Bulgarian Chemical Communications, Volume 43, Number 2 (pp. 320–324) 2011

Variation of the unit cell parameters of the $REBa_2Cu_3O_y$ (RE = Gd, Er) ceramics in function of the oxygen content

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Received January 16, 2011; Revised April 12, 2011

High temperature $Gd_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ ($y = 6.5 + \delta$) superconducting ceramics were prepared via solid-state reaction. The amount of oxygen in the synthesized samples was varied as they were kept at 460±5 ºC in flowing argon. The oxygen non-stoichiometry content, δ was determined by measuring the absorption of the blue colored I_3^--starch compound. The unit cell parameters were determined from powder XRD patterns. A correlation between c unit cell parameter and y-oxygen coefficient in $Er_1Ba_2Cu_3O_y$ and $Gd_1Ba_2Cu_3O_y$ ceramics was established. The derived new relations can be used for the rapid semi-quantitative analysis of the oxygen content in the mentioned ceramics.

Key words: superconducting ceramics, oxygen stoichiometry coefficient, I_3^--starch compound, X-ray.

INTRODUCTION

Since the discovery of $Y_1Ba_2Cu_3O_y$ ($y = 6.5+\delta$) high temperature superconducting ceramics (HTSC) many attempts to improve their critical temperature (T_c) and current (J_c) have been made: by optimizing the preparation procedure and conditions, by doping with different atoms, by introduction of pining centers, by replacing Yttrium with rare earths such as Er, Gd, etc. [1]. One of the key moments in the production of rare earth HTSC is the determination of oxygen content as the superconducting properties are correlated with its value. When the oxygen coefficient y is in the range 6.5–7.0, $RE_1Ba_2Cu_3O_y$ (RE = Y, Er, Gd, etc.) ceramics are superconducting and their structure is orthorhombic. An orthorhombic to tetragonal phase transition, occurring around $y \approx 6.5$ is responsible for the loss of the superconducting properties.

Many wet methods have been developed for the determination of the non-stoichiometric oxygen coefficient δ in $RE_1Ba_2Cu_3O_y$ samples [2–5]. Oxygen content could also be obtained by methods such as Raman spectrometry and X-ray diffraction if appropriate mathematical relations "oxygen content–physical parameter" are preliminary found [6, 7]. Such mathematical relation between c-axis unit cell parameter (determined from Inorganic Crystal Structure database (ICSD) data) and the y-oxygen coefficient (determined by iodometric titrations) has been derived data for $Y_1Ba_2Cu_3O_y$ HTSC [7]. It will be usefully to find the relations "oxygen content–c-unit cell parameter" for other $RE_1Ba_2Cu_3O_y$ HTSC, to verify if the relation can be extrapolated for other RE. We decided to compare the relation with $Gd_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ HTSC because the ionic radii of Gd (0.938 nm), Er (0.890 nm) and Y (0.900 nm) are similar [8]. Unfortunately a limited number of orthorhombic $Gd_1Ba_2Cu_3O_y$ [14, 19–23] and $Er_1Ba_2Cu_3O_y$ [9–18] structures have been reported in the ICSD thus no satisfactory correlation between c-unit cell parameter and oxygen content could be derived. Therefore the aim of the present work is to produce $RE_1Ba_2Cu_3O_y$ (RE = Gd, Er) superconducting ceramics with different oxygen content, to determine their oxygen coefficient, y and c-unit cell parameter, and to derive the relations between y-coefficient and c-parameter.

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EXPERIMENTAL

Samples preparation

A solid-state reaction was used to prepare the $Gd_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ HTSC samples. The triple heat treatment regime with intermediate grindings was used. The first step includes mixing and milling of appropriate amounts of Gd_2O_3, Er_2O_3, CuO, $BaCO_3$, and calcination in flowing oxygen at 900 ºC for 21h. The second step of the heat treatment was conducted at 930 ºC for 21h in the same atmosphere, followed by annealing at 450 ºC for 2h. The last step (third) started with grinding and pressing of the powder in pellets, followed by sintering at 940 ºC for 23 h, slow cooling to 450 ºC and holding at that temperature for 23 h. Pieces of the synthesized superconducting samples were grinded and kept at 460±5 ºC in flowing argon for various times (0–120 h) then quenched to room temperature.

