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THERMOANALYTICAL STUDIES OF Ga-SUBSTITUTED $MBa_2Cu_3O_{7-\delta}$ SUPERCONDUCTING COMPOUNDS FORMATION (*M*=Yb, Eu)

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Abstract

A thermoanalytical study in non-isothermal conditions was realized on Ga-substituted $MBa_2Cu_3O_{7-\delta}$ superconducting compounds formation (*M*=Yb, Eu). The presence of different oxides in the reaction mixtures leads to different reactivity of the system. The type of lanthanoide ion present in the studied compositions determines the reactivity of the system. In the system containing Eu the solid state reactions start at lower temperature than in the system containing Yb. Ga-substitution does not change evidently the thermal behavior of the unsubstituted samples. Different reactivities of the studied reaction mixtures led, after similar thermal treatment in isothermal conditions, to samples with different structure and superconducting properties.

Keywords: Ga-substitution, superconducting compounds, thermal analysis

Introduction

The superconducting ceramics known as '1-2-3' is represented by the $YBa_2Cu_3O_{7-\delta}$ compound. The substitution of Cu [1–3] or Y [4–10], by different ions (Eu, Gd, Dy, Yb), is well known, the resulted compounds being superconducting, as well.

A special influence on the superconducting behavior could be determined by gallium substitution. Gallium is located, as well as Y, in the third group of the periodic table, leading to compounds in which it shows three valencies, but the ionic radius for Ga^{3+} is half of that of Y^{3+}. The substitution of Ga in the Y position could lead to the decrease of the Cu–O interplanar distances, that may influence the superconducting properties of the resulted compounds, especially the transition temperature of the superconducting ceramics.

The multi-ionic substitutions in the 1-2-3 type superconducting materials lead not only to the modification of the electrical properties, but determine changes in the solid state reactions that takes place during high temperature processing.

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The aim of the present work consists in the thermoanalytical study of the solid state reactions which occur during the formation of Ga-substituted $MBa_2Cu_3O_{7-\delta}$ type compounds, (*M*=Yb, Eu).

Experimental

Reagent grade $BaCO_3$ and Yb_2O_3, Eu_2O_3, Ga_2O_3, CuO (all Merck) were used for samples preparation. The mixtures have been obtained by wet homogenisation in isopropyl alcohol.

DTA curves of initial mixtures were performed in static air in the temperature range 20–1020°C by means of a derivatograph OD-102 (MOM, Budapest) at a heating rate of 10°C min^{-1}.

In order to obtain dense samples, the following thermal treatment was used, after wet homogenisation, the dry blends were annealed three times, in air at 800°C for 4 h; the sample was weighed after each annealing. The resulting powder was cold-pressed into pellets with the diameter of 10 mm using a manual preset at 3000 daN.

The pressed samples were heat-treated at 950°C during 7 h and furnace cooled down to room temperature.

The phase composition of the sample obtained after the thermal treatment was determined by X-ray diffraction method, using a DRON-2 diffractometer and CrK_α (λ=2.92092 Å).

The electrical measurements were realized using the four points method.

Results and discussion

The results of the DTA/TG analysis are summarized in Table 1.

The well-known behavior of CuO and $BaCO_3$ was confirmed. All samples present slight mass loss at low temperatures, that could be assigned to the adsorbed water and isopropyl alcohol (used in the mixing of the samples) evolution (reaction 1).

In the case of CuO the well-known reduction to Cu_2O at temperatures above 1000°C was noticed (reaction 2).

The pure $BaCO_3$ does not start its decomposition at temperatures lower than 1000°C. The only thermal effect observed in this case is the endothermic effect at about 830°C assigned to $BaCO_3$ phase transformation from rhombohedral to hexagonal form (reaction 3).

When a mixture of CuO:$BaCO_3$, in 3:2 molar ratio, was analyzed the $BaCO_3$ decomposition started at temperatures lower than 1000°C, mainly at 940°C, due to the solid state reaction between $BaCO_3$ and CuO.

