Synthesis of Y–Ba–Cu–O ceramic using metallic Y as starting component

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Abstract

This work presents the results obtained for a high-temperature superconducting ceramic, of the Y–Ba–Cu–O system, synthesized by solid state reaction from Y_2O_3, Y, $BaCO_3$ and CuO, in one case, and Y instead of Y_2O_3 in the other. Its properties and structure depend on the choice of the starting states of Y. Use of elemental Y as a starting component made it easier to form a defect perovskite structure with lower values of cell parameters, compared with those obtained from Y_2O_3.

Keywords: Synthesis; $YBa_2Cu_3O_{7-x}$; Superconductors; Thermal analysis

1. Introduction

The physical properties, characteristics and structure of superconducting ceramic materials of a copper-oxide-based system, of $YBa_2Cu_3O_{7-x}$ type, synthesized by a solid state reaction technique, primarily depend on the processing conditions and the choice of starting components [1–5]. The resulting products of this method of preparation mostly have multiphase compositions with the presence of non-superconducting phases or impurities at grain boundaries, which lead to a decrease in the critical current density [6,7]. The critical temperature of transition in the superconducting state for the $YBa_2Cu_3O_{7-x}$ composition is a function of the oxygen content in the defect orthorhombic structure, i.e. the ratio of Cu^{2+} to Cu^{3+} ions [8]. The perovskite structure with cation ratio Y:Ba:Cu = 1:2:3 and oxygen content $7-x$, is stable for x from 0.35 to 0.095, where the latter value corresponds to the maximum critical temperature value [8]. The $YBa_2Cu_3O_{7-x}$ phase appears in two modifications: an

orthorhombic (O), low-temperature, superconductive phase, for $x \sim 0$; and a tetragonal (T), high-temperature, non-superconductive one, for $x \sim 1$.

These two modifications are separated by an O–T transformation, which is a function of temperature and oxygen partial pressure [9]. In recent reports [10,11], the influence of the starting forms of the components on the superconducting behaviour of Y–Ba–Cu–O ceramic produced from Y_2O_3 $BaCO_3$ and CuO has been investigated, but in neither was Y used as a starting material in the process of synthesis. Therefore, our attention was directed to the influence of elemental Y on the synthesis of $YBa_2Cu_3O_{7-x}$. Samples produced were examined by thermal, X-ray, and metallographic analyses.

2. Experimental

To determine the influence of various starting forms of components on the mechanism of synthesis and the T_c value of the Y–Ba–Cu–O system, the samples were prepared from $BaCO_3$, CuO and Y_2O_3, and from $BaCO_3$, CuO and Y in the case of the second sample, by the solid state reaction technique [12,13]. Appropriate quantities of the starting components (at a stoichiometric ratio Y:Ba:Cu = 1:2:3) were weighed and first mixed in a porcelin mortar with a pestle. To obtain the parameters of the thermal treatment, DTA–TG–DTG analyses were made. Based on these results, the homogenized mixture of starting components was calcined at 1173 K for 3 h. The cooled samples were homogenized again, then pressed and sintered at 1223 K for 4 h. The thermal treatments were carried out in air, and the cooling rate was 40 K h^{-1}.

The measurements of T_c values were made by an indirect method based on monitoring and measuring the time of Maissner's effect [14]. The composition of samples was investigated by X-ray analysis.

Optical microscopy was used to determine the microstructure of samples previously prepared by the ordinary polishing methods used for this kind of investigation.

3. Results and discussion

The measured values of the critical temperature transition were 89 and 99 K for the samples synthesized from Y_2O_3 and Y, respectively. The synthesis, carried out in air, was investigated by comparative DTA–TG–DTG analysis using the method of non-isothermal kinetics. The maximum temperature during thermal treatment was 1273 K, and the heating rate was 10 K min^{-1}. The activation energies for characteristics processes during synthesis of the superconducting phase $YBa_2Cu_3O_{7-x}$ were calculated by Daniel's method [15,16], based on following expressions

$$\ln k = n + E_a/RT$$

$$k_i = T_i/(A-a_i) \text{ at } T_i$$

where k is the rate constant, k_i the rate constant of the i-segment, E_a the activation energy (kJ mol^{-1}); R the universal gas constant (kJ mol^{-1} K^{-1}), T the temperature of

the i-segment (K), a_i the area of the i-segment of the peak (mm^2), T_i the temperature change in the i-segment (from the measured curve in mm), and A the area of the whole peak (mm^2).