Critical temperature measurement (T_c)

The critical temperature T_c was obtained from resistivity measurements by the Four probe contact method. The temperature was stabilized by typical scheme including PID controller with 10mK accuracy [24]. Both synthesized samples $RE_1Ba_2Cu_3O_y$ are superconducting and the values of their critical temperature T_c are as follows: 91.5K for $Gd_1Ba_2Cu_3O_y$ and 90.4 K for $Er_1Ba_2Cu_3O_y$.

Samples analysis by spectrophotometric method

The non-stoichiometric oxygen coefficient, δ was determined by the spectrophotometric method based on the formation of the I_3^--starch compound [2]. The samples are dissolved in HCl and KI solution under inert atmosphere and the iodine liberated is bounded with Starch in a blue colored compound. The absorption is measured by differential mode and the non-stoichiometric oxygen coefficient δ is obtained as a relation of two absorptions.

Samples analysis by X-ray method

Powder X-ray diffraction (XRD) data were recorded at room temperature using Bragg-Brentano geometry with Co *Kα* radiation. Step scans were performed over the angular range $8 < 2\theta < 70$ for $Er_1Ba_2Cu_3Oy$ and $8 < 2\theta < 90$ for $Gd_1Ba_2Cu_3O_y$ with the step size of 0.02 º/sec. The diffractograms were indexed using DICVOL [25] and the obtained unit cell parameters were refined using the X'pert Highscore program [26]. The peak shape was described by a pseudo-Voigt function. The background level was defined by a polynomial function. For each diffraction pattern the scale factor, the peak asymmetry and the unit-cell dimensions were refined while the instrumental zero shifts were kept constant.

RESULTS AND DISCUSSION

The average results for non-stoichiometric coefficient δ for $Gd_1Ba_2Cu_3O_y$ and $Er_1Ba_2Cu_3O_y$ HTSC samples (initially synthesized as well as annealed under argon flow) obtained by the spectrophotometric method are listed in Table 1. Each result is a mean value of at least three parallel determinations. The standard deviation is in the limits of ±0.002. A decrease of the oxygen coefficient *y* in function of the annealing time is observed (Fig. 1).

From the trends observed in Fig.1a it is visible that for $Gd_1Ba_2Cu_3O_y$ the process of oxygen release is very

Table 1. Non-stoichiometric coefficient δ and unit cell parameter for c-axis

Samples	Annealing time, [h]	non-stoichiometric coefficient δ	*c*-unit cell parameter
$Er_1Ba_2Cu_3O_y$	0	0.420	11.670(2)
	12	0.365	11.682(2)
	24	0.293	11.686(4)
	48	0.214	11.695(2)
	72	0.183	11.697(2)
$Gd_1Ba_2Cu_3O_y$	0	0.376	11.692(4)
	12	0.243	11.708(7)
	36	0.239	11.710(8)
	96	0.225	11.720(5)
	120	0.206	11.724(2)

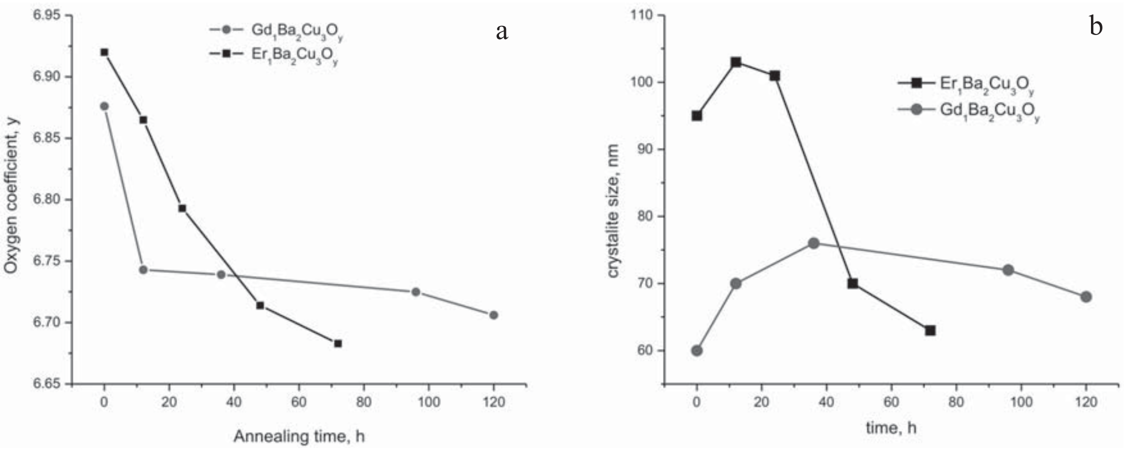

Fig. 1. Decrease of the oxygen coefficient y (a) and crystallite size (b) of the studied HTSC in function of the annealing time

rapid during the first 12 h. After the 12th hour the oxygen decrease is time-consuming. For Er$_1$Ba$_2$Cu$_3$O$_y$ the loss of oxygen at the beginning is almost proportional to the annealing time. The plateau in the oxygen content variation starts around the 48 h of the annealing. This difference of oxygen loss may be related to the differences in crystallite size and thus to the specific surface area and porosity.