The samples corresponding to compositions containing Yb with different Ga-substitutions present much complex DTA curves (Fig. 1).

The phase transformation of $BaCO_3$ at about 830°C was noticed for all samples (reaction 3).

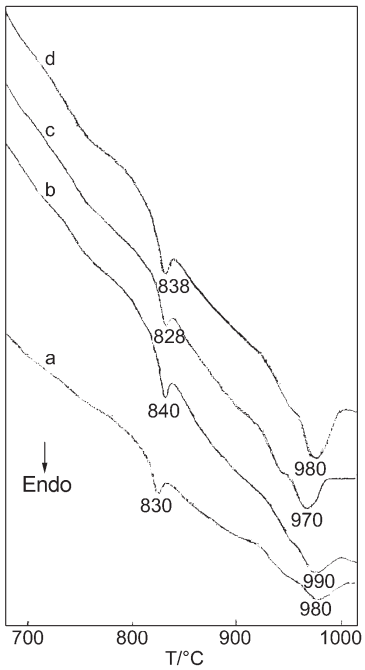

Fig. 1 DTA curves of the samples with nominal composition: a – $Yb_1Ba_2Cu_3O_{7-\delta}$; b – $Yb_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$; c – $Yb_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$; d – $Yb_{0.97}Ba_2Ga_{0.003}Cu_3O_{7-\delta}$

The $BaCO_3$ decomposition starts for all samples at about 900°C, due to the solid state reaction of $BaCO_3$ with the oxides present in the system and proceeds in three steps noticed as shoulders in the DTA curves. The main peak of the global endothermic effect is situated at about 9800°C (reaction 4).

The Ga-substitution in the mentioned system causes the increase of the mentioned thermal effects.

Compared to the pure $BaCO_3$ and to the binary CuO:$BaCO_3$ mixture, increasing the complexity of the system led to decreasing of the temperature at which $BaCO_3$ starts its decomposition due to the solid state reactions with other oxides in the system. However, the $BaCO_3$ decomposition is not fully accomplished in the studied temperature range (Table 1).

In the samples containing Eu with different Ga-substitution (Fig. 2) the solid state reaction of $BaCO_3$ with the other oxides in the system starts at 800°C, lower with 100°C than in the similar samples prepared with Yb. The $BaCO_3$ phase transformation (reaction 3) could be however observed, as at low temperature the rate of solid state reaction of $BaCO_3$ with the other oxides in the system is very slow and unreacted $BaCO_3$ in high amount is still present in the samples at about 830°C. Although the solid state reactions of $BaCO_3$ with other oxides present in the system (reaction 4) start with 100°C earlier than in the former case, they are not fully accom-

Table 1 DTA/TG results of the studied samples

Sample	Temperature range/°C	Mass loss%		Thermal effects/°C	Assignment
		experim.	theoretical		
CuO	20–1000	1.0			(1)
	1000–1100	2.0	22.30	>1100	(2)
$BaCO_3$	20–1020	2.5		–	(1)
			22.30	830	(3)
CuO:$BaCO_3$ (3:2)	20–940	1.4		–	(1)
				842	(3)
	940–1100	11.40	13.89*	1020	(4)
$YbBa_2Cu_3O_{7-\delta}$	20–900	1.66		–	(1)
				830	(3)
	900–1020	9.00	10.62*	970 sh	
				980 sh	(4)
				1010	
$Yb_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$	20–900	1.66		–	(1)
				840	(3)
	900–1020	9.0	10.63*	930 sh	
				970 sh	(4)
				990	
$Yb_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$	20–900	3.18		–	(1)
				828	(3)
	900–1020	10.45	10.65*	910 sh	
				950 sh	(4)
				970	
$Yb_{0.97}Ba_2Ga_{0.03}Cu_3O_{7-\delta}$	20–900	1.87		–	(1)
				838	(3)
	900–1020	10.30	10.65*	900 sh	
				965 sh	(4)
				980	
$EuBa_2Cu_3O_{7-\delta}$	20–800	1.96		–	(1)
				842	(3)
	800–1020	10.83	10.90*	970 sh	
				1010	(4)
$Eu_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$	20–800	2.22		–	(1)
				852	(3)
	800–1020	10.54	10.91*	950 sh	
				1017	(4)
$Eu_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$	20–800	2.18		–	(1)
				850	(3)
	800–1020	10.54	10.92*	940 sh	
				1010	(4)
$Eu_{0.97}Ba_2Ga_{0.03}Cu_3O_{7-\delta}$	20–800	1.54		–	(1)
				850	(3)
	800–1020	10.20	10.93*	940 sh	
				1005	(4)

