Thermochimica Acta, 162 (1990) 69–74
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A HEAT CAPACITY STUDY OF THE HIGH-T_c SUPERCONDUCTING COMPOUNDS $MBa_2Cu_3O_{7-x}$ (M ≡ Y, Eu, Ho) NEAR T_c *

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(Received in final form 24 October 1989)

ABSTRACT

Heat capacity results for single-phase, polycrystalline samples of high-T_c ceramic superconductors $YBa_2Cu_3O_{6.98}$, $EuBa_2Cu_3O_{6.80}$ and $HoBa_2Cu_3O_{6.90}$ are reported. The samples were obtained from the sintered products of well-reacted M_2O_3, BaO_2 and CuO powders.

The calorimetric measurements were performed in a continuous-heating, computer-controlled calorimeter in the temperature range 77–300 K.

The heat capacity behaviour of $YBa_2Cu_3O_{6.98}$ in different low magnetic fields is also reported.

INTRODUCTION

Although two reviews have recently appeared on the thermal properties of $MBa_2Cu_3O_{7-x}$ compounds [1,2], they refer, for the most part, to the yttrium-based superconductor. To date, the thermal properties of the rare-earth-based superconductors have not been studied to the same extent in a comparative way even through they can give important information on the theoretical aspects of superconducting transitions. Moreover, there are few comparisons of well-characterised samples obtained by the same laboratory.

This work was initially directed to the study of the effect of yttrium substitution by a rare earth element carrying a different magnetic moment [3,4] on the superconducting transition temperature (T_c). In this paper we compare the heat capacity data of $YBa_2Cu_3O_{7-x}$, $EuBa_2Cu_3O_{7-x}$ and $HoBa_2Cu_3O_{7-x}$, and present the heat capacity results of $YBa_2Cu_3O_{7-x}$ performed in zero magnetic field, 20 Oe and 90 Oe.

The literature [5,6] shows that, although most rare earth atoms are more or less magnetic, these substitutions do not change T_c by more than ±10%. Moreover in this paper, we show that the T_c values of the rare-earth-substituted superconducting oxides do not change at all (within the experimental accuracy of 0.1 K) at least when using the isoentropic method proposed by Junod et al. [7].

* Presented at the 10th AICAT, Pisa, Italy, 11–14 December 1988.

0040-6031/90/$03.50

Some more questions concerning $YBa_2Cu_3O_{7-x}$ remain unanswered; for example, whether a first-order phase transition is superimposed on the specific heat jump at T_c, as observed by Butera [8], or whether the different T_c values found in the literature are in effect due to a low oxygen content and not to the substitution of Y by a rare earth.

EXPERIMENTAL

The $MBa_2Cu_3O_{7-x}$ compounds were prepared by a solid-state reaction proposed by us [9], which is based on the thermal decomposition of BaO_2 instead of $BaCO_3$. Details are reported elsewhere [10].

Batches of about 30 g were prepared from well-dried stoichiometric amounts of Y_2O_3 (4 N, Atlantic Equipment Engineers), Eu_2O_3 (4 N, Strem Chemicals), Ho_2O_3 (4 N, Strem Chemicals), BaO_2 (2 N, Material Research) and CuO (2 N, Merck) powders mixed thoroughly in a rotating mixer. The samples were first reacted in air at about 1220 K for 8 h (heating rate, 5–10 K min^{-1}), and then slowly cooled to room temperature.

The compounds were weighed to determine the reaction weight-loss, and then finely powdered, dry sieved and structurally characterised [11]. X-ray analysis indicated single-phase samples with the orthorhombic *Pmmm* structure-type and lattice parameters in agreement with the literature data. The powders were characterised magnetically by their diamagnetic susceptibility in a 100–300 Oe field measured on a laboratory scale using a simplified Faraday balance.

They were then pressed into cylinders and sintered in O_2 for 12 h at temperatures of 1210 K, for Eu- and Ho-based compounds, and 1250 K for the Y-based compound. The sintered samples were checked magnetically, and by X-ray and microprobe analyses, to confirm that they were superconducting above 90 K and single-phased. Micrographic analysis of each batch after conventional polishing and etching with a dilute solution of CH_3COOH showed a single-phase structure and well-formed grains.

The oxygen content of all the samples was determined by a crystallographic method that uses accurate determination of the crystallographic constant, *c*. This can easily be correlated to the oxygen content [12,13].

The stoichiometry of the samples was found to be $YBa_2Cu_3O_{6.98}$, $EuBa_2Cu_3O_{6.80}$ and $HoBa_2Cu_3O_{6.90}$.

The samples for the heat capacity measurements were obtained from the sintered product by cutting pellets of 13 mm diameter weighing 2–3 g.

The calorimetric measurements were performed in a computer controlled, continuous heating adiabatic calorimeter [14]. The measurements are reproducible to 1%; the absolute accuracy strongly depends on the thermal conductivity of the samples, especially at high temperatures, and is estimated to 5% below 150 K for YBCO samples. Calorimetric measurements in

magnetic field were performed by cooling the sample in zero field, and generating the magnetic field externally before starting the heat capacity measurements.

RESULTS AND DISCUSSION

The C_p/T versus T data, comparing the heat capacity of $MBa_2Cu_3O_{7-x}$ compounds with different magnetic moment carried by two rare earths or yttrium [4], are shown in Fig. 1.

It should be noted that the absolute heat-capacity values for the three samples are different, However, as the differences with respect to the total heat capacity are around 5%, they may not be significant.