The results of XRD analyses of the all Er$_1$Ba$_2$Cu$_3$O$_y$ and Gd$_1$Ba$_2$Cu$_3$O$_y$ samples are shown on Figures 2 and 3, respectively. The peak positions and intensities of the obtained phase correspond well to these of the known superconducting erbium and gadolinium 123 HTSC phase. All samples were indexed as orthorhombic with $a \sim 3.82$ $b \sim 3.88$ and $c \sim 11.68$ [1]; the values of the refined c-axis unit cell parameter are listed in Table 1. As expected the c-axis cell parameter increases with the decrease of the non-stoichiometric oxygen coefficient δ.

The variation of crystallite size obtained from the XRD patterns is shown on Fig. 1b. After an initial increase of the size the tendency is reversed and the diminution is somewhat consistent with oxygen content depletion and reaching of a plateau (probably a stage before orthorhombic to tetragonal phase transition).

Based on the spectrophotometric and XRD data the regression equations of the correlation between the non-stoichiometric oxygen coefficients δ and c cell parameter for the studied HTSC were obtained (Table 2). The equations $y = f(c)$ were also derived (Table 2) and are shown on Figure 4. One can see that the graphical relation for Er$_1$Ba$_2$Cu$_3$O$_y$ is very close to that of Y$_1$Ba$_2$Cu$_3$O$_y$ HTSC plotted from the

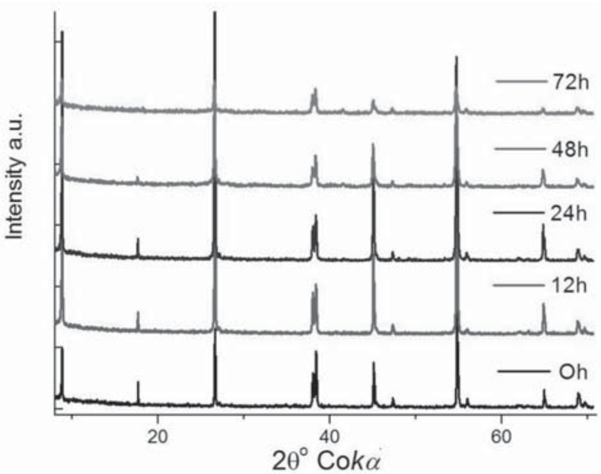

Fig. 2. XRD patterns of the synthesized and annealed in flowing argon Er$_1$Ba$_2$Cu$_3$O$_y$ sample

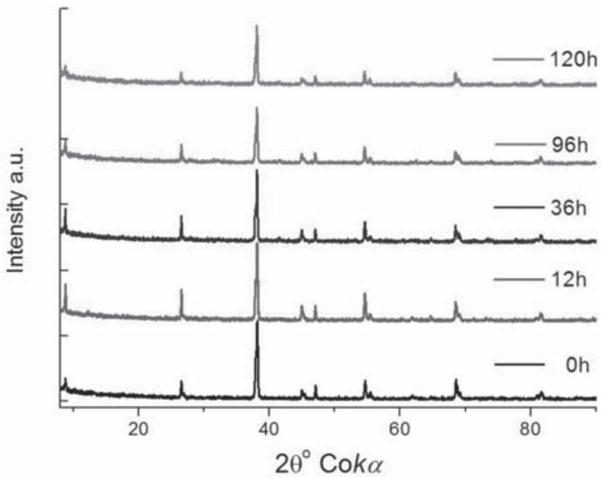

Fig. 3. XRD patterns of the synthesized and annealed in flowing argon Gd$_1$Ba$_2$Cu$_3$O$_y$ sample

Table 2. Results of the correlation

	Regression equation $c = k_0 - k_1\delta$	Error		Equation $y = f(c)$
		k_0	k_1	
$Er_1Ba_2Cu_3O_y$	$c = 11.718 - 0.107\delta$	0.004	0.013	$y = 116.01 - 9.346\ c$
$Gd_1Ba_2Cu_3O_y$	$c = 11.755 - 0.172\ \delta$	0.010	0.038	$y = 74.843 - 5.814\ c$

