ELSEVIER

Thermochimica Acta 298 (1997) 155–159

thermochimica
acta

A thermogravimetric study of the stability and reduction of the precursors for mercury-based superconductors

A. Kareiva*

Department of General and Inorganic Chemistry, Vilnius University, 2006 Vilnius, Lithuania

Received 10 April 1996; accepted 18 December 1996

Abstract

The precursor powders of the $Ba_2Ca_{n-1}Cu_nO_{2n+1+\delta}$ (n=1, 2, 3) are prepared by sol–gel route. The stability and thermal behaviour of these oxides during vacuum calcination has been investigated. The suitability of the obtained samples for the synthesis of Hg-based high-T_C superconductors as well as a preparative peculiarities of their synthesis are discussed. © 1997 Elsevier Science B.V.

Keywords: Superconductors; Mercury; Precursors

1. Introduction

The recently discovered mercury-based superconductors $HgBa_2CuO_{4+\delta}$ (Hg-1201), $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) and $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223) represent a large family of high-T_C superconductors, formulated $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ [1–3]. The highest T_C reported for the Hg-1223 superconductors was 133.5 K, which is the highest ever reported T_C for all copper-oxide superconductors. It is as a consequence of their unique properties that there is continued interest in the development of new synthetic methods for their preparation.

The sol–gel synthesis route have been proposed for the preparation of different types of ceramic materials [4–8]. It is known, that sol–gel technique significantly improves the chemical homogeneity of high-temperature superconducting powders and precursors attempted for superconducting ceramics [9–13]. Our numerous studies have been published to describe the successful use of sol–gel technique for synthesizing $Ba_2CaCu_2O_{5+\delta}$ and $Ba_2Ca_2Cu_3O_{7+\delta}$ precursors for the preparation of Hg-1212 and Hg-1223 superconductors, respectively [14–16]. Contrary, Peacock et al. [17] have reported that it was only possible to synthesize Hg-1201 sample by sol–gel method, but failed when they tried to prepare the higher Hg-1212 and Hg-1223. To clarify such different results, the precursor samples were characterized by thermogravimetric analysis as indispensable tool for the characterization of materials, including high-temperature superconductors [18–20].

The aim of this contribution is to determine the stability and thermal behaviour of synthesized by sol–gel method $Ba_2Ca_{n-1}Cu_nO_{2n+1+\delta}$ precursors discussing their applicability for the preparation of Hg-based superconductors.

---

*Corresponding author.

PII S0040-6031(97)00039-7

2. Experimental

The ternary Ba–Ca–Cu and double Ba–Cu gels were prepared using stoichiometric amounts of analytical-grade metal acetates as starting materials and tartaric acid as complexing agent [14–16]. The dried gels were ground in an agate mortar and preheated for 5 h at 750°C and 10 h at 850°C in air with intermediate grindings. Since the gels were very combustible, slow heating (at 2°C min^{-1}) between 150 and 350°C was used. The powders obtained were annealed for 10 h at 850°C in a vacuum furnace (the pressure of residual gases was $<10^{-2}$ Pa). After vacuum calcination the prepared precursor specimens were placed immediately in the thermogravimetric analyzer.

The thermogravimetric measurements in flowing air up to 1000°C were performed with a Perkin–Elmer TGA7 thermogravimetry apparatus using a heating rate of 10°C min^{-1}. About 30 mg of sample in a platinum crucible was used for each TG run.

3. Results and discussion

The properties of Hg-based superconductors depend strongly on the powder-processing conditions. The main requirement of synthesized precursors for the preparation of $HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$ superconductors is that it should be free of carbonate so that the desirable superconducting phase could form as a major phase. In general, most of the syntheses by the sol–gel technique are based on carbon-containing precursors. Thus, the $BaCO_3$ or $CaCO_3$ formation is a problem in the sintering of superconducting materials. For example, in the case of Bi–(Pb)–Sr–Ca–Cu–O superconductor the residual carbonate concentration remains 20% of its initial value even after 20 h sintering at 860°C in air [21]. Furthermore, the formation of an intermediate oxycarbonate phase in different systems, such as $Ba_{44}Cu_{48}(CO_3)_6O_{87.9}$, $(Y_{1-x}Ca_x)_2Ba_4Cu_5(CO_3)O_{11}$ and $YBa_2Cu_{2.95}(CO_3)_{0.35}O_{6.6}$ was reported [22–25].