In effect, as already pointed out by Junod et al. [7], large differences in the heat capacity data ($\pm 10\%$), beyond the experimental accuracy of the calorimetric apparatus, have been observed in different YBCO samples prepared under various conditions. A similar dependence on the preparation could also be expected for the heat capacity of samples in which yttrium is replaced with a rare earth.

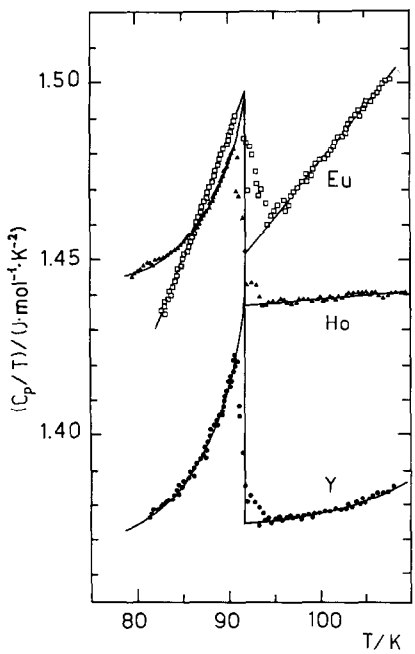

Fig. 1. C_p/T vs. T data around the critical temperature for $YBa_2Cu_3O_{6.98}$ (●), $EuBa_2Cu_3O_{6.80}$ (□) and $HoBa_2Cu_3O_{6.90}$ (▲). Continuous lines show the equal-area construction of the ideal jump (see text).

In contrast, the fact that T_c is clearly the same is quite remarkable. It must be stressed that the same extrapolation method was used, in which the T_c is determined by plotting C_p/T versus T. In this representation, the area under the experimental curve is an entropy. The smoothed behaviour below 90 K and above 93 K permits a straightforward extrapolation so as to obtain the ideal jump, $\Delta(C_p/T)$, of about 59 mJ mol^{-1} K^{-2} for $YBa_2Cu_3O_{6.98}$ and $HoBa_2Cu_3O_{6.90}$. The lower jump of $EuBa_2Cu_3O_{6.80}$ is due to its lower oxygen content, which leads to a lower amount of superconducting phase at 91 K [7].

The temperature of the ideal jump is drawn so as to preserve the entropy balance; the net areas between the ideal, continuous line and the smoothed, experimental data above and below T_c are zero.

None of our samples displayed the lambda transition at 86.6 K reported by Butera [8] nor did we detect latent heat at the critical temperature (91.5 K) in zero magnetic field. However, because he worked with a 30 g sample whereas we used 2–3 g pellets, it is possible that our technique was not sufficiently sensitive.

In contrast, lambda transitions have been observed by McConville and Serin [15] in conventional superconductors subjected to a magnetic field.

A first-order superconducting–normal-state transition is expected if the sample is measured in a magnetic field: the relative thermal effect can be

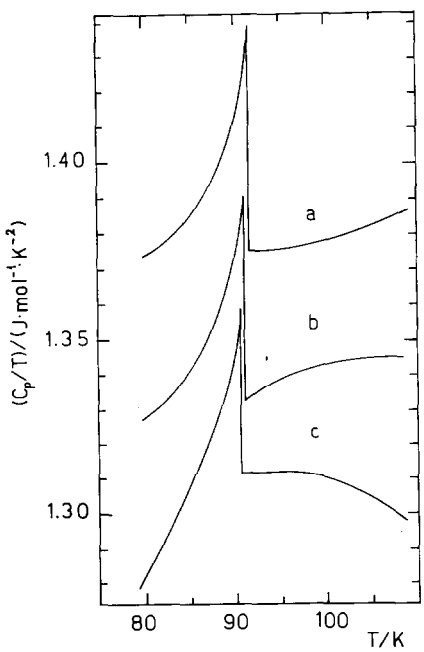

Fig. 2. Comparison of the C_p/T vs. T data for $YBa_2Cu_3O_{6.98}$ in different magnetic fields: a, $H = 0$ Oe; b, $H = 20$ Oe; and c, $H = 90$ Oe.

calculated from the relationship

$$q = -(\mu_0/4\pi)TH_cV_s(dH_c/dT)$$

where H_c is the thermodynamic critical field and V_s is the superconducting molar volume. Therefore, the heat capacity of YBCO in magnetic fields of 20 and 90 Oe was studied.

Figure 2 shows the measurements in magnetic fields of 0, 20 and 90 Oe near T_c. The experimental points are omitted for clarity. A dependence of the critical temperature, T_c, on the magnetic field ($dT_c/dH \simeq -15$ mK Oe^{-1}) was indeed observed, but no lambda divergences were seen.

These results are in agreement with those obtained by Salomon et al. [16]. In higher magnetic fields, they found that the heat capacity of the YBCO phase shows a slight dependence of T_c on H, and an enlargement of the transition. This behaviour is similar to that caused by a depletion of oxygen, as we have reported elsewhere [13].

The absolute value of the heat capacity was also found to depend on the magnetic field, as if a latent heat were emitted in a broad transition. The sign, however, was opposite to that expected from the relationship stated above. Therefore, even though it was also observed by Salomon et al. [16], this effect may have an unknown instrumental origin. Work is in progress to ascertain the exact nature of this effect in the rare earth analogues of $YBa_2Cu_3O_{7-x}$ as well.

ACKNOWLEDGEMENTS

Professors G.L. Olcese and A. Iandelli are gratefully thanked for helpful discussions and suggestions.

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