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Upper critical field of Me–Y–Ba–Cu–O (Me = Zr, Hf)

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The properties of the ceramic high-T_c superconductors Me–Y–Ba–Cu–O (Me = Zr, Hf) have been measured in applied magnetic fields up to 20 T. The temperature dependencies of the upper critical field B_{c2} were determined for a wide range of concentration (5–60 mol%) of the doping elements. The major effect of this method of doping is to improve the mechanical properties. The slope $\partial B_{c2}/\partial T$ near T_c depends on the type of doping element and on the doping concentration.

An important factor which sets a limit to the extensive use of high-T_c materials in microelectronic devices and superconducting wires is their high brittleness and low strength. The search for materials that combine good superconductive properties at a high transition temperature with suitable mechanical properties is a very active field in contemporary materials science.

Doping of high-T_c superconductors has been widely used in an attempt to optimize the superconducting properties. In the case of $YBa_2Cu_3O_{7-\delta}$, the substitution of other rare earth elements for Y usually has little effect, with the notable exception of Pr. Substitution with Zn or magnetic elements such as Fe leads to a rapid decrease of the critical temperature. Alloying with noble metals such as Au or Ag is found to improve the critical current at grain boundaries, and there are indications that low concentrations of Au improve the superconducting properties of single crystals.

In this paper we report the results of a high magnetic field investigation of the transport properties of ceramic samples of $YBa_2Cu_3O_{7-\delta} + xMeO_2$ (Me = Zr, Hf). This research was inspired by our previous results which showed that the mechanical properties of these ceramics could considerably be improved [1–4]. The hardness increased to 2–4 times the value for the undoped materials, and at elevated temperatures a near plastic deformation was found possible. Doping with concentrations up to $x = 0.6$ was possible with only little effect on the superconducting transition temperature. Preliminary measurements indicate in contrast that the critical current of the ceramics increased. At concentrations above 0.6 the material became electrically insulating.

We prepared our samples from the mixtures of Y_2O_3, CuO, MeO_2 (Me = Zr, Hf) and the carbonate $BaCO_3$, which were fired at 980°C for at least 40 h. The thoroughly mixed powers were pressed into pellets at a hydrostatic pressure of 10 kbar. The pellets were sintered at 980°C for 12 h in air, and subsequently annealed in pure oxygen.

It was observed that all the samples we prepared are of multiphase nature. The basic phase found in the samples was $YBa_2Cu_3O_{7-\delta}$ [3]. The Me-upgraded phase is situated on the $YBa_2O_{7-\delta}$ granular surface as well as in the intergranular space. Microprobe phase analysis indicated that the metal dopant is mainly incorporated in the form of $ZrBaO_3$ or $HfBaCuO_4$. The volume content and morphology of the Me-upgraded phase depends on the nature of the doping elements and dopant concentration.

The electrical properties of the Me–Y–Ba–

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Cu–O (Me = Zr, Hf) systems were studied in magnetic fields up to 20 T for a wide range of dopant concentrations (5–60 mol%). The resistive transition was measured in a variable-temperature cryostat. In the applied magnetic field, temperature was regulated using a capacitance thermometer which was calibrated in zero field against a germanium resistor. The resistance was determined with a standard four-probe technique, with the leads glued to the sample using carbon black paint. The current density was kept below 5×10^{-3} A/cm^2 to avoid ohmic heating or exceeding the critical current density. The normal state resistivity of a typical sample is of the order of 1–10 mΩ cm. In zero field the 10–90% width of the resistive transition for our systems was 0.5–1.5 K. The resistive transitions become significantly broader in an applied magnetic field (see fig. 1). The critical field value as a function of temperature was determined with the 50% criterion from the midpoints of the superconductive transitions, and $B_{c2}(T)$ is shown in figs. 2 and 3, for samples with several different dopant concentrations. The slope $\partial B_{c2}/\partial T$ was determined for a number of concentrations of Me, where the metallic elements were Zr and Hf in the research covered by this report. The slope

