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A THERMOGRAVIMETRIC INDEX FOR THE PREDICTION OF THE PROCESSING TEMPERATURE OF $REBa_2Cu_3O_{7-x}$ HIGH Tc SUPERCONDUCTING MATERIALS

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ABSTRACT

Production of ceramic high Tc superconductors using BaO_2 as precursor requires careful determination of the processing temperature. In this paper we introduce a thermogravimetric index to select the proper temperature. The method has been tested for $Ho_2O_3/4BaO_2/6CuO$ and $Eu_2O_3/4BaO_2/6CuO$ systems and the predictions are rather consistent with the experimental results.

INTRODUCTION

In a previous publication some of these authors |1| have shown that monophasic sample of $YBa_2Cu_3O_{7-x}$ can be prepared using BaO_2 instead of $BaCO_3$ as raw material . This processing is advantageous with respect to the traditional one in that it gives directly the superconducting phase without heat treatments in oxygen after the formation of the 1:2:3 compound.

Composition and temperatures at which the samples will be treated are critical in the new process. This paper has been worked out with the aim of finding a thermogravimetric index to select and predict the temperature and the composition more suitable to start the isothermal treatment for producing the monophasic superconducting compounds.

Besides we like to show that the use of BaO_2 as precursor can be useful in obtaining superconducting materials such as $REBa_2Cu_3O_{7-x}$ where RE stands for Europium and Holmium.

EXPERIMENTAL

Samples were prepared by weighing stoichiometric amounts of Eu_2O_3 (3N-

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pure) or Ho_2O_3 (3N-pure), CuO and BaO_2 (reagent grade) powders. Powders (about 20 g) were intimately mixed in an automatic rotating mixer.

Then the samples were placed in alumina crucibles within a thermobalance using a heating rate equal to 10 °C/min with an up and down program to 1150 °C in dynamic oxygen environment. Sample weights were 200 mg and the thermobalance sensitivity was equal to 0.1 mg. Simultaneously the DTA curves were recordered with sensitivity equal to 0.2 mV.

Production of superconducting powders was done according to the standard ceramic process. 15 g of initial reagents were placed in an alumina crucible in a furnace with air as gaseous environment. The samples were heated up to 940-960 °C if the initial mixture was $Eu_2O_3/4BaO_2/6CuO$ and to 920-940 °C if initial oxides were $Ho_2O_3/4BaO_2/6CuO$. The heating period for all runs was carried out at 10 °C/min. Then in "quasi-isothermal" conditions the specimen was left for 12 hours and finally the furnace was cooled down to room temperature at a rate equal to 5 °C/min.

Characterization of the final products was made by XRD using Kα Cu radiation.

Diamagnetic susceptibility was made using a simplified Faraday balance in a 100-300 Oe field.

RESULTS AND DISCUSSION

Figure 1 gives typical thermogravimetric traces for ternary mixtures $Eu_2O_3/4BaO_2/6CuO$ (a) and $Ho_2O_3/4BaO_2/6CuO$ (b) treated in oxygen. The interpretation of the detailed steps controlling the weight loss of Fig. 1 is not easy and it includes a liquid phase formed by the melting of BaO_2 (360 °C). However within the precision related to the chemical purity of the raw materials, it appears reasonable to say that oxygen is the gaseous phase that evolves from the starting mixture through chemical reactions of BaO_2.

Furthermore a basic guide line to produce the 1:2:3 phase should be that the sample is treated at such a temperature that there is sufficient oxygen in the solid phase to form the superconducting compound.

The literature |2| shows that the stoichiometric oxygen composition has to range between x = 0 and x = 0.20 in order to obtain good high temperature superconducting materials. Accordingly, if the only oxide which looses weight is BaO_2, the temperature at which the required oxygen composition is left within the solid phase can be derived from the thermogravimetric traces.

Points K and Q and points G and M represent this boundary condition respectively for $Ho_2O_3/4BaO_2/6CuO$ and $Eu_2O_3/4BaO_2/6CuO$ mixtures. While the optimum temperature at which the subsequent isothermal treatment has to be chosen within this range, it should be noted that if the isothermal working temperature is greater than that corresponding to the $REBa_2Cu_3O_{6.5}$ no superconducting phase can be obtained. Indeed as we proved experimentally, the weight loss behind the $REBa_2Cu_3O_{6.5}$ cannot be recovered by the sample during further oxygen high temperature treatment.

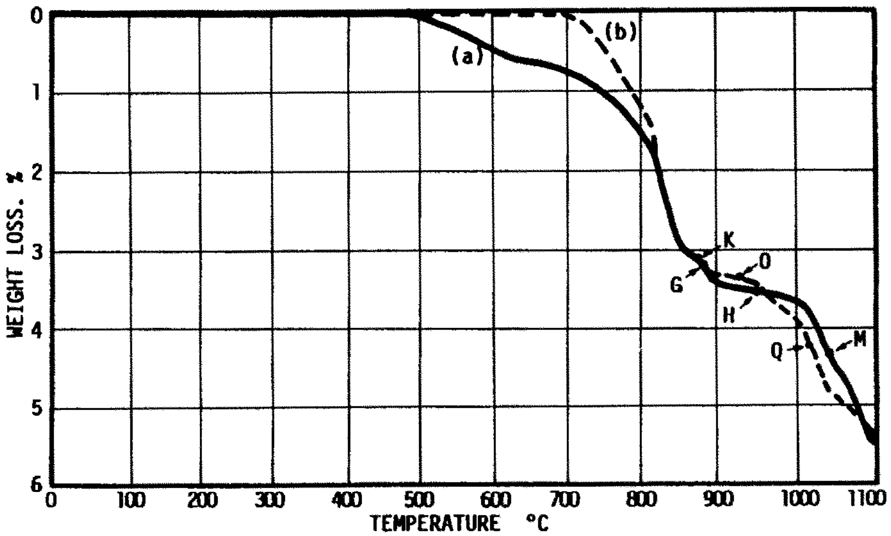

Fig. 1. TG curves of ternary mixtures $Eu_2O_3/4BaO_2/6CuO$ (a) and $Ho_2O_3/4BaO_2/6CuO$ (b) treated in dynamic oxygen environment.