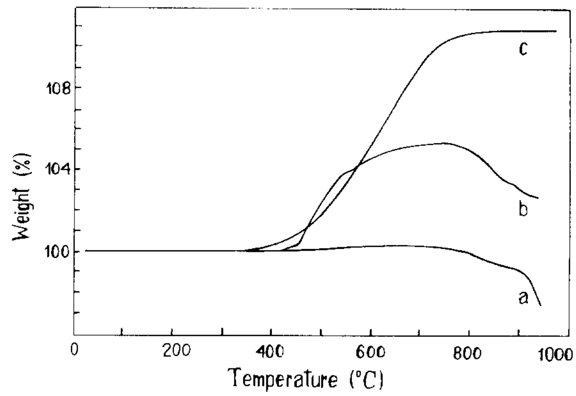

Fig. 1. TG curves for the $Ba_2Ca_2Cu_3O_x$ precursor samples annealed in (a) air and (b) vacuum and (c) for Cu_2O at heating rate of 10°C min^{-1}.

For a complete decomposition of carbonate in air, high temperatures cannot be used due to the appearance of liquid phase. Besides, it was reported [26] that destruction of the perovskite structure of superconducting $Yba_2Cu_3O_7$ starts at ~900°C, when the samples were analyzed by thermogravimetry in high vacuum. So, in order to reduce the carbonate amount in synthesized samples as much as possible a vacuum calcination at 850°C was used [15,16]. Fig. 1 shows TG analysis curves for the ternary $Ba_2Ca_2Cu_3O_x$ precursor annealed in vacuum and air. When the powders were heated in air (Fig. 1a), the decomposition of carbonate at >800°C takes place. A corresponding thermogravimetric analysis for the precursor that had been preheated in vacuum is shown in Fig. 1(b). The weight increase, starting from ca. 400°C is possibly due to conversion of Cu(I) to Cu(II) [14]. For comparison, Cu_2O was also heated using the same experimental conditions (Fig. 1c). A weight increase of 10.93% at 350–800°C was observed. This is in a good agreement with theoretical weight increase of 11.11% which proves that the following reaction occurs:

$$Cu_2O + 1/2O_2 = 2CuO \tag{1}$$

Thus, the high temperature vacuum calcination of precursors leads to copper reduction, schematically according to the following equation:

$$Ba_2Ca_2Cu(II)_3O_7 \rightarrow Ba_2Ca_2Cu(I)_3O_x + (7-x)/2O_2 \tag{2}$$

However, TG curve of the vacuum annealed sample shows a total gain in weight of 5.2%, which is a little higher as compared to the theoretical (3.8%). This negligible discrepancy may be caused not only by oxygen nonstoichiometry of the sample. The formation of carbonates if air gas used contains even small

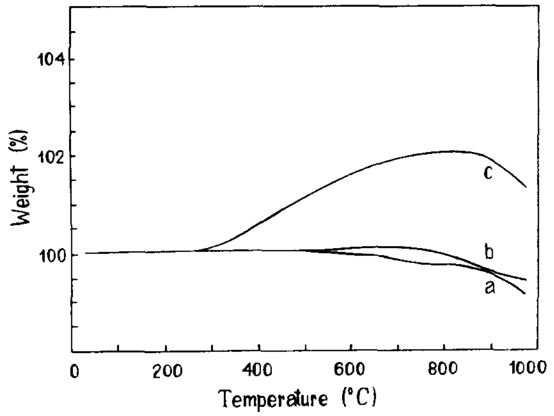

Fig. 2. TG curves for the $Ba_2CaCu_2O_x$ precursor samples annealed in (a) oxygen, (b) air and (c) vacuum at heating rate of 10°C min^{-1}.

amount of CO_2 as impurity is possible. This explanation is not unexpected, since the weight loss above 800°C was found (Fig. 1b).

