Introduction of Artificial Pinning Centres in „$Bi_2Sr_2CaCu_2O_8$" Ceramics

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Abstract

Considering the phase equilibrium diagram of the system Bi_2O_3-SrO-CaO-CuO, single phase „$Bi_2Sr_2CaCu_2O_8$" ceramics have been transformed by a simple annealing procedure into multi phase samples. The transformation results in the formation of second phases and in an increase of the intra grain critical current density at 1 T of five times. This increase is believed to express improved pinning properties of the superconducting crystals. The prepared pinning centres are believed to be e.g. coherent precipitates (Guinier-Preston-zones) within the superconducting crystals.

1. Introduction

"$Bi_2Sr_2CaCu_2O_8$" (2212 phase, Tc 94 K) and "$(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$" (2223 phase, Tc = 110 K) exhibit weak internal pinning at temperatures above 20 K resulting in a decrease of the critical current density of about two orders of magnitude in an applied magnetic field of up to 2 T [1-5]. Therefore, an application of these materials in devices under magnetic fields is still not possible yet. Effective pinning centres are assumed to may not exceed about 10 nm [6,7]. Therefore, in this article a processing route is presented resulting in superconducting bulk ceramics with very fine (« 1 µm) precipitates of second phases and enhanced pinning properties using temperature dependent solubility lines. In addition, the microstructure of the

prepared samples has been studied in order to clarify the nature of the produced pinning centres.

2. Experimental

Samples with the composition $Bi_{2.18}Sr_{1.7}Ca_{1.3}Cu_2O_{8+d}$ using Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO as starting material (purity 99 %) were prepared. The mixed and ground powders were calcined at 750 °C and 800 °C for 24 h and pressed into cylindrical pellets (15 mm long and 4 mm in diameter, 625 MPa). The pellets were sintered at 820 °C in air for 90 h with intermediate grinding and pressing, furnace cooled and subsequently annealed at 885 °C for 10, 15, 22.5, 25, 30, 37.5, 45, 60, 180 and 360 minutes (Fig. 1). Finally, the samples were air quenched on a copper plate.

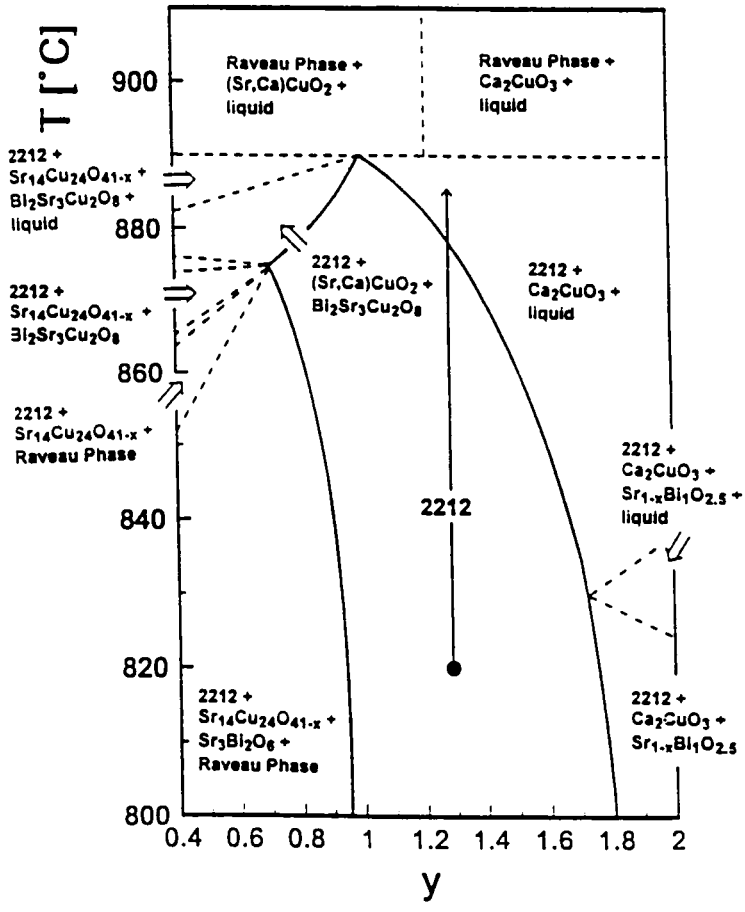

Fig. 1: Temperature vs. Ca content [8] including the performed annealing step to precipitate Ca_2CuO_3 + liquid.