The DTA–TG–DTG results for the synthesis of $YBa_2Cu_3O_{7-x}$ (from different starting components) are illustrated in Fig. 1. According to the presented curves (Fig. 1) and the results in Ref. [17], it can be concluded that a superconducting ceramic of the Y–Ba–Cu–O system was formed by a multiphase reaction. The initial mass loss obtained by TG analysis in the temperature region below 473 K was found to correspond to the water loss from the carrier sample, and therefore this was not taken into consideration during the calculation of the superconducting phase stoichiometry.

For the sample synthesized from elemental Y, Fig. 1(b), a characteristic "hump" on the TG curve, in the temperature range from 798 to 953 K, is observed. The mass increase of 9 mg is a consequence of a two-step Y oxidation, and is in agreement with the stoichiometric amount of oxygen needed here, 8.3 mg.

The appearance of an endothermic peak at 1003 K on the DTA curves, not followed by a mass loss, is characterstics of the superconducting phase decomposition and represents the O–T transformation [18]. The presence of these peaks on DTA curves in the process of synthesis of both the samples, Fig. 1, can be attributed to the mentioned transformation of a small quantity of the superconducting phase which was obtained during the homogenization process of the starting components. The peak appearing at 1083 K on the DTA curves in Fig. 1, also characteristic for both samples, presents a rhombic–hexagonal transformation of unreacted $BaCO_3$ [18]. The intensity of the peak can be used as a measure of the superconducting phase quality achieved in the process of synthesis [19]. Endothermic peaks (DTA curves, Fig. 1) that partially overlap in the higher temperature region (about 1173 K) for both samples, mostly correspond to the mass loss due to the release of CO_2 from $BaCO_3$ and, partially, of O_2

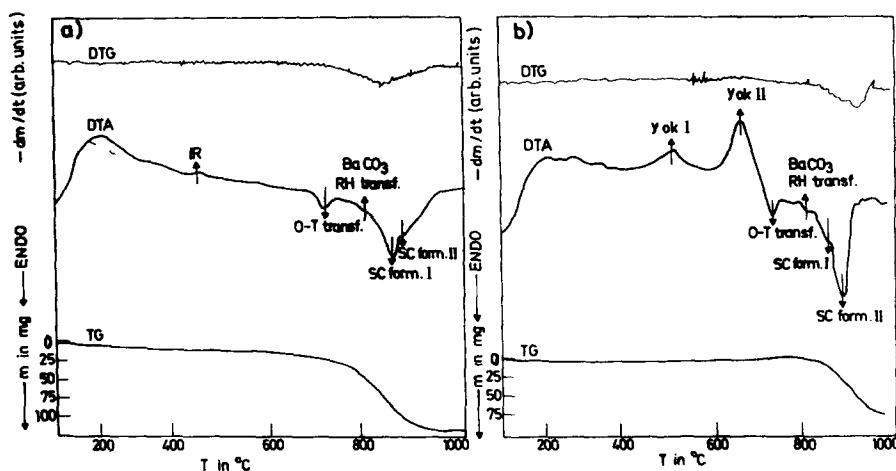Fig. 1. DTA, TG and DTG curves of $YBa_2Cu_3O_{10}$ synthesized from: (a) Y_2O_3,$BaCO_3$ and CuO; (b) Y, $BaCO_3$ and CuO.

from the superconductor synthesized at higher temperature [19]. From these data, the values of parameter x in the starting formula were calculated. For an initial sample weight of 500 mg, the calculated quantity of CO_2 released from $BaCO_3$ is 79.529 mg. The mass losses according to the curves for the sample synthesized from Y_2O_3 and Y are 83 mg and 80 mg, respectively, and based on these results, the determined values of parameter x are 0.29 and 0.04, respectively.

The lines in Fig. 2 to the following processes:

– line IR, the initial reaction in the homogenous mixture of Y_2O_3, $BaCO_3$ and CuO;
– line Y ox., I and II, oxidation of Y in two stages (stages I and II);
– line OT transf., orthorhombic–tetragnonal transformation;
– line RH transf., rhombic–hexagonal transformation of $BaCO_3$;
– line SC form., I and II, formation of superconducting phase in two stages (stages I and stages II).