sh – shoulder, * calculated considering that it occurs only by $BaCO_3$ decomposition
Reaction (1): adsorbed water or/and alcohol evolution; Reaction (2):$CuO \rightarrow Cu_2O$
Reaction (3): $BaCO_3$ rhombohedral→hexagonal phase transformation
Reaction (4): solid state reaction of $BaCO_3$ with the oxides present in the mixtures

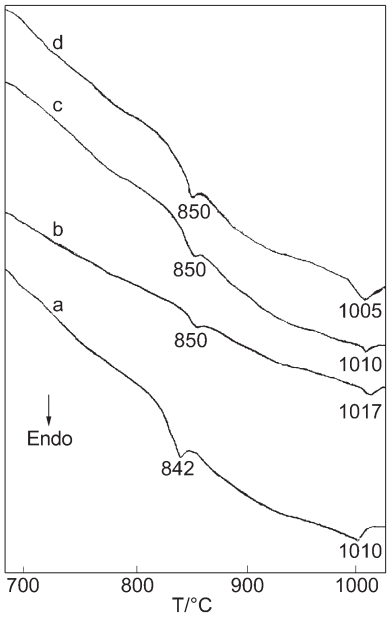

Fig. 2 DTA curves of the samples with nominal composition: a – $Eu_1Ba_2Cu_3O_{7-\delta}$; b – $Eu_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$; c – $Eu_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$; d – $Eu_{0.97}Ba_2Ga_{0.003}Cu_3O_{7-\delta}$

plished to 1020°C. The thermal effect assigned to $BaCO_3$ decomposition by its interaction with the oxides present in the system is broad and much less evidenced than in the case of the mixtures containing Yb. The main peak of the endothermic effect is displaced to higher temperature, over 1000°C (Fig. 2).

In the system containing Eu, the Ga-substitution has a less evident effect on the position and the intensity of the registrated thermal effects.

The results of the thermoanalytical study of the Ga-substituted $MBa_2Cu_3O_{7-\delta}$ superconducting compounds (*M*=Yb, Eu) led to the conclusion that the overall reactivity of the system is determined by the presence of the lantanoide oxides, mainly Yb or Eu. In the presence of Eu the solid state reaction between the components of the system starts at 800°C, while in the presence of Yb the similar reaction starts only at 900°C. Ga-substitution has a less evidenced effect on the reactivity of the studied systems.

The different behavior of the studied systems, noticed in non-isothermal conditions, may explain the different phase composition obtained by isothermal thermal treatment of the same samples.

In Figs 3 and 4 the X-ray diffraction patterns of the samples thermally treated in isothermal conditions are presented. The XRD patterns have shown for all samples containing Eu, no matter the Ga-substitution, a pure orthorhombic 1-2-3 phase. In the case of the samples containing Yb besides the 1-2-3 phase, the so-called 'green phase' could be observed.