In the case of $Ba_2CaCu_2O_{5+\delta}$ precursor, the similar results were obtained. Fig. 2 shows the TG curves obtained for the samples preheated in vacuum, oxygen and air. For the samples preheated in oxygen and air no changes in weight up to carbonate decomposition temperature were observed. As seen, for the vacuum annealed sample the weight gain starts at approximately same temperature as for Cu_2O or $Ba_2Ca_2Cu_3O_x$ precursor. It proves that again the copper reduction Cu(II)→Cu(I) under vacuum annealing occurs. Calculations suggested that copper mainly exists as Cu(I) in the $Ba_2CaCu_2O_x$ precursor after vacuum calcination.

Completely different situation was revealed for the precursor $Ba_2CuO_{3+\delta}$ during vacuum annealing. In the 820–930°C range, the reduction of copper to metallic instead of the reduced phase $Ba_2Cu(I)O_x$ formation [27] was determined. The following equations can describe this process assuming that full copper reduction occurs:

$$Ba_2CuO_3 \rightarrow 2BaO + Cu + 1/2O_2 \quad (3)$$

or partial reduction according to [28] coexists:

$$3Ba_2CuO_3 \rightarrow 6BaO + Cu + Cu_2O + O_2 \quad (4)$$

This is not surprising, since according to Mullens et al. [29], the decomposition of copper oxalate even in an inert atmosphere goes to metallic copper. Besides that, the melting of formed products follows the reduction process. Thus, contrary to Ref. [17] the synthesis of high purity $HgBa_2CuO_{4+\delta}$ superconductor using sol–gel technique proposed became complicated or even impossible.

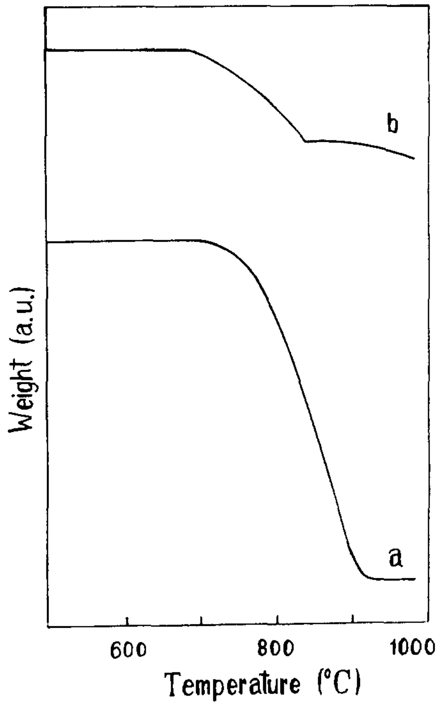

Fig. 3. (a) The decomposition of pure $CaCO_3$ and (b) mixture of $CaCO_3$, $BaCO_3$ and CuO at heating rate of 10°C min^{-1}.

A number of possible explanations of such results obtained could be suggested. It is known, that the introduction of various metallic elements, such as Cd, Ca, Sr in the cuprates can influence on the valency of copper [30], as well as on the oxygen content of synthesized ceramics [31]. From the structural point of view the introduction of Ca into the cuprates can stabilize the higher copper oxidation state. These type of compounds are all characterized having blocks $[(CuO_2)(Ca)]_{n-1}(CuO_2)$ with a perovskite-like structure [32–34].