The search for the optimum temperature at which the sample has to be treated requires that the solid phase needs to be stable with respect the oxygen loss during the isothermal treatment. This requirement might be satisfied by those solid phases which do not loose weight within the temperature range determined above. The existence of such a phase and its stability range might depend upon different variables that we are actually studying (3). For the systems presented here, the temperatures corresponding topoints O and H can be figured out respectively for $Ho_2O_3/4BaO_2/6CuO$ and $Eu_2O_3/4BaO_2/6Cuo$ systems. Table 1 summarizes these results.

Accordingly the isothermal temperatures at which the Holmium system is treated have to be less than that corresponding to those for the Europium system. Furthermore these selected temperatures indicate that the oxygen stoichiometry composition for the Holmium compound should be closer to $x = 0.08$, while that for Europium phase should be closer to $x = 0.15$. This prediction holds only in the case that no further change in oxygen stoichiometry occurs during the isothermal treatment.

TABLE 1

Temperature and weight losses for selected points in the TG curves of Fig. 1.

Chemical composition	Point	Weight Loss. %	Temperature. °C
$Eu_2O_3/4BaO_2/6CuO$	Start	----	----
$EuBa_2Cu_3O_7$	G	3.17	875
$EuBa_2Cu_3O_{6.5}$	M	4.25	1035
$EuBa_2Cu_3O_{7-x}$	H	3.50	940
$Ho_2O_3/4BaO_2/6CuO$	Start	----	----
$HoBa_2Cu_3O_7$	K	3.13	870
$HoBa_2Cu_3O_{6.5}$	O	4.17	1015
$HoBa_2Cu_3O_{7-x}$	Q	3.30	920

Even if the superconducting materials have been produced in air and therefore further studies are required to establish the role of the gaseous environment |3|, it is suggested that the predictions derived from Table 1 are verified for the production of Holmium and Europium samples.

Indeed to obtain superconducting Ho-based compounds a temperature which is about 20 °C lower than that required for Eu-based superconductors is needed.

Furthermore the selected temperatures for Eu-based and Ho-based superconductors gave at the end of the 12 hours heat treatment the monophasic compounds with the orthorhombic Pmmm structure-type and lattice parameters in agreement with most recent Literature data |4|: a = 3.844(1) Å, b = 3.894(1) Å and c = 11.674(7) Å for $EuBa_2Cu_3O_{7-x}$; a = 3.818(1) Å, b = 3.879(1) Å and c = 11.649(6) Å for $HoBa_2Cu_3O_{7-x}$.

XRD patterns of the solid phases obtained which correspond to points O and H in Figure 1 are given in Figure 2.

It should be noted that a certain amount of superconducting phase along with binary oxides $BaCuO_2$ is formed during the heating treatment.

The thermogravimetric index here determined therefore gives a temperature which is thermodynamically feasible to produce the 1:2:3 phase. The long period of time at which the samples are left under isothermal conditions is consequently related to kinetic steps concerning the solid state reactions.

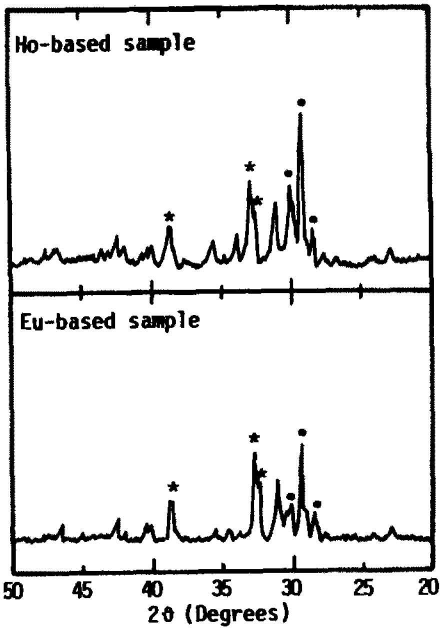

Fig. 2. XRD patterns of Eu-based and Ho-based mixtures heated in thermobalance in dynamic oxygen environment at 940 °C and 920 °C respectively (see points H and O of Fig. 1). Stars indicate the most evident peaks of 1:2:3 phase; analogously full circles indicate $BaCuO_2$ phase.

CONCLUSIONS

A thermogravimetric index to predict the processing temperature for $REBa_2Cu_3O_{7-x}$ high Tc superconducting materials has been derived using two guide-parameters:

1. The amount of oxygen loss during the heating period has to be such that the oxygen left in the reacting mixture is equal to that required by the 1:2:3 phase stoichiometry.
2. The mixture corresponding to the above said temperature should not loose further weight for a convenient temperature range.

Gaseous environment and detailed mechanism steps associated with the decomposition process might affect the temperature of processing as well as the thermal stability with respect to the oxygen phase.

Our further studies will be on these topics |3|.

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