Table 3. Values of the difference Δy: $\Delta y = yEr/Gd - yY$

c-axis value [Å]	11.675	11.680	11.685	11.690	11.695	11.700	11.705	11.710
$\Delta y = y_{Er} - y_Y$	–0.015	0.003	0.021	0.038	0.055	0.073	0.091	0.108
$\Delta y = y_{Gd} - y_Y$	–0.084	–0.084	–0.084	–0.084	–0.084	–0.084	–0.084	–0.085

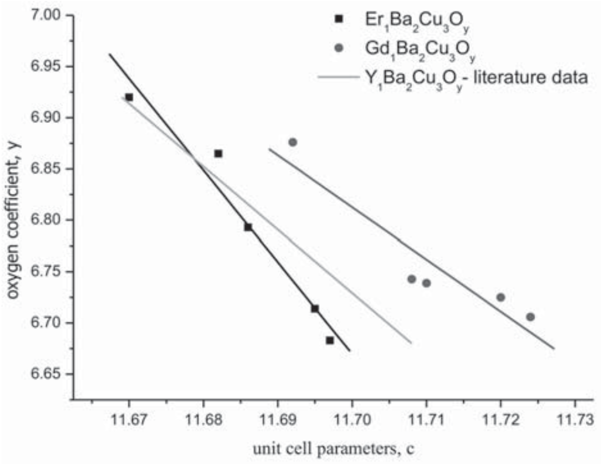

Fig. 4. Variation the oxygen content in function of the c-axis parameter

equation y = 75.250-5.856c [7]. The $Gd_1Ba_2Cu_3O_y$ relation is a little distant from that of $Y_1Ba_2Cu_3O_y$ – almost parallel to it. The differences between y coefficients calculated by the equations for gadolinium/erbium and ref. 7 yttrium ceramics are given in Table 3. In view of the fact that the difference Δy in almost all cases is greater than the errors of the spectrophotometric and XRD methods one can conclude that relation "oxygen content – c cell parameter" is specific for each ReBCO. Interestingly the observed deviations are in accordance with the difference between the ionic radii of Gd-Y and Er-Y and Y, with respective values of 0.04 nm (for Gd) and 0.01 nm (for Er). The development of a more complex relation, taking into account additional physical, chemical, structural etc. parameters may be envisaged with the accumulation of additional data.

CONCLUSIONS

The crystallite size of $Er_1Ba_2Cu_3O_y$ and $Gd_1Ba_2Cu_3O_y$ ceramics diminishes with depletion of oxygen. Both the oxygen content, y and crystallite size reach a "plateau", more rapidly for samples with smaller crystallites.

A correlation between c-unit cell parameter and y-oxygen coefficient in $Er_1Ba_2Cu_3O_y$ and $Gd_1Ba_2Cu_3O_y$ ceramics is established. The new derived equation can be used for the rapid semi-quantitative analysis of the oxygen content in the cited HTCS ceramics. The relation "oxygen content–c cell parameter" obtained for $Y_1Ba_2Cu_3O_y$ HTSC could not be employed to calculate precisely the oxygen content value, y for $Er_1Ba_2Cu_3O_y$ and $Gd_1Ba_2Cu_3O_y$ superconducting samples.

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ИЗМЕНЕНИЯ НА ПАРАМЕТРИТЕ НА ЕЛЕМЕНТАРНА КЛЕТКА НА $REBa_2Cu_3O_Y$ (RE = Gd, Er) КЕРАМИКИ В ЗАВИСИМОСТ ОТ КИСЛОРОДНОТО СЪДЪРЖАНИЕ

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Постъпила на 26 януари, 2011 г.; приета на 12 април, 2011 г.

(Резюме)

Високо температурни $Gd_1Ba_2Cu_3O_y$ и $Er_1Ba_2Cu_3O_y$ ($y = 6.5 + \delta$) свръхпроводими керамики бяха получени. Количеството на кислород в образците бе променяно като образците бяха отгрявани на 460±5 ºC в аргонова атмосфера. Нестехиометричното кислородно съдържание, δ, бе определено спектрофотометрично. Параметрите на елементарна клетка бяха определени чрез прахова рентгенова дифракция. Изведена бе зависимостта между *c* параметъра на елементарната клетка и съдържанието на кислород, *y*. Получените зависимости могат да се използват за бързо полуколичествено определяне на съдържанието на кислород.