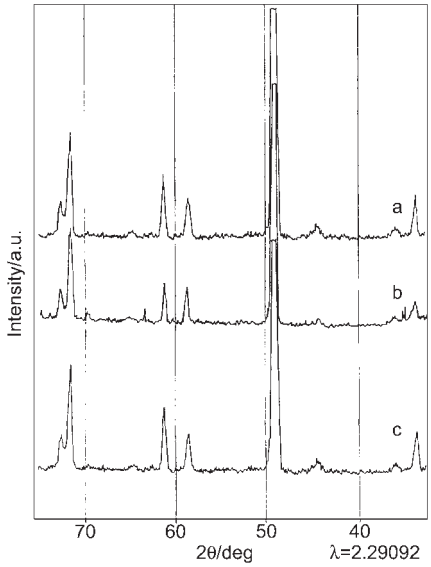

Fig. 3 XRD patterns of the samples thermally treated in isothermal conditions, with nominal composition: a – $Eu_1Ba_2Cu_3O_{7-\delta}$; b – $Eu_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$; c – $Eu_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$

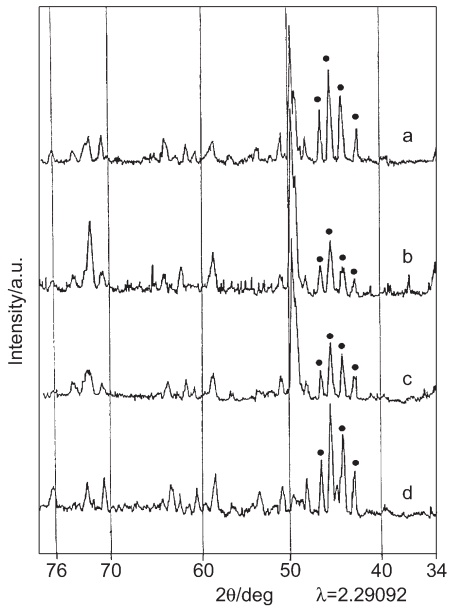

Fig. 4 XRD patterns of the samples thermally treated in isothermal conditions, with nominal composition (● – 'green phase'): a – $Yb_1Ba_2Cu_3O_{7-\delta}$; b – $Yb_{0.99}Ba_2Ga_{0.01}Cu_3O_{7-\delta}$; c – $Yb_{0.98}Ba_2Ga_{0.02}Cu_3O_{7-\delta}$; d – $Yb_{0.97}Ba_2Ga_{0.003}Cu_3O_{7-\delta}$

As mentioned in the experimental part, the reaction mixtures, in powder, were annealed three times, in air at 800°C for 4 h, followed by a heat-treatment at 950°C during 7 h as pellets.

According to the results obtained in non-isothermal conditions, the samples containing Eu starts the solid state reaction of the components of the system at 800°C. In this way, the preliminary thermal treatment at 800°C is effective in the superconducting phase formation.

In the case of samples containing Yb the solid state reaction of components of the mixture starts only at 900°C. In this way the preliminary thermal treatment at 800°C is not effective for the superconducting phase formation.

The superconducting transition temperature of the obtained samples is presented in Figs 5 and 6.