The addition of Ca to barium cuprates influences both the microstructural evolution and the thermal decomposition temperature. Fig. 3 clearly demonstrates that the temperatures of decarbonation in flowing oxygen for pure $CaCO_3$ and for mixture of $CaCO_3 : BaCO_3 : CuO=1 : 2 : 2$ differ considerably. For pure $CaCO_3$, decarbonation started at 700°C

Table 1
Decarbonation temperatures for the mixtures of $BaCO_3$ and CuO

Molar ratio (Ba : Cu)	Temperature, °C (Initial reaction)
1 : 0.4	860
1 : 0.5	860
1 : 0.75	855
1 : 1	845
1 : 1.5	840
1 : 2	840

and completed at 915°C. For the mixture of $CaCO_3$, $BaCO_3$ and CuO, decarbonation of $CaCO_3$ started at 680°C and completed at 840°C. Apparently, in this case the rapid decomposition took place in a more narrow temperature range. Furthermore, the decarbonation can be accelerated by sintering the precursor under evacuated conditions. These results are in good agreement, reported by Katsumata et al. [21], and leads us to speculate that solid-state reaction between CaO and CuO preferably occurs instead of following reaction:

$$CuO \rightarrow Cu + 1/2O_2 \quad (5)$$

On the other hand, the metallic copper formation during vacuum sintering of the precursor $Ba_2CuO_{3+\delta}$ takes place.

Besides that, we can see from Table 1 that the decarbonation of $BaCO_3$ for the mixtures of $BaCO_3$ and CuO starts at different temperatures depending on molar ratio of the constituents. With increasing copper amount the decomposition temperature of $BaCO_3$ slightly decreases. These results do not contradict with those obtained above showing the connection between formation and stability of precursors $Ba_2Ca_{n-1}Cu_nO_{2n+1+\delta}$ and the decarbonation temperatures of $CaCO_3$ and $BaCO_3$. Nevertheless, it is obvious that additional investigations are needed to better explain this connection.

4. Conclusions

The stability and thermal behaviour during vacuum annealing of $Ba_2CuO_{3+\delta}$, $Ba_2CaCu_2O_{5+\delta}$ and $Ba_2Ca_2Cu_3O_{7+\delta}$ fabricated by sol–gel technique as the precursor material were studied by means of thermogravimetric analysis method. Results showed that reduction of Cu(II) to Cu(I) in the systems of Ba–Ca–Cu–O takes place, when the specimens were calcinated under vacuum conditions. However, in case of the Ba–Cu–O precursor vacuum heat treatment, the reduction to metallic copper occurs. Hence, the proposed synthesis of the first member $HgBa_2CuO_{4+\delta}$ of the homologous series of mercury-based superconductors, using our sol–gel method is complicated. Attempts to explain such different behaviour of analyzed samples were made. It was determined that for the mixture of $CaCO_3$, $BaCO_3$ and CuO the decarbonation of $CaCO_3$ occurs at lower temperatures preventing probably full copper reduction. Moreover, the decarbonation temperature of $BaCO_3$ slightly depends on Ba : Cu molar ratio in the sample and should be higher in $Ba_2CuO_{3+\delta}$ precursor case.

Acknowledgements

The author wishes to thank Prof. L. Kihlborg and Dr. I. Bryntse, Arrhenius Laboratory, Stockholm University, Sweden for use TG analyzer and for helpful discussions.

References

[1] S.N. Putilin, E.V. Antipov, O. Chmaissem and M. Marezio, Nature, 362 (1993) 226.
[2] A. Schilling, M. Cantoni, J.D. Guo and H.R. Ott, Nature, 363 (1993) 56.
[3] R.L. Meng, L. Beauvais, X.N. Zhang, Z.J. Huang, Y.Y. Sun, Y.Y. Xue and C.W. Chu, Physica C, 216 (1993) 21.
[4] P. Audebert, P. Griesmar, P. Hapiot and C. Sanchez, J. Mater. Chem., 2 (1992) 1293.
[5] G.R. Lee and J.A. Crayston, Adv. Mater., 5 (1993) 434.
[6] J.D. Mackenzie, J. Sol–Gel Sci. Techn., 1 (1993) 7.
[7] G. Westin and M. Nygren, J. Mater. Chem., 3 (1993) 367.
[8] B. Dunn, G.C. Farrington and B. Katz, Solid State Ionics, 70/71 (1994) 3.
[9] P. Catania, N. Hovnanian, L. Cot, M. Pham Thi, R. Kormann and J.P. Ganne, Mater. Res. Bull., 25 (1990) 631.
[10] A. Kareiva, M. Karppinen and L. Niinistö, J. Mater. Chem., 4 (1994) 1267.
[11] P. Karen and A. Kjekshus, J. Am. Ceram. Soc., 77 (1994) 547.
[12] Y.G. Metlin and Y.D. Tretyakov, J. Mater. Chem., 4 (1994) 1659.
[13] A. Kareiva, I. Bryntse, M. Karppinen and L. Niinistö, J. Solid State Chem., 121 (1996) 356.
[14] A. Kareiva and I. Bryntse, J. Mater. Chem., 5 (1995) 885.

