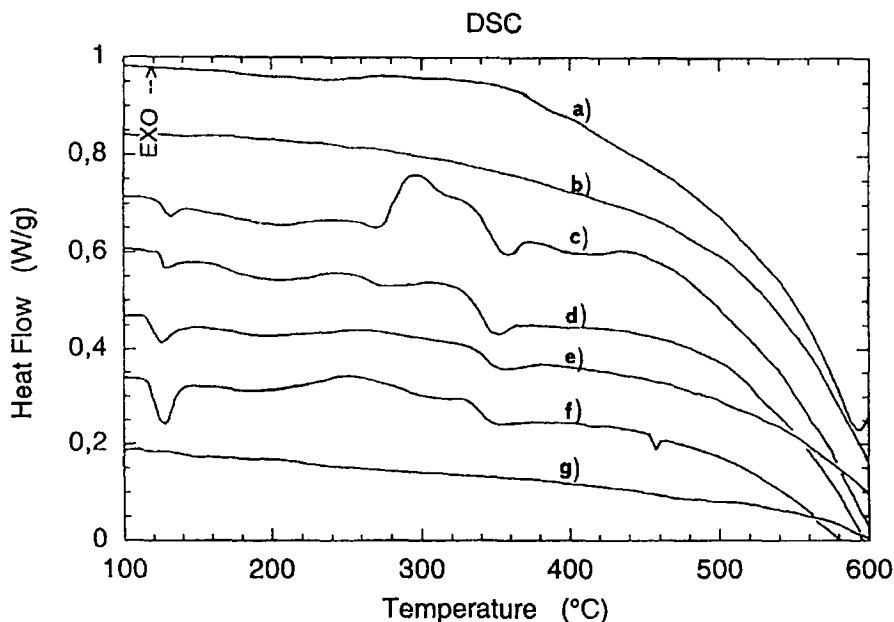


Fig. 2 DSC in air at $30^\circ\text{C min}^{-1}$ for pure samples and mixtures at different molar ratio: a) BaCO_3 -CuO (1:0.5); b) BaCO_3 ; c) BaO_2 -CuO (1:1); d) BaO_2 -CuO (1:0.5); e) BaO_2 - BaCO_3 (1:1); f) BaO_2 ; g) CuO

sented. The BaO_2 powder shows large thermal effects during DSC, probably due to impurities. In particular, at about 115°C is well evident the onset of an endothermic effect connected to crystallisation water loss. The following exothermic effect between $200\text{--}310^\circ\text{C}$ is connected to atmosphere reactions involving barium ions and oxygen or carbon dioxide. The weak endothermic effect at 450°C (melting point of BaO_2) suggests the presence of only a small amount of crystalline phase. This can explain the DSC curve inflection between $325\text{--}343^\circ\text{C}$ as due to glass transition of the BaO_2 powders. XRD analysis carried out at 400°C confirms this hypothesis: there are no reflections of crystalline BaO_2 . The absence of evident thermal effects during DSC of BaCO_3 , CuO , and $\text{BaCO}_3\text{--CuO}$ (1:0.5 mol), demonstrates their thermal stability. The DSC of $\text{BaO}_2\text{--BaCO}_3$ (1:1 mol) shows only the thermal effects due to the BaO_2 presence; this indicates that these two phases do not react in the tested temperature range.

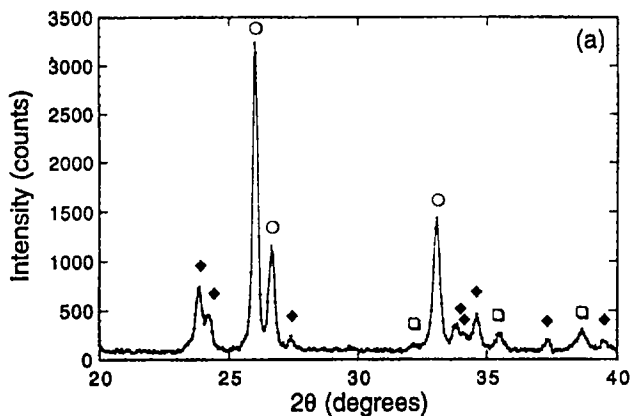


Fig. 3a X-ray diffraction pattern of $\text{BaCO}_3\text{--BaO}_2\text{--CuO}$ mixture (3:1:1 mol) in air at 300°C . BaCO_3 (♦), BaO_2 (○) and CuO (□)

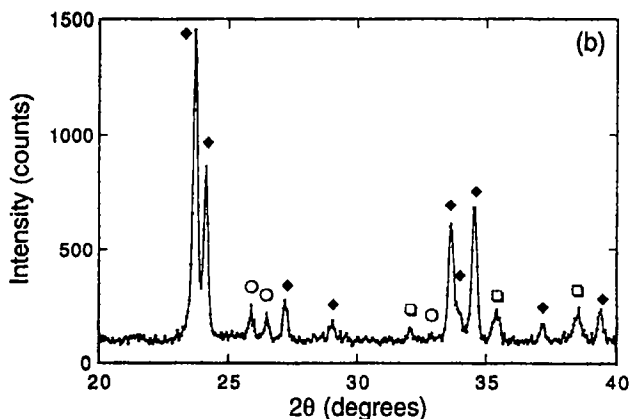


Fig. 3b X-ray diffraction pattern of $\text{BaCO}_3\text{--BaO}_2\text{--CuO}$ mixture (3:1:1 mol) in air at 400°C . BaCO_3 (♦), BaO_2 (○) and CuO (□)

