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Note

HIGH TEMPERATURE DTA OF CERAMIC SUPERCONDUCTOR $YBa_2Cu_3O_{7-\gamma}$

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During DTA of the $YBa_2Cu_3O_{7-\gamma}$ (1 2 3) ceramic oxide superconductor fired at 950 °C for 50 h in a stream of oxygen four endothermic effects are detected within the range 950–1350 °C $YBa_2Cu_3O_{7-\gamma}$ decomposes reversibly to Y_2BaCuO_5, $BaCuO_2$ and CuO at 999 °C having a ternary eutectic at 957 °C

Ozawa and co-workers [1,2] found the formation of a perovskite phase in the temperature region above 750 °C and ca 970 °C they observed melting followed by decomposition and phase separation above this temperature De Leeuw et al [3] reported a reversible decomposition of $YBa_2Cu_3O_{7-\gamma}$ above 1000 °C in air into Y_2BaCuO_5 and CuO, and above 1200 °C into Y_2O_3, $BaCu_2O_2$ and CuO

EXPERIMENTAL

For our high temperature thermal investigation we used a commercial DTA apparatus by Netzsch equipped by a DDK measuring head with Pt crucibles The temperature was calibrated by ICTA/NBS temperature standards and Al_2O_3 was used as reference A powdered sample of about 100 mg was heated in an oxygen and/or air stream at a rate of 5 K min^{-1} and temperature changes were detected with a sensitivity of 0 1 mV/25 cm by the thermocouple Pt–Pt10Rh The 1 2 3 sample was prepared by mixing, powdering and firing of analysed oxides [4] finally tempered at 950 °C for 50 h, followed by slow cooling to ambient temperature

RESULTS AND DISCUSSION

Figure 1 shows the DTA curves for the 1 2 3 sample heated in oxygen up to 1350 °C for the first and the second time Four endothermic effects can be seen with a mutual intensity ratio of 14 100 · 3 5 34 the last being

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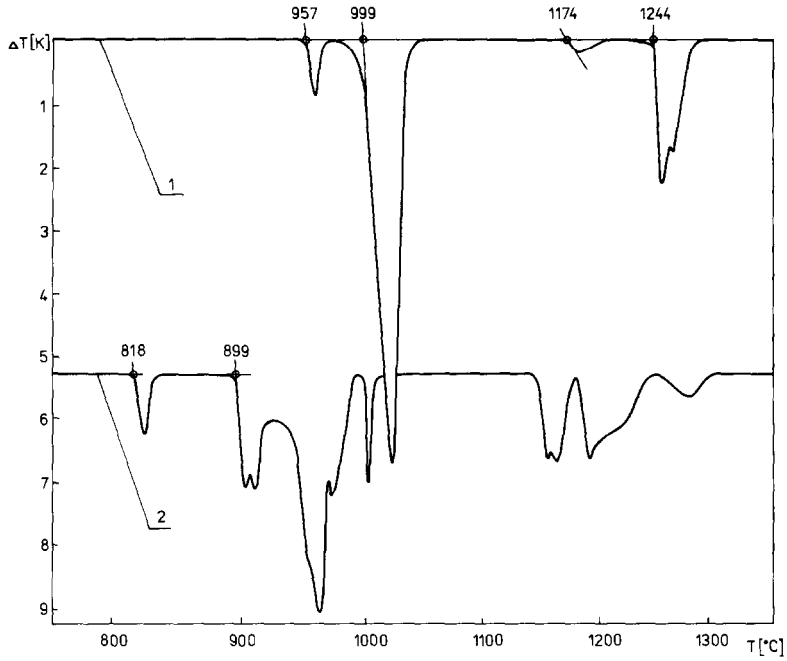

Fig 1 DTA curves of $YBa_2Cu_3O_{7-\gamma}$ in dynamic oxygen atmosphere (1) first run, (2) second run of the same sample

twisted By comparing with the DTA of known single phases of $BaCuO_2$, $YCuO_{2\,5}$ and Y_2BaCuO_5 we can deduce that the first effect is connected with an eutectic of the ternary $YO_{1\,5}$–BaO–CuO system

The second effect is associated with the decomposition of the 1 2 3 phase into Y_2BaCuO_5 and $BaCuO_2$ instantly dissociating into BaO and CuO, respectively The third is probably decomposition of the binary $Y_xBa_yO_x$ phase which occurs together with the Y_2BaCuO_5 phase The last decomposes above 1244 °C as is indicated by the last twisted peak The first decomposition was proved by an independent X-ray diffraction analysis on quenched samples If DTA is limited to below 1050 °C the peak of the 1 2 3 phase decomposition is reversible and the sample remains superconductive

In contrast with the result of De Leeuw et al [3] we observed irreversible decomposition at temperatures above 1244 °C During the second heating of the same sample the DTA pattern substantially changes due to the formation of new high temperature phases initiated by the formation of a liquid phase The eutectics at 818 and 900 °C (twisted) are remarkable, these appear during cooling and remain during repeated runs In consequence the portion of the desired superconducting phase 1 2 3 decreases (more than four times with respect to the intensity ratios) because of the Y_2BaCuO_5 phase and the unknown phase formation It follows that the maximum

temperature for the 1 2 3 superconductor phase formation should not exceed the temperature of the second peak, i e 999 °C which is in accordance with the temperature of 960 °C recommended by Ozawa et al [1]. When carrying out the DTA in air the temperatures of the two first peaks decrease to 911 and 977 °C respectively

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