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THERMAL STUDY OF SUPERCONDUCTING $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho)

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ABSTRACT

Polycrystalline black coloured samples of $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho) have been prepared from mixtures of BaO_2, CuO and R_2O_3, which were ground, pelletized and heated in air at 975 °C for 3 days, and slowly cooled in an oxygen-enriched air atmosphere. The resulting products are pure orthorhombic phases, S.G. Pmmm No. 47, Z = 1. Structural data are given. The TG studies carried out in both hydrogen and nitrogen dynamic atmospheres, have allowed to establish the oxygen content of the samples, which compare with those determined from populations of the oxygen positions after refining the X-ray diffraction intensities.

INTRODUCTION

During the last quarter of the last year the superconducting phase in the system Ba-Cu-Y-O has been identified by several groups as orthorhombic $Ba_2Cu_3YO_{7-x}$, having a critical temperature, T_c, of about 90 K. In this phase Y can be replaced by the stable trivalent rare earths without significantly altering either T_c or the orthorhombic structure. It is known that the oxygen content in these oxides determines properties such as the magnetic susceptibility, the electrical resistivity, the lengths of the unit-cell parameters, and the T_c temperature. In this paper the authors establish the oxygen content of four $Ba_2Cu_3RO_{7-x}$ samples by two methods, X-ray powder diffraction and thermogravimetric (TG) analysis, in order to compare both results.

EXPERIMENTAL

Samples of $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho) were obtained from analytical grade BaO_2, CuO and R_2O_3 (R = Y, Eu, Gd, Ho) which were mixed, ground in an agate

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mortar, pelletized, heated in air at 975 °C for 3 days, and slowly cooled in an oxygen-enriched air atmosphere. Susceptibility and resistivity measurements showed that these compounds are high T_c superconductors, being the values of the corresponding T_c (K) 88, 90, 92 and 92 for R = Y, Eu, Gd and Ho respectively.

The samples were characterized by X-ray powder diffraction as indicated elsewhere[1]. For thermogravimetric studies a Mettler TA 3000 system was used. The samples were heated up to 900 °C at rates of 4 °C.min^{-1} and 10 °C.min^{-1} under a flux of 50 ml.min^{-1} of hydrogen and nitrogen respectively. TG residua and the products of thermal treatments at intermediate temperatures were identified by X-ray diffraction as indicated for the initial samples.

RESULTS AND DISCUSSION

I) THERMAL STUDIES

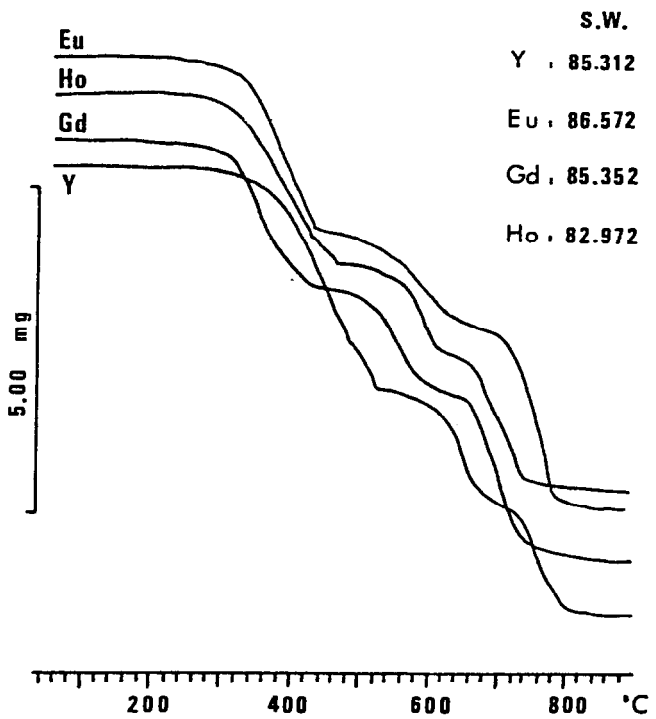

Fig. 1. Thermogravimetric curves in hydrogen dynamic atmosphere of the compounds $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho), at a heating rate of 4 °C.min^{-1}.

