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COMPARISON OF DILATOMETRIC MEASUREMENTS OF $YBa_2Cu_3O_{7-x}$ IN OXYGEN, AIR AND ARGON ATMOSPHERE

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ABSTRACT

The results of the comparison of the thermal dilatometric measurements for two specimens of $YBa_2Cu_3O_{7-x}$ prepared at different conditions-reacting the constituents at 930°C for 18 h (sample I) and 950°C for 24 h (sample II) in air atmosphere and sintering the samples at 950°C for 24 h (sample II) and 900°C (sample II) in flowing oxygen - are presented. The measurements are performed in flowing oxygen, air and argon atmospheres. Experimental results of percentage thermal expansion $\frac{\Delta l}{l}$ and the coefficient of the linear thermal expansion α show that the phase transition $O_1 \longrightarrow O_2$ is followed by an increase of $\frac{\Delta l}{l}$ and α, while their values decrease by the $O_2 \longrightarrow T$ phase transformation. A hysteresis effect by heating and cooling is observed (especially strong in argon). Independent on the gas atmosphere, the $O_1 \longrightarrow O_2$ phase transition takes place at about 400°C for the sample I. For the sample II in oxygen this transition takes place at 575°C and in air it is completed at 550°C. $O_2 \longrightarrow T$ phase transition temperature for sample II is higher than the one for sample I and it decreases with the gas atmosphere changing: oxygen → air → argon.

The results of dilatometric measurements carried out on the $YBa_2Cu_3O_{7-x}$ compound are reported. They were undertaken in order to determine the temperature of the transition between both orthorhomic and a tetragonal phase in oxygen, air and argon atmosphere. These results are

compared with our dilatometric measurements /1/ on the sample prepared by the other conditions.

The sample was prepared by mixing appropriate amounts of $BaCO_3$ (99.8%), Y_2O_3 (spectral purity) and CuO (99.9%) /2,3/, grinding and heating at 950°C in air for 24 h. After slow cooling, this raw powder material was reground, pressed into pellets and sintered in flowing oxygen at 900°C for 20 h. Then the sample was slowly cooled down to 200°C in O_2. We denote this "sample" as "sample II" to differ it from the "sample I" we have investigated earlier /1/, prepared by reacting the same constituents at 930°C for 18 h in air and sintered for one day at 950°C in flowing oxygen.

The X-ray diffraction examinations of both samples /1,2/ have shown that the products were single phase orthorhombic compounds with a good cristallinity and the unit cell parameters: a = 0.3822 nm, b = 0.3891 nm and c = 1.1665 nm, being in good agreement with the data of Greedan et al. /4/. This phase has been identified as the high T_c superconductive phase and denoted as orthorhombic phase 1 (O_1) characterized by lattice constants $a<b=\frac{c}{3}$, /1,2,5/. The transition from orthorhombic O_1 phase to orthorhombic O_2 phase, characterized by $a<b<\frac{c}{3}$, /5,5/, takes place at about 400°C /1,6/. Another phase transition at about 700°C was identified as a transition of O_2 phase to a tetragonal one (T) /1,6/.

The electrical resistance and magnetic susceptibility measurements /1,2/ have shown that the transition to a superconducting state takes place at 92 K for the sample I and at 90 K for the sample II.

The measuring equipment contained the Netzsch high temperature electronic dilatometer (type 402 E). The temperature range used extends from 20°C to 950°C. The measurements on the sample were taken successionally in flowing oxygen, air and argon gas atmospheres.

Fig. 1a. shows the temperature dependence of the percentage thermal expansion $\frac{\Delta l}{l}\%$ of the $YBa_2Cu_3O_{7-x}$ ceramic at different gas atmospheres.

Fig. 1b. shows the temperature dependence of the coefficient of the linear thermal expansion calculated on the basis of these data.

For comparison, in Figs. 2a. and 2b. are presented $\frac{\Delta l}{l}$ and α as a function of temperature for the sample I /1/.

Comparison of the results obtained in this work (sample II) and the results of measurements /1/ (sample I) indicates that:

- the phase transitions at $\sim$ 400°C and $\sim$700°C correspond to $O_1 \rightarrow O_2$ and $O_2 \rightarrow$ T transformations respectively. If we denote the phase transition temperatures for the samples under consideration as T_I, T_{II} for

$O_1 \rightarrow O_2$ and T'_I, T'_{II} for O_2 — T transition, it is visible that (in air and argon) $T_I > T_{II}$, while $T'_I < T'_{II}$ (in oxygen, air and argon);

- there is no visible O_1 — O_2 transitions at 400°C for the sample II (in oxygen) but it takes place at 575°C. It is pointed out too that in air the $O_1 \rightarrow O_2$ transitions, which begins at 363°C, is completed at 550°C;

- at high temperatures for both specimens the hysteresis behaviour of $\frac{\Delta l}{l}$ is observed;

- in argon atmosphere (Fig. 2b) the value of α at temperatures 400-600°C is very high.

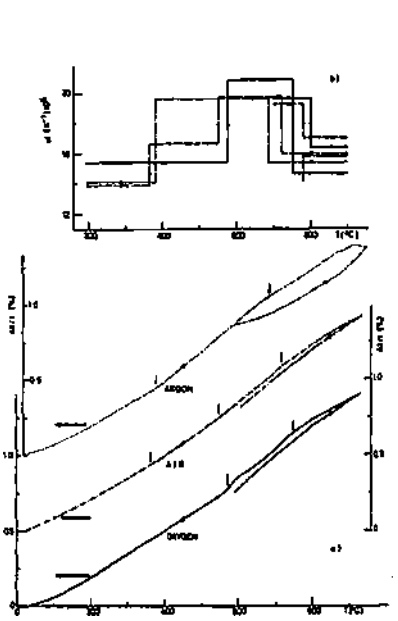

Fig. 1

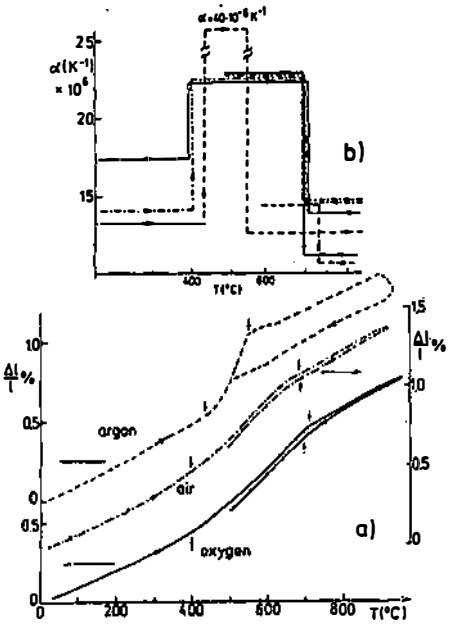

Fig. 2

Thermal dilatometric measurements have also indicated an influence of the gas atmosphere on the phase transition temperatures, as well as on the values of the linear thermal expansion coefficient α. This dependence is a result of oxygen removal. The thermogravimetry data show that in this temperature region a change in oxygen stoichiometry is observed above 400°C /7,8/. This change is very strong for an inert gas atmosphere (N_2, Ar, He) and smaller for oxygen and air.

For both samples in different phase regions the different values of α are observed. The observed increase in the value of α in the O_2 phase is probably connected with the diffusion of the oxygen from the (0, 1/2, 0) to (1/2, 0, 0) position /9/.

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