Superconducting phase formation in random neck syntheses: a study of the Y–Ba–Cu–O system by magneto-optics and magnetometry

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Abstract
Magneto-optical imaging and magnetization measurements were applied to investigate the local formation of a superconducting phase effected by a random neck synthesis in the Y–Ba–Cu–O system. Polished pellets of strongly inhomogeneous ceramic samples show clearly the appearance of superconducting material in the intergrain zones of binary primary particles reacted under different conditions. Susceptibility measurements allowed evaluation of the superconducting critical temperature, which turned out to be close to that of optimally doped YBa2Cu3O7−x.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Recently, a combinatorial approach for searching for new oxide superconductors was presented [1–4]. The basic idea is to generate the most inhomogeneously reacted ceramic samples in order to synthesize new superconducting compounds [1–3]. Starting with a mixture of grains of several initial components, due to their statistical distribution, various combinations of original grains are created in different parts of a sample. If such a mixture is heated up to temperatures sufficient to start a chemical reaction between neighboring grains, one can obtain a significant variety of resulting products. In this case, it is preferable that the initial grains are not completely used up since a longer reaction will lead to some averaging (see [5] for details). Because the reaction predominantly occurs in neck zones between randomly distributed grains, it was called a random neck synthesis (RNS) [5]. After reaction, the resulting ceramic material can be ground to small particles and a magnetic separation procedure may be used in order to selectively take out grains exhibiting superconductivity [4, 5]. A key issue for the functioning of such an approach is to find the conditions that would lead to the formation of superconducting phases within volumes large enough for further processing. In this work, we employ magneto-optical imaging (MOI) as a technique to visualize superconducting regions in inhomogeneously reacted samples. We demonstrate that by RNS in a mixture of two component (i/j) prereacted BaO2/Y2O3, BaO2/CuO and CuO/Y2O3 particles, superconducting YBa2Cu3O7−x with Tc ≈ 92 K can be obtained and detected. Superconducting regions appear embedded in a matrix of non-superconducting products of the reaction.

2. Experimental details

The magneto-optical (MO) Faraday effect allows visualization of the magnetic field distribution down to micrometer resolution [6]. Due to expulsion of the field from superconducting regions, they can be identified in MO images of non-uniform samples. A film made of lutetium doped ferrimagnetic iron garnet [7] was used as a MO layer. In order to visualize the magnetic field distribution, the MO layer was placed directly onto the polished surface of a ceramic sample. Linearly polarized light for illumination and a microscope equipped with a CCD camera were used for observation and data acquisition. An additional polarizer situated between the...
CuO, Y2O3 and BaO2 were mixed according to compositions. The oxides were prereacted by classical solid state chemistry. First, the powders were heated in air at 950°C for 24 h. Then, they were heated for an additional 24 h at 1100°C of the corresponding (i/j) oxide mixtures. A homogeneous distribution of components was achieved by joint ball milling of the corresponding (i/j) oxide mixtures. The resulting powders were pressed into disk shaped pellets. These pellets were heated in air at 950°C for 24 h. 2BaO-Y2O3 pellets were then heated for an additional 24 h at 1100°C.

Each set of pellets belonging to one of three element combinations was independently transformed into particles of about 80–100 μm. This was done by breaking the pellets in a mortar and sieving out the corresponding size fraction. Then, equal amounts of these three types of (i/j) particles were thoroughly mixed together and this mixture was used for making samples, i.e., pressed into pellets and heated at 930°C in an oxygen atmosphere. Heating and cooling rates were 300°C h⁻¹ and 15°C h⁻¹, respectively. The sample S1 was kept at 930°C for one week and the sample S2 for three weeks. More details on the RNS procedure can be found elsewhere [5].

After such a procedure, pellets were fragile. In order to improve their stability and make them suitable for MOI experiments, they were placed in an epoxy resin EPO-TEK 305 and polymerized under a N2 pressure of 6 bar. After removal of excess resin, the flat surfaces were polished with a fine diamond powder. This was necessary in order to obtain a close contact between the sample surface and the MO layer, which is essential to ensure a high spatial resolution. A photograph of the sample S2 is shown in figure 1. We note that both samples looked practically identical.

The basic idea behind the RNS approach is to provide reactive contacts between grains of different compositions. If volumes of starting grains are not used up during the reaction time, all phases that may exist in the Y–Ba–Cu–O system at given conditions (temperature, total pressure and partial pressure of oxygen) should be formed in neck zones between different grains. As the original particles were chosen to be sufficiently large, product particles may also acquire a size suitable for further handling and analyses.