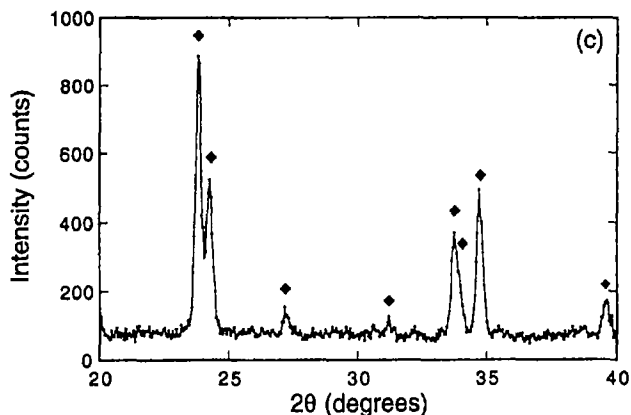
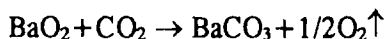


Fig. 3c X-ray diffraction pattern of BaCO₃-BaO₂-CuO mixture (3:1:1 mol) in air at 500°C. BaCO₃ (◆), BaO₂ (○) and CuO (□)

On the contrary, the mixtures BaO₂-CuO (1:1 and 1:0.5 mol) show two exothermic effects at 200–275°C and 278–356°C, respectively. The second peak in the BaO₂-CuO (1:1 mol) DSC curve, suggests that CuO tends to catalyse the exothermic reactions. The ternary mixtures BaCO₃-BaO₂-CuO show some distinct features that are most evident for molar ratios close to 3:1:1.

HTXRD patterns collected at 300, 400 and 500°C, for the BaO₂-BaCO₃-CuO system (Figs 3a, 3b, 3c), show that BaO₂ peaks tend drastically to decrease between 300 and 400°C while BaCO₃ peaks increase. This result and the DSC thermal effect can be explained by the transformation of BaO₂ in BaCO₃ following the reaction:



This is well demonstrated by the EGA measurements on BaCO₃-BaO₂-CuO mixture (3:1:1 mol) sample as reported in Fig. 4. In fact the atmosphere analysed during the thermal analysis test, at about 200°C shows an oxygen increase and a simultaneous carbon dioxide decrease. Figure 5 shows the DSC and TG analysis of the BaCO₃-BaO₂-CuO (3:1:1 mol) mixture. Also in this case, the evident thermal effect is associated with the reduction of the BaO₂ that tends to transform to BaCO₃. This is confirmed by TG analysis, where first appears a weight loss due to BaO₂ reduction, followed by an increase of weight due to carbon dioxide absorption.

In the DSC curve of Fig. 5, an unexpected large endothermic peak is present, with onset at about 390°C. It seems reasonable that this effect is not related to any melting process; in fact, XRD of the sample in this temperature range (Figs 3b, 3c) does not show any phases which may undergo melting. On the contrary the only evidence is the disappearance of CuO reflections: this suggests that the endothermic peak is only connected with a new phase formation, obtained with dissolution of CuO in a BaCO₃-like structure.