The critical current densities of the pellets have been obtained by measuring of the magnetic susceptibility at 30 K up to 1 T and calculating J_c from these data using Bean's model [9]. The magnetic susceptibility has been measured at 30 K, as at this temperature an increase of the pinning properties is expected to become most obvious. The second phase content of the samples have been determined by optical and electron microscopy. The critical temperatures (onset) of the pellets have been determined by AC susceptibility measurements. Phase identification has been performed using electron microscopy with energy dispersive x-ray analysis (EDX), optical microscopy using polarized light, x-ray diffraction ($CuK\alpha_1$, XRD) and transmission electron microscopy (TEM).

3. Results

The as-sintered 2212 samples are single phase (> 99 vol.-%) refering x-ray analysis, as well as, electron and optical microscopy. According to the phase equilibria, the annealing of the samples results in the formation of Ca_2CuO_3 and liquid (Fig. 2 and 3) combined with a reduction of the Ca content of the 2212 phase.

Fig. 4 shows the susceptibility vs. temperature plots of a starting sample and the 30 min post annealed sample. It is seen that the critical temperatures T_c of the samples and the trend of the susceptibility lines have not be changed significantly by the post annealing ($\Delta T_c \approx 5$ K). The graphic analysis (Fig. 5) shows that the

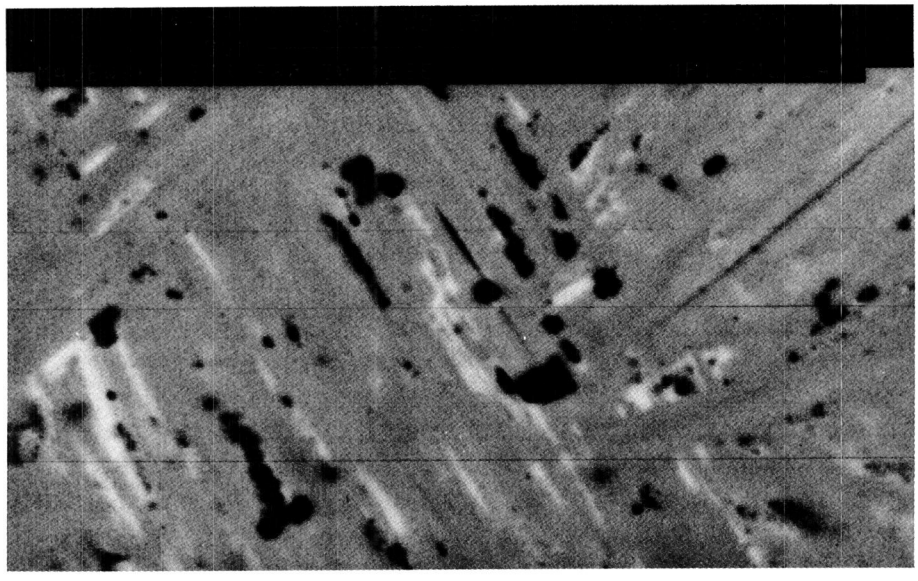

Fig. 2: SEM/BSE image of the 30 min annealed sample. Black: Ca_2CuO_3 precipitates, grey: 2212 phase, white: liquid.