Figure 1 shows the TG curves obtained in hydrogen stream at a heating rate of 4 °C.min^{-1} for $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho). The X-ray patterns of the calcination products at temperatures around 800 °C, showed that residua were constituted by Cu metal, BaO and either R_2O_3 (R = Y, Gd, Ho) or EuO. The weight loss allowed to establish the oxygen content for each sample, 6.80 for R = Y, Gd and Ho, and 6.70 for R = Eu. Figure 2 includes the TG curve in nitrogen atmosphere for $Ba_2Cu_3YO_{7-x}$, as representative of the TG curves for the family of compounds $Ba_2Cu_3Ro_{7-x}$, since all of them have the same profile, the only difference being the value of the weight loss. The resulting product of this thermal treatment is the $Ba_2Cu_3RO_{6.0}$ tetragonal phase. The oxygen content values obtained under these conditions agree with those provided by the thermogravimetric study carried out in hydrogen atmosphere.

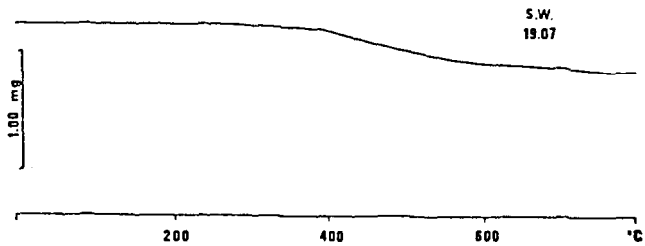

Fig. 2. Thermogravimetric curve in nitrogen dynamic atmosphere of $Ba_2Cu_3YO_{7-x}$.

Because the calcination product at 800 °C for R = Y, Gd, Ho is a mixture of Cu metal, BaO and R_2O_3 (R = Y, Gd, Ho), only the copper present in the sample is reduced. In the three cases the first inflexion point observed in the curve corresponds to the reduction of 4-coordinated (planar) copper, which is accomplished at lower temperatures than the reduction of the 5-coordinated (square pyramidal). On the other hand, for R = Eu the calcination product at 840 °C is Cu metal, BaO and EuO, which means that both copper and europium are reduced. The X-ray diffraction powder of a sample taken at the temperature corresponding to the first inflexion point shows that the residuum is constituted by Cu, CuO, BaO, Eu_2O_3 and EuO; the weight loss value until the first inflexion point coincides with that corresponding to the reduction of 4-coordinated copper and two fifths of the europium present in the sample. The X-ray diffraction powder of the residuum in the second inflexion point shows that all the Eu^{3+} has been reduced to Eu^{2+} given that this residuum is constituted by Cu, CuO, BaO, and EuO.

For R = Y, Gd, Ho, the heating rate of 10 °C.min^{-1} leads to identical reduction products as those obtained heating at 4 °C.min^{-1}. However, for R = Eu and a heating rate of 10 °C.min^{-1}, the residuum at 800 °C is a mixture of Cu metal, BaO, Eu_2O_3 and EuO. Thus, all the Eu^{3+} present in the sample is not reduced to Eu^{2+}. Given that for R = Y, Gd, Ho heated at 10 °C.min^{-1}, the thermogravimetric curves do not present a significant difference with respect to those obtained at 4 °C.min^{-1}, figure 3 only shows the curve for R = Eu, which presents two steps. The first weight loss, until 420 °C approximately, agrees with the oxygen losses of 4-coordinated copper and two fifths of the europium present, and the second one, until 700 °C approximately, corresponds to the reduction of 5-coordinated copper.