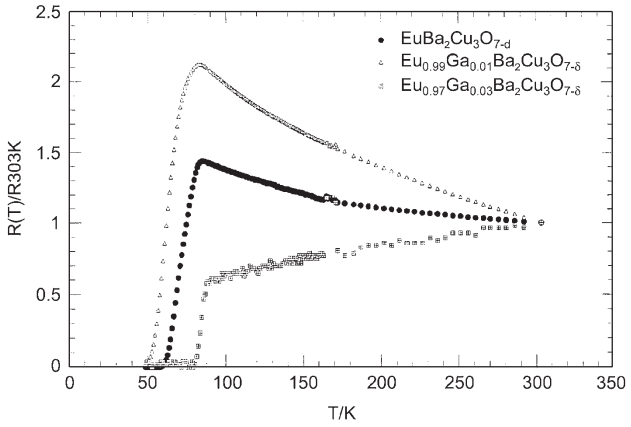

Fig. 5 Superconducting transition temperatures T_c for samples containing Eu

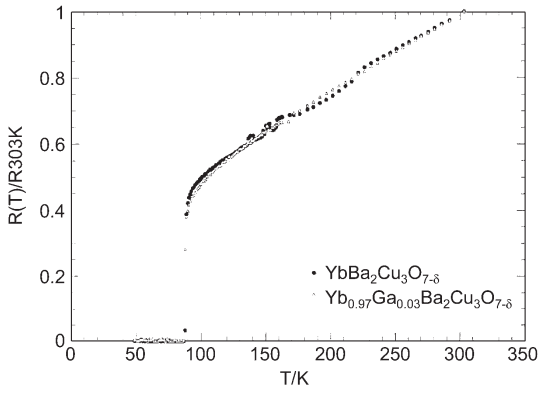

Fig. 6 Superconducting transition temperatures T_c for samples containing Yb

In the case of samples containing Eu, the presence of different amounts of Ga in the mixture, determines different superconducting behavior. The sample containing the highest amount of Ga presents the highest value for T_c and the less pronounced semiconducting behavior, as well. The semiconducting properties emphasized by the Eu containing samples were confirmed previously by magnetic measurements [11–13]. In this case the transition to diamagnetism marked the T_c transition temperature. The dependence of the superconducting properties with the Ga content indicated that during the isothermal treatment Ga was completely incorporated in the Eu containing samples.

In samples containing Yb, the superconducting behavior is not influenced by the Ga-substitution. The fact could be correlated with the incomplete incorporation of the Ga in the superconducting lattice due to an incomplete solid state reaction, which is underlined by the presence of the 'green phase' in the mixtures.

Conclusions

A thermoanalytical study in non-isothermal conditions on Ga-substituted $MBa_2Cu_3O_{7-\delta}$ superconducting compounds formation (M=Yb, Eu) was realized.

The presence of different oxides in the reaction mixtures leads to different reactivity of the system. The overall reactivity of the system is determined by the presence of the lanthanoide oxides, mainly Yb or Eu. In the system containing Eu the solid state reactions starts at lower temperature than in the system containing Yb, the Ga-substitution having a less evidenced effect on the superconducting compounds formation.

The different reactivity of the studied reaction mixtures noticed in non-isothermal conditions, led, after thermal treatment in isothermal conditions, to samples with different phase composition and superconducting properties.

References

1 J. Piechota and A. Pajaczkowska, Phys. Stat. Sol (a), 119 (1990) 271.
2 A. M. Balagurov, J. Piechota, A. Pajaczkowska, G. M. Mironova and H. Szymczak, Z. Phys. B-Condensed Matter, 76 (1989) 153.
3 Gh. Ilonca, A. V. Pop, D. Benea, M. Mehbod, L. Lanckbeen and R. Deltour, Romanian Report in Physics, 46 (1994) 147.
4 M. J. Kramer, A. Karion, K. W. Dennis, M. Park and R. W. McCallum, Enhanced Superconductivity, TMS-94 Febr. 24, 1994.
5 S. K. Malik, C. V. Tomy, D. T. Adroja, R. Nagarajan, Raw Prasad and N. C. Soni, Solid State Communication, 66 (1988) 1097.
6 Yu. Mei, S. M. Green, G. G. Reynols, T. Wiczynski, H. L. Luo and C. Politis, Z. Phys. B-Condensed Matter, 66 (1987) 303.
7 P. Allenspach, B. W. Lee, D. Gajewski and M. B. Maple, J. Appl. Phys., 73 (1993) 6317.
8 C. Jiang, Yu Mei, S. M. Green, H. L. Luo and C. Politis, Z. Phys. B-Condensed Matter, 68 (1987) 15.

9 M. B. Maple, Y. Dalichaouch, J. M. Ferreira, R. R. Hake, B. W. Lee, J. J. Neumeier, M. S. Torkiachvili, K. N. Yang, H. Zhou, R. P. Guertin and M. V. Kuric, Physica, 148B (1987) 155.
10 E. Burzo and V. Pop, J. Mat. Sci., 27 (1992) 5253.
11 I. Pop, R. Redac, I. Burda and V. Ioncu, Modern Phys. Let. B, 10 (1966) 809.
12 I. Pop, R. Redac, Gh. Borodi and V. Ioncu, Modern Phys. Let. B, 11 (1967) 593.
13 R. Redac and I. Pop, Romanian J. Phys., 42 (1997) 739.