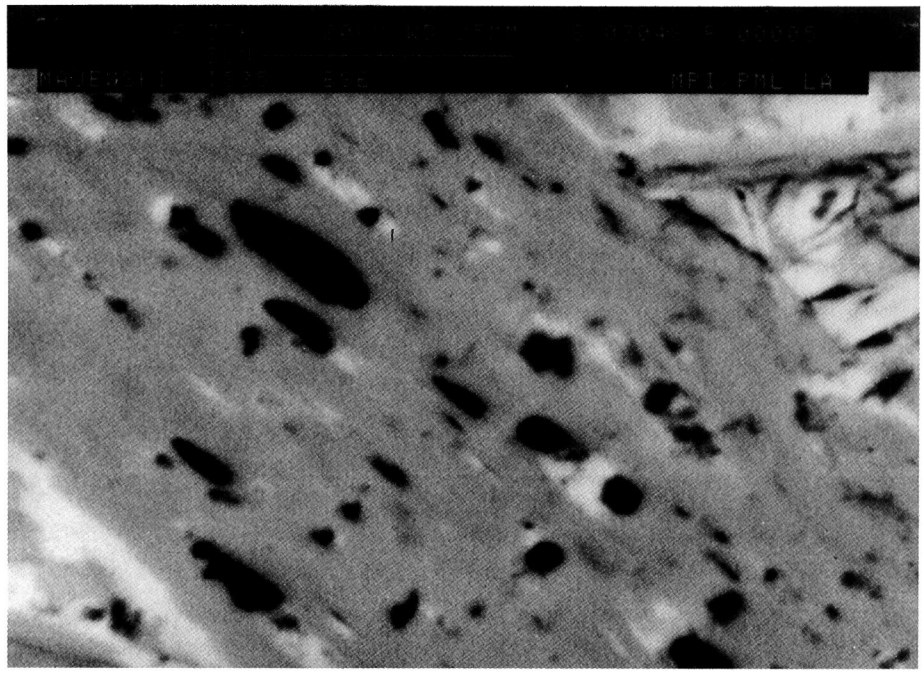

Fig. 3: SEM/BSE image of the 60 min annealed sample. Description see Fig. 2.

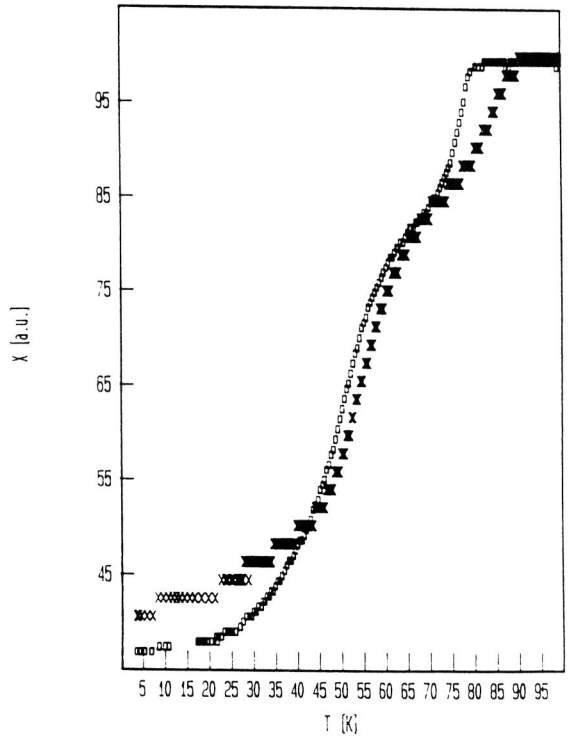

Fig. 4: Susceptibility vs. temperature plot of the starting samples (corsses) and the 30 min annealed samples (triangles).

$J_{c(1T)}/J_{c(0t)}$ values which represent the pinning force exhibit a distinct maximum at an annealing time of about 20 min. With increasing and decreasing annealing time the values decrease. The J_c vs. B plot of the starting samples and the 15 min annealed sample are depicted in Fig. 6. The samples have a J_c of 4000 A/cm^2 at zero magnetic field.

Fig. 7 shows the grain size distribution curves of the Ca_2CuO_3 precipitates of different samples. It is clearly seen that the grain size of the precipitates increases with increasing annealing time. Precipitates smaller than 100 nm have not been determined due to the resolution of the electron microscope. To overcome this drawback TEM-studies of the starting sample and the 15 and 30 min annealed samples have been performed. Nevertheless, even using the TEM precipitates with a grain size smaller than about 100 nm have not found. In addition, the size of the liquid precipitates which form unregularly shaped streaks also exceeds 10 nm.