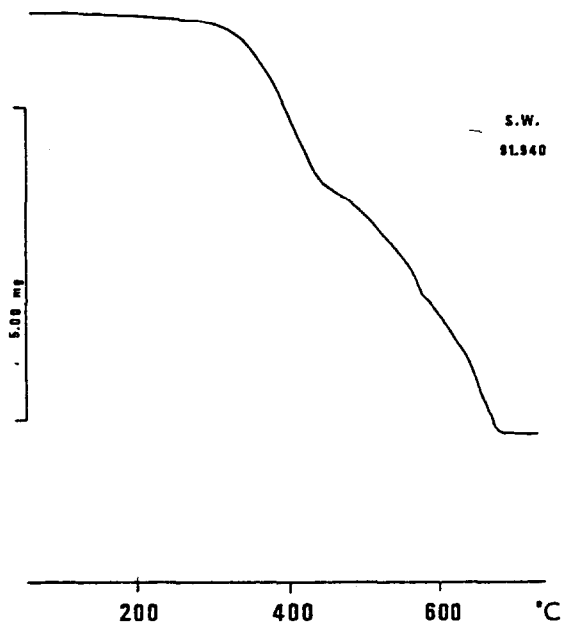

Fig. 3. Thermogravimetric curve in hydrogen dynamic atmosphere of $EuBa_2Cu_3O_{7-x}$, at a heating rate of 10 °C.min^{-1}.

II) X-RAY DIFFRACTION STUDY

The four superconducting oxides studied were single crystallographic phases, which were indexed in the orthorhombic system. The unit-cell parameters were refined using the program LSUCRE[2].

Table I. Unit-cell parameters for $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho)

R	a(Å)	b(Å)	c(Å)	V(Å^3)
Y	3.8174(4)	3.8825(4)	11.683(2)	173.17(2)
Eu	3.8451(5)	3.9032(4)	11.728(1)	176.02(2)
Gd	3.8376(5)	3.904(1)	11.700(1)	175.27(4)
Ho	3.819(1)	3.888(1)	11.689(4)	173.56(6)

X-ray intensities, I_o, were collected by step scanning with increments of $0.01°2\theta$ and a counting time of 4s each step, being the goniometer controlled by a DACO-MP V2 computer, which carried out the integration of the diffraction peaks and the background correction. Seventy-two reflections for R = Y, eighty-four for R = Eu, forty-five for R = Gd and seventy-three for R = Ho, were considered as observed. From these intensities a number of 9 structural parameters (scale factor, atomic positional parameters, occupancy factors for two oxygen atoms and the overall temperature factor) were refined by means of a full-matrix least squares method[3], which minimizes the function $\Sigma W(|F_o|^2 - s_f |F_c|^2)^2$, where W, F_o, F_c and s_f are the weight of each reflection, the observed and calculated structure factors and the scale factor, respectively. The observed intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and correction terms for anomalous dispersion were taken from the International Tables[4]. The discrepancy factors were computed as $R = \Sigma(|F_o|^2 - s_f |F_c|^2)/\Sigma|F_o|^2$. A previous refinement was made including the overlapping reflections, 0 0 3 and 0 1 0 for instance; from here the relative contribution of each reflection was obtained and used in a second refinement. This refinement was performed in the space group Pmmm, No. 47, and led to the atomic positions and occupancy factors, f, given in Table II. These occupancy factors indicate that the oxygen content values of the four compounds $Ba_2Cu_3RO_{7-x}$ are 6.80, 6.87, 6.90 and 6.90 for X = Y, Eu, Gd and Ho, respectively. These values compare with those obtained from thermogravimetric studies.

Table II. Atomic positional and occupancy factors (f) for $Ba_2Cu_3RO_{7-x}$ (R = Y, Eu, Gd, Ho).

Atom	Position	x/a	y/b	z/c				f			
				Y	Eu	Gd	Ho	Y	Eu	Gd	Ho
Ba	2t	½	½	0.1846(3)	0.1836(3)	0.184(1)	0.1844(3)	1	1	1	1
Cu 1	1a	0	0	0	0	0	0	1	1	1	1
Cu 2	2q	0	0	0.3576(6)	0.3523(6)	0.354(2)	0.3546(6)	1	1	1	1
R	1h	½	½	½	½	½	½	1	1	1	1
O 1	1e	0	½	0	0	0	0	0.68(8)	0.80(4)	0.5(2)	0.75(7)
O 2	2s	½	0	0.379(2)	0.380(2)	0.376(7)	0.380(2)	1	1	1	1
O 3	2r	0	½	0.379(2)	0.375(2)	0.374(7)	0.379(2)	1	1	1	1
O 4	2q	0	0	0.164(3)	0.158(3)	0.170(12)	0.162(3)	1	1	1	1
O 5	1b	½	0	0	0	0	0	0.12(8)	0.07(5)	0.4(2)	0.14(7)

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