From the ln k–1000/T plots in Fig. 2, the values of activation energies E_a for the previously mentioned processes were calculated and are given in Table 1. A comparasion of these values with the results published by Gadalla and Hegg [19] shows good
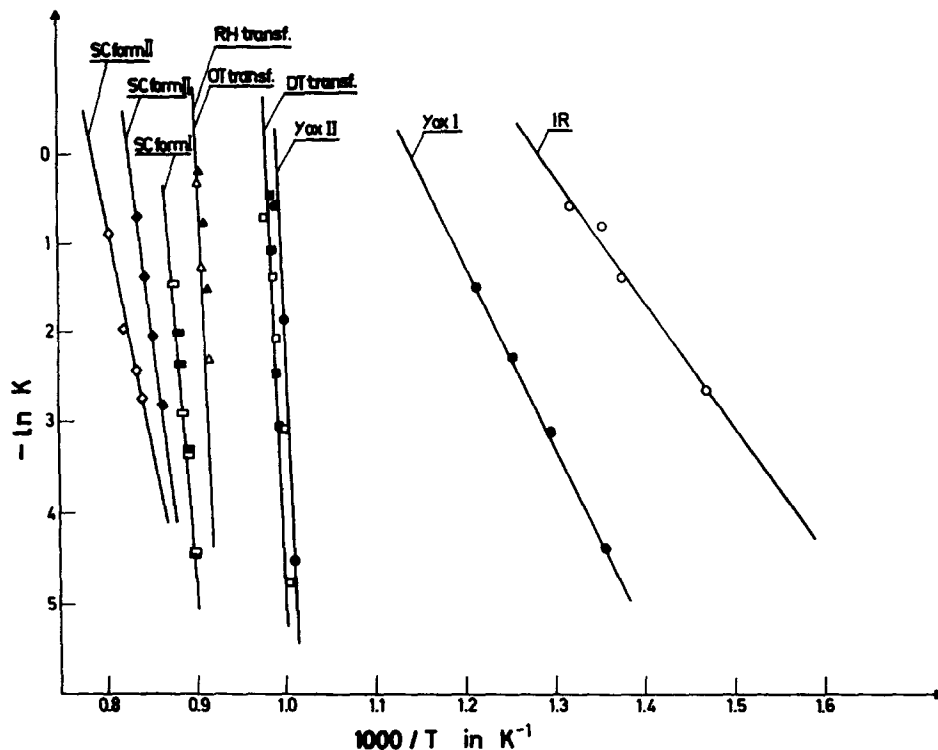

Fig. 2. ln K–1000/T plot: open marks, synthesis from Y_2O_3, $BaCO_3$ and CuO; closed marks, synthesis from Y, $BaCO_3$ and CuO.

Table 1
Activation energy values (E_a) for $YBa_2Cu_3O_{7-x}$ synthesis

Type of process (peak marks in Fig. 1.)	$E_a/kJ\,mol^{-1}$	
	$YBa_2Cu_3O_{7-x}$	Synthesized from
	Y_2O_3	Y
Initial reaction (Peak IR)	140	–
Oxidation of Y (Peak Y ox I)	–	180
in two steps (Peak Y ox II)	–	460
O–T transformation (Peak OT transf.)	380	320
R-H transformation (Peak R-H transf.)	290	280
Superconducting formation in two steps (Peaks SC form. I)	250	250
(Peak SC form. II)	200	230

agreement for the last multiple peaks (designated SC form. I and II on Figs. 1 and 2) for both samples. Comparing E_a for the sample produced from elemental Y as a starting material are lower than those obtained for the sample produced from Y_2O_3 as a starting material.