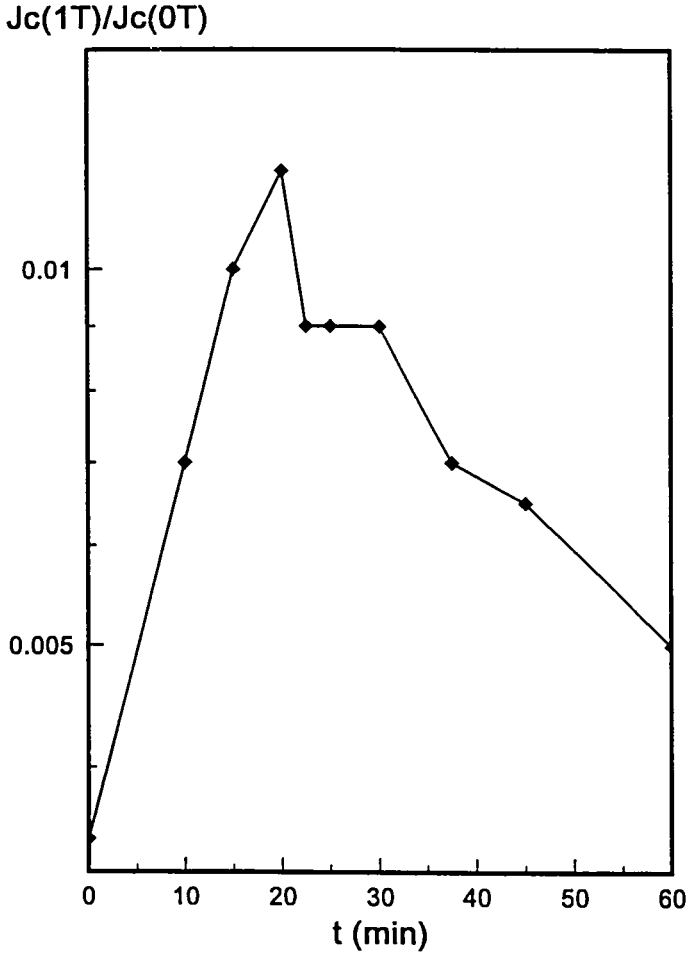

Fig. 5: $J_{c(1T)}/J_{c(0T)}$ at 30 K vs. the post annealing time of the samples.

Fig. 8 shows the mean grain size of the samples vs. the square rout of the annealing time revealing a linear dependence which suggests a diffusion controlled growth of the precipitates. Considering this diagram, it is clearly seen that a mean grain size of the precipitates of about 10 nm can be maintained at annealing times of only about 1 min. However, considering Fig. 5 a significant shift of the pinning properties can not be expected for a annealing time of only 1 min.