[15] I. Bryntse and A. Kareiva, Mater. Res. Bull., 30 (1995) 1207.
[16] I. Bryntse and A. Kareiva, Physica C, 251 (1995) 115.
[17] G.B. Peacock, A. Asab, J.P. Hodges, I. Gameson and P.P. Edwards, Physica C, 235-240 (1994) 911.
[18] K. Leroy, J. Mullens, J. Yperman, J. Van Hees and L.C. Van Poucke, Thermochim. Acta, 136 (1988) 343.
[19] J. Šestak, T. Hanslik, M. Nevriva, D. Zemanova, E. Pollert, A. Triska and J. Tlaskal, J. Therm. Anal., 33 (1988) 947.
[20] J. Mullens, A. Vos, A. De Backer, D. Franco, J. Yperman and L.C. Van Poucke, J. Therm. Anal., 40 (1993) 303.
[21] T. Katsumata, K. Maekawa, T. Ohtaki, Y. Seki, Y. Minami, H. Imagawa and H. Fujinuma, Mater. Res. Bull., 29 (1994) 777.
[22] M.A.G. Aranda and P. Attfield, Angew. Chem. Int. Ed. Engl., 32 (1993) 1454.
[23] B. Domenges, Ph. Boullay, M. Hervieu and B. Raveau, J. Solid State Chem., 108 (1994) 219.
[24] F.J. Gotor, P. Odier, M. Gervais, J. Choisnet and Ph. Monod, Physica C, 218 (1993) 429.
[25] F.J. Gotor, N. Pellerin, P. Odier, E. Cazy, J.P. Bonnet, A.R. Fert and J. Ayache, Physica C, 247 (1995) 252.
[26] K. Nagase, H. Yokobayashi, M. Kikuchi, A. Tokiwa, Y. Syono and Y. Morioka, Thermochim. Acta, 175 (1991) 207.
[27] W. Wong-Ng and L.P. Cook, Powder Diffr., 9 (1994) 1.
[28] J.T.S. Irvine and C. Namgung, J. Solid State Chem., 87 (1990) 29.
[29] J. Mullens, A. Vos, R. Carleer, J. Yperman and L.C. Van Poucke, Thermochim. Acta, 207 (1992) 337.
[30] A. Maignan, D. Groult, R.S. Liu, T. Rouillon, P. Daniel, C. Michel, M. Hervieu and B. Raveau, J. Solid State Chem., 102 (1993) 31.
[31] V.E. Prusakov, R.A. Stukan, K.S. Pigal'skii, E.F Makarov, A.G. Kazakevich, V.P. Shashkin and A.O. Panfilov, Russian J. of Inorganic Chemistry, 38 (1993) 1341.
[32] G. Van Tendeloo, C. Chaillout, J.J. Capponi, M. Marezio and E.V. Antipov, Physica C, 223 (1994) 219.
[33] O. Chmaissem, L. Wessels and Z.Z. Sheng, Physica C, 230 (1994) 231.
[34] B. Raveau, C. Michel, M. Hervieu and A. Maignan, J. Mater. Chem., 5 (1995) 803.