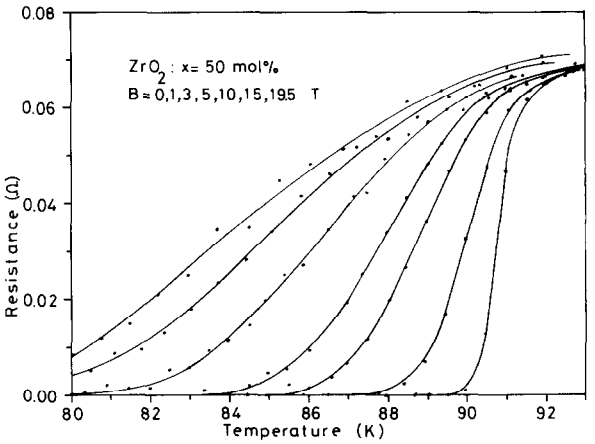

Fig. 2. Resistance of $YBa_2CU_3O_{7-\delta}$ + 50 mol% ZrO_2 as a function of temperature for different values of the magnetic field.

was found to vary between 0.9 and 2 T/K near T_c, and between 2 and 4.5 T/K in the high-field part. For a given temperature, just below T_c, there is an optimum in the value of the dopant concentration at which the upper critical field reaches a maximum, both for the Zr-doped and Hf-doped systems. The optimum concentration is in the range 45–50 mol% MeO_2.

It is an important and remarkable observation

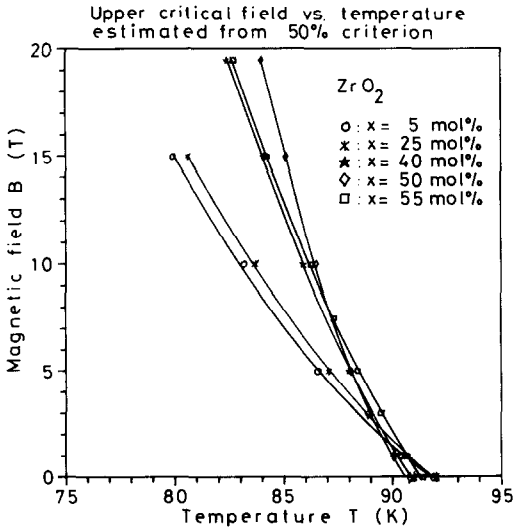

Fig. 1. Upper critical magnetic field of $YBa_2Cu_3O_{7-\delta}$ + $xZrO_2$ samples versus temperature for different values of dopant concentration x.

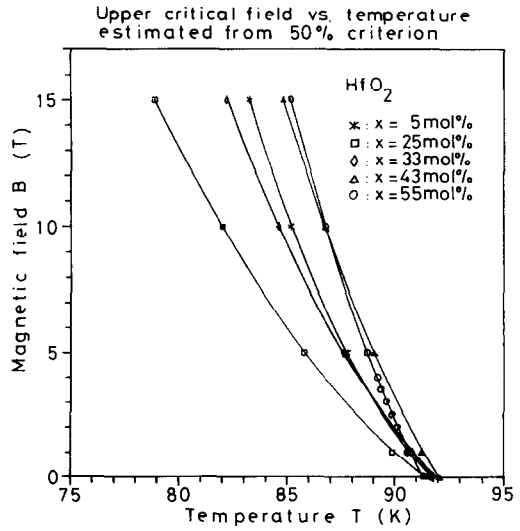

Fig. 3. Upper critical magnetic field of $YBa_2Cu_3O_{7-\delta}$ + $xHfO_2$ samples versus temperature for different values of dopant concentration x.

that just at these concentrations, improvement of the mechanical properties of these ceramic materials was also found. From measurements of the acoustic attenuation and sound velocity the elastic properties was determined. The elastic modulus and the value of the longitudinal strength of the metal-doped ceramics was found to increase in comparison to the undoped $YBa_2Cu_3O_{7-\delta}$, and it became possible for the material to undergo significant plastic deformation at higher temperatures without degradation of the superconducting properties [1, 3].

To gain some insight into the potential of this doping technique to increase the transport critical current in this type of samples, we have started an AC-susceptibility study. The preliminary results indicate an enhancement of the intergrain critical current.

In conclusion, we have found that there exists an optimum value for the metalic dopant concentration at which the upper critical field of the Zr- or Hf-doped $YBa_2Cu_3O_{7-\delta}$ superconductor reaches a maximum value. Therefore, by doping $YBa_2Cu_3O_{7-\delta}$ with metallic dopants in the way described in our reports, significant improvements can be realised in the magnetic and mechanical properties of this superconducting material. The mechanism for the improvement of the intergrain transport properties is not yet totally clear; it may be related to enhanced pinning of the flux lattice.

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