Magnetization measurements were carried out on a SQUID magnetometer with a 5 T magnet (Quantum Design). Because some measurements were made in very low magnetic fields, we note that there was some residual magnetic field \( H_0 \approx 0.5 \) Oe. Most probably \( H_0 \) corresponds to the magnetic field of the Earth. In our data, we indicate the actual magnetic field, which includes \( H_0 \).

3. Sample preparation

In view of a ceramic combinatorial approach providing maximum chemical diversity within a single sample [1–4], three binary (i/j) combinations of Cu/Y, Cu/Ba and Ba/Y oxides were prereacted by classical solid state chemistry. First, CuO, Y2O3, and BaO2 were mixed according to compositions Ba2O2–CuO, 2CuO–Y2O3, and 2BaO–Y2O3. A homogeneous distribution of components was achieved by joint ball milling of the corresponding (i/j) oxide mixtures. The resulting powders were pressed into disk shaped pellets. These pellets were heated in air at 950°C for 24 h. 2BaO–Y2O3 pellets were then heated for an additional 24 h at 1100°C.

Figure 1. A photographic image of the sample S2 after polishing (horizontal size corresponds to 3 mm). Gray areas correspond to the green phase (Y2BaCuO5).

4. Results

4.1. MO imaging

MO images of the sample S1 are shown in figure 2. The sample was cooled down to \( T = 10 \) K in a zero magnetic field. Then, the magnetic field \( H = 160 \) Oe was applied perpendicularly to the sample surface. A crossed polarizer and analyzer were used for observation. In this case, areas with a non-zero magnetic field are seen as bright, while superconducting regions, due to expulsion of magnetic flux, can be identified as darker spots (figure 2(a)). As expected, superconducting inclusions are distributed irregularly throughout the sample. After taking this image, the field was increased to \( 2.5 \) kOe and then switched off. The resulting image of the same area is shown in figure 2(b). As may be seen, dark spots became bright after switching off the magnetic field. This is clear evidence of a magnetic flux trapped inside these areas, which is a secure identification of superconductivity.

Having a closer look at the flux density distribution shown in figure 2(a), some particular features are apparent. The most extended superconducting regions exhibit lateral dimensions of 150–200 μm, being a bit larger than typical grains that were preliminary chosen (80–100 μm). Another interesting feature is that the shape of the superconducting regions provides convincing evidence that the superconducting phase was predominantly formed around some sufficiently big grains. Figure 2(c) underlines this fact. We also note that dark areas of the image, corresponding to superconducting regions, are not uniform but consist of smaller black spots connected by gray areas. This reflects non-uniform superconductivity inside superconducting regions. One can imagine that, during the reaction, a superconducting phase was initially formed in several reaction centers around some particular grains and their subsequent growth resulted in the formation of somewhat...
Figure 2. (a) MO image of the sample S1 obtained at $T = 10$ K and $H = 160$ Oe after zero-field cooling. Superconducting areas are visible as dark structures. (b) The same area of the sample in the remanent state after $H$ was increased to 2.5 kOe and then reduced to zero. (Horizontal size of the image is 1.2 mm.) (c) Magnified areas of the MO image. Superconducting regions exhibit typical shapes of intergrain contacts with the superconducting phase formed around some particular grains as is indicated by the dotted lines.

Figure 3. The MO contrast $P$ as a function of temperature. The results were obtained in the remanent state as shown in figure 2(b). The solid line is a guide to the eye drawn in a way that $P$ vanishes at $T_c = 91.6$ K evaluated from magnetization measurements. The inset shows a part of the MO image, which was used for evaluation of $P$.

Figure 4. (Left panel) A MO image of the sample S2 at $T = 10$ K and $H = 40$ Oe after zero-field cooling. Superconducting regions are dark. A part of the image from figure 2(a), scaled to the same size, is shown in the right panel for comparison.

weaker superconducting links between them. As we discuss below, similar conclusions can be drawn from the analysis of the magnetization data.

In order to quantify the results of the MOI experiments, we introduce the magneto-optical contrast $P$ as the difference between light intensities coming from superconducting and normal regions of the sample. The particular superconducting region, which was used for calculation of $P(T)$ data, is indicated by the white circle in the inset of figure 3. The remanent state was created at $T = 10$ K as described above. Then, $P$ was measured as a function of increasing temperature. The results are plotted in figure 3. Obviously, $P$ must vanish at $T = T_c$. As may be seen, the results of the MOI experiments are in agreement with $T_c = 91.6$ K, evaluated from magnetization data as is described below.

A MO image of the sample S2, which underwent a much longer thermal treatment, is shown in the left panel of figure 4. Although this image is similar to those of the sample S1, there are considerable differences. While the sizes of
superconducting regions are about the same, their