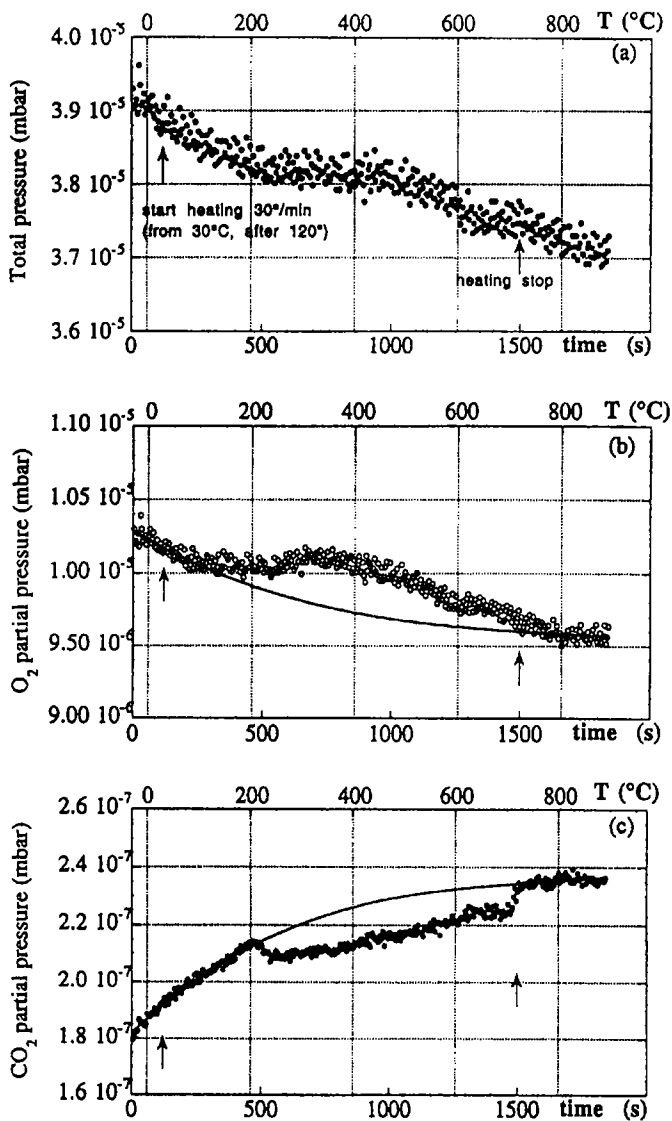


Fig. 4 Evolved Gas Analysis of BaCO₃-BaO₂-CuO mixture (3:1:1 mol)

Conclusions

The combined results of TG, DSC and EGA and high temperature XRD are consistent with the formation of a new phase in the Ba-Cu-C-O system. The new phase is isomorphous with BaCO₃ and, due to a very peculiar combination of ordered and disordered sublattices, is not detectable by standard diffraction techniques. However, its formation from a mixture of BaCO₃, BaO₂ and CuO

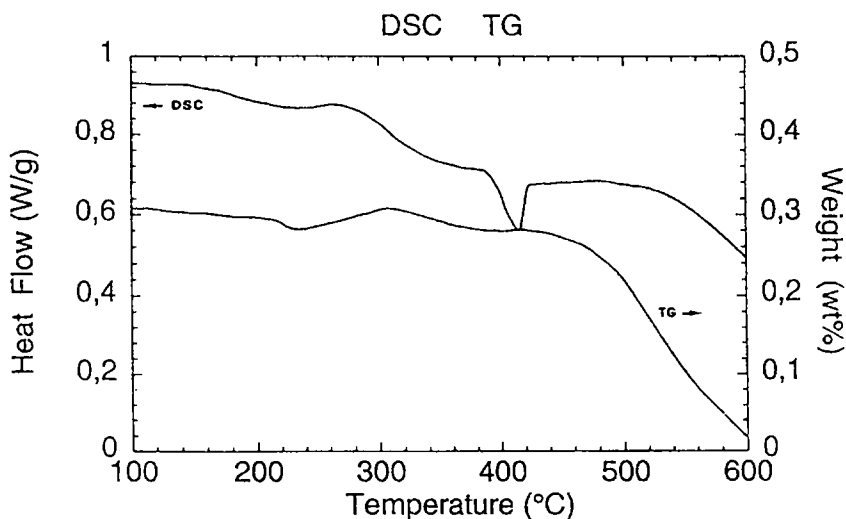


Fig. 5 DSC and TG in air and at $30^{\circ}\text{C min}^{-1}$ for $\text{BaCO}_3\text{-BaO}_2\text{-CuO}$ mixture (3:1:1 mol)

powders 3:1:1 is well evidenced by the DSC curves. We interpret the endothermic feature peaked around 410°C as the sign of the incorporation of crystalline CuO and amorphous BaO_2 in the BaCO_3 structure. Consistently, in the same temperature range the CuO diffraction peaks disappear and no other Cu-containing crystal phase shows in the XRD powder patterns. Interesting side effects that have been detected, concern the catalytic role of the CuO in the carbonation of the impurity fractions contained in the BaO_2 powders and in promoting the crystalline/amorphous phase transformation of this latter compound at 320° .

References

- 1 H. Müller-Buschbaum, *Angew. Chem. Int. Ed. Engl.*, 28 (1989) 1472.
- 2 see for example: K. Kinoshita and T. Yamada, *Nature*, 357 (1992) 313; B. Raveau, M. Huvé, A. Magnain, M. Hervieu, C. Michel, B. Domenges and C. Martin, *Physica C*, 209 (1993) 163; M. Kikuchi, E. Ohshima, N. Ohnishi, Y. Muraoka, S. Nakajima, E. Aoyagi, M. Ogawa, J. Akimitsu, T. Oku, K. Hiraga and Y. Syono, *Physica C*, 219 (1994) 200; T. Kawashima, Y. Matsui and E. Takayama-Muromachi, *Physica C*, 227 (1994) 95; D. Pelloquin, M. Herwicw, C. Michel, A. Maiggnan and B. Raveau, *Physica C*, 227 (1994) 215.
- 3 G. Calestani, P. Ganguly, F. C. Maticotta, P. Nozar, A. Migliori, K. A. Thomas and A. Tomasi, *Physica C*, 247 (1995) 359.
- 4 G. Calestani, F. C. Maticotta, A. Migliori, P. Nozar, L. Righi, K. A. Thomas, *Physica C.*, under publication.
- 5 M. A. G. Aranda and J. P. Attfield, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1454.
- 6 F. C. Maticotta, G. Calestani, A. Migliori, P. Nozar, P. G. Radaelli, P. Scardi and K. A. Thomas, *Angew. Chem. Int. Ed. Engl.*, submitted.