From Fig. 3, which presents the weight loss of investigated samples versus temperature, it is clear that the oxidation of metallic Y is followed by a mass increase, while the
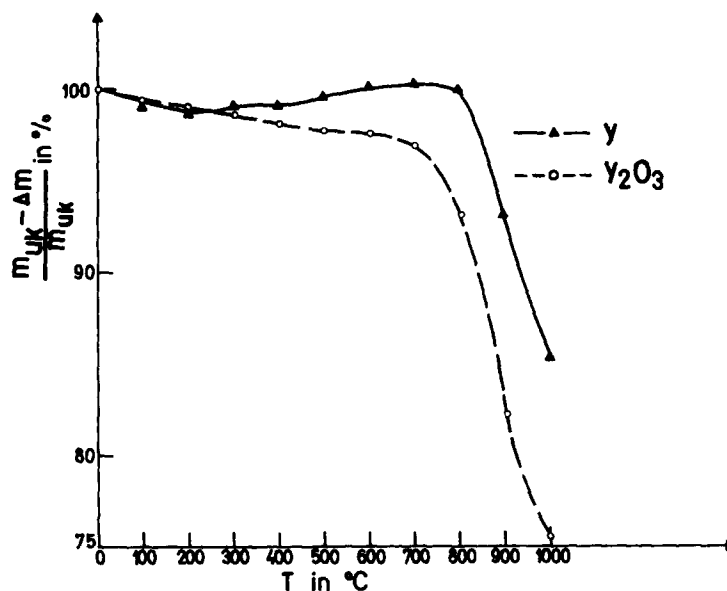

Fig. 3. Weight loss vs. temperature.

superconducting phase formation causes a mass decrease (the end of the curve, designated "Y").

The unit cell dimensions and the indices of the plane position were determined from the diffractograms obtained and are summarized in Table 2. The results of X-ray anlaysis, given in Table 2, indicate that the peak with the maximum intensity, for both investigated samples, is obtained at $\theta = 16.5°$ (plane 1 1 0), confirming the perovskite structure. For the sample produced from elemental Y, the calculated values of the cell parameters (a, b and c) are lower than the lattice parameters for the sample prepared from Y_2O_3. It should be pointed out that the lattice parameters for the sample produced from Y_2O_3 are in good agreement with the results obtained by Sugiyama et al. [20] and Kumar et al. [21]. Optical microscopy, Fig. 4, showed that the sample synthesized from elemental Y (Fig. 4a) is characterized by a greater content of the superconducting $YBa_2Cu_3O_{7-x}$ phase, and a better disposition and shape of the grains of the same size, compared with the sample obtained Y_2O_3, Fig. 4b. Grain boundaries are important because they play a significant role in flux pinning, and the mechanical properties and sensitivity of the material to environmental effects [11,22,23]. The sharper edged grains and lower content of impurities, for the same sample obtained from elemental Y, are in agreement with the higher T_c value, compared to the sample obtained from Y_2O_3, as mentioned before in the text.

Table 2
Results of X-ray analysis

Y_2O_3,$BaCO_3$,CuO $a = 0.3817$ nm $b = 0.3886$ nm $c = 1.1728$ nm				Y,$BaCo_3$,CuO $a = 0.3727$ nm $b = 0.3824$ nm $c = 1.1667$ nm			
d/nm	h	k	l	d/nm	h	k	l
0.13606	2	0	6	0.13606	2	0	6
0.15659	2	1	3	0.15659	2	1	3
0.15806	1	2	3	0.15806	1	2	3
0.16647	1	2	2	0.16647	1	2	2
0.17411	0	1	6	0.17337	0	1	6
0.17713				0.17776			
0.18396				0.19120	2	0	0
0.19434	2	0	0	0.20250			
0.22262	1	1	3	0.22262	1	1	3
0.23258	1	0	4	0.23258	1	0	4
0.25150				0.24610	1	1	2
0.27356	1	1	0	0.27380	1	1	0
0.29402				0.29780			
0.30701				0.30480			
0.31999	1	0	2	0.31999	1	0	2
0.38175	1	0	0	0.37280	1	0	0
0.39094	0	0	3	0.38890	0	0	3
0.58892				0.58892			

a   b

Fig. 4. Optical micrograph of $YBa_2Cu_3O_{7-x}$ synthesized from: (a) Y_2O_3, $BaCO_3$ and CuO; (b) Y, $BaCO_3$, and CuO.

4. Conclusions

The presented results indicate that the use of elemental Y, as a starting component, made it easier to form a superconducting phase, providing lower values of E_a for all steps of the reaction. For the sample obtained from elemental Y, based on the results of X-ray analysis, a decrease in the lattice parameters a, b and c was observed. From the results of optical microscopic analysis it can be concluded that both samples are multiphase, with irregular configuration of the grains. Sharper edged grains and a greater content of superconducting phase are characteristics of the samples produced from metallic Y. Improved characterstics of the sample produced from elemental Y results in the higher T_c values.

Acknowledgements

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