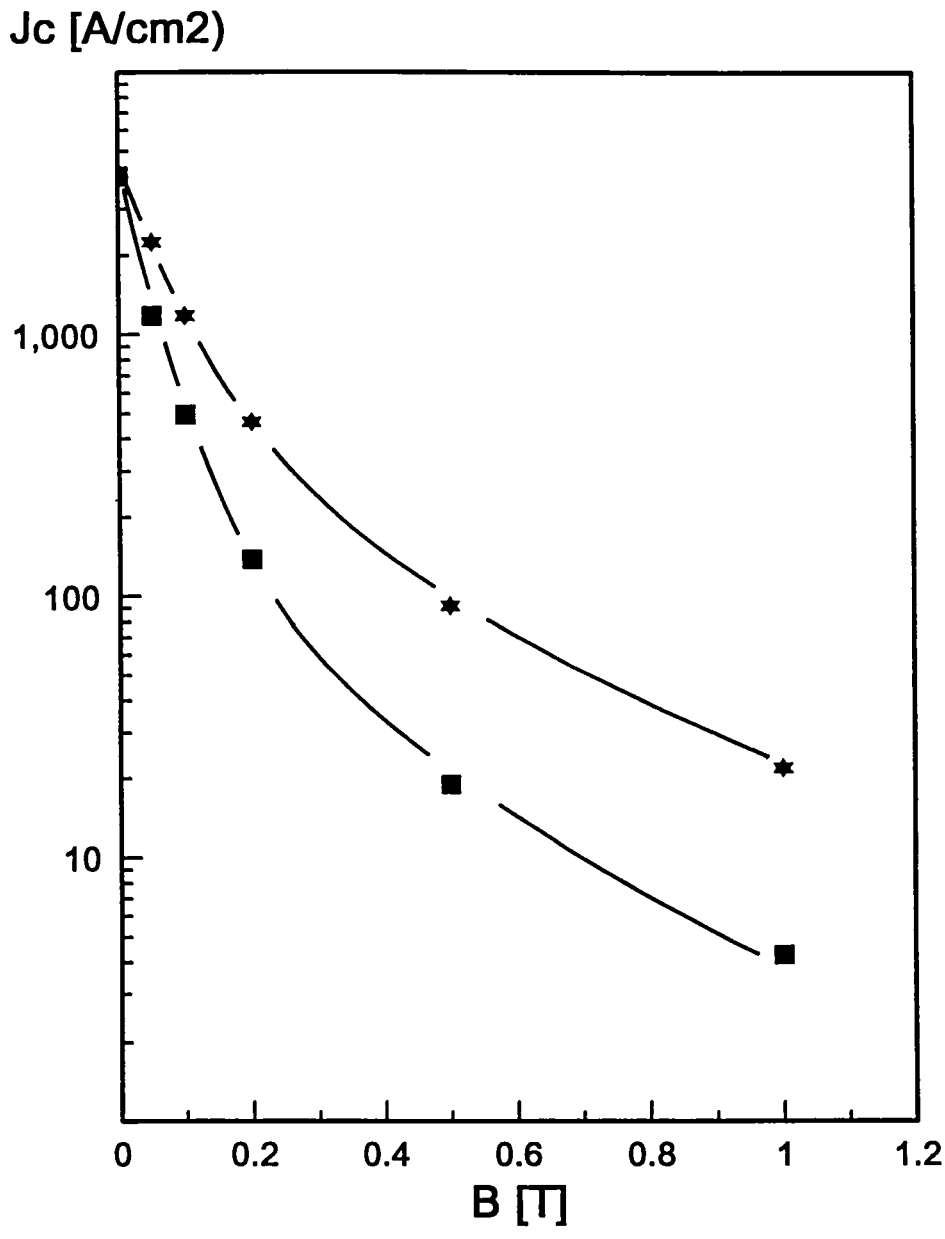

Fig. 6: J_c vs. the applied magnetic field of the starting sample (squares) and the 15 min annealed sample (stars). T = 30 K.

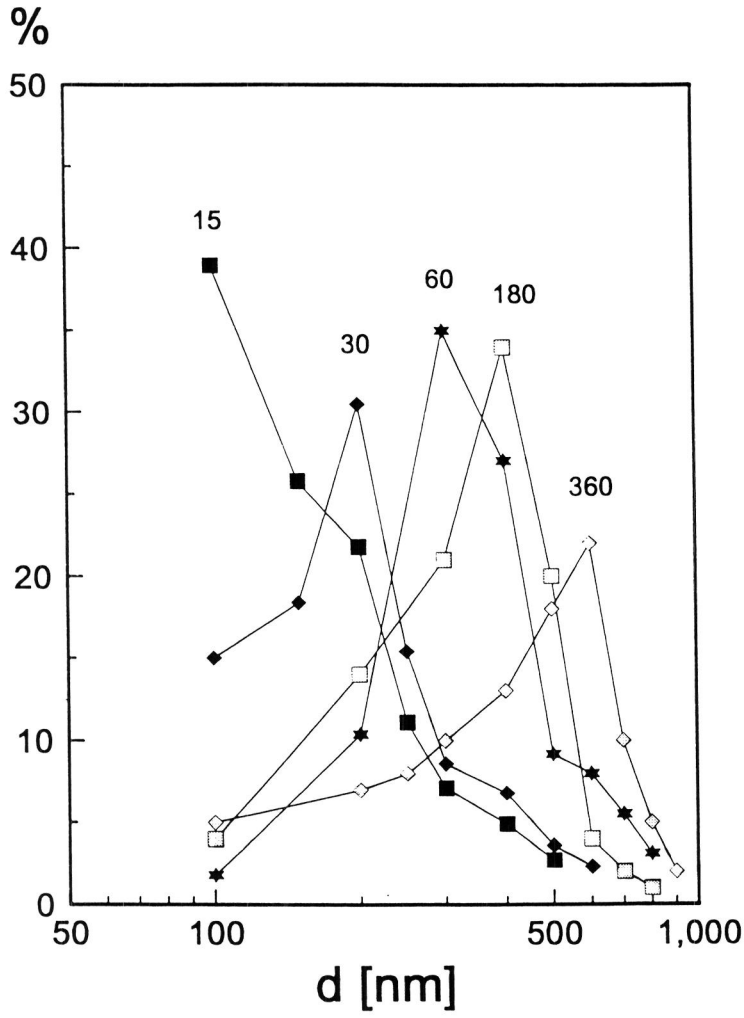

Fig. 7: Grain size distribution lines of the Ca_2CuO_3 precipitates. The values at the lines indicate the post annealing time (min).

The results of the analysis of the XRD-pattern of the samples are shown in Fig. 9, where the full width at half maximum of different reflections of the 2212 phase are plotted vs. the duration of the post annealing. The full width at half maximum of all considered reflections show a maximum at the 15 and 30 min annealed samples, which suggest an inceased lattice distortion of the 2212 crystals of these samples. In addition, TEM studies of the microstructure of the 15 and 30 min annealed samples and the starting sample show that the annealed samples exhibits an significantly higher density of dislocation of about 5×10^9 cm^{-2} compared to the starting samples. In addition, it is remarkable that the dislocation lines are concentrated at the a-b-planes of the crystals (Fig. 10).

Fig. 10: TEM image of the a-b-plane of a 2212 crystal of the 30 min annealed sample.

4. Discussion and Conclusions

The increase of the J_c at magnetic fields above 0.1 T with annealing shows a strong evidence for the improvement of the pinning properties of such samples by the precipitation of second phases. The decrease of the pinning effect with increasing annealing time might be due to coarsening of the second phases. However, the grain size of the Ca_2CuO_3 precipitates significantly exceeds 10 nm and therefore, it can be concluded that the precipitates are not effective pinning centres, if at all.

It has to be taken into account that besides the possible effect of such second phases the increased pinning can also be caused by defects in the 2212 phase itself resulting from the phase transformation due to the reactions:

2212 (Ca rich) $\Leftrightarrow$ 2212 (lower Ca content) + Ca_2CuO_3 + liquid

Such defects could be e.g. lattice distortions which may act as pinning centres. In this case, the observed decrease of J_c with increasing annealing time could be explained by the defect healing.

A strong evidence for the existence of an increased amount of lattice distortions e.g. coherent precipitates within the post annealed samples is the increased value of the full width at half maximum of different reflexes of the 2212 phase of the 15 and 30 min annealed samples and the higher density of dislocation lines of the annealed samples compared to the as sintered sample.

Considering this facts, it is extremly remarkable that especially these samples exhibits the highest increase of the pinning properties. Therefore, the increased pinning properties of the 15 to 30 min post annealed samples is believed to be caused by an increased amount of lattice distortions e.g. coherent precipitates (Guinier-Preston-zones) within the 2212 crsytals due to the precipitation of Ca_2CuO_3 and liquid. The Ca_2CuO_3 and liquid precipitates observed within these samples are believed to be too large to act as pinning centres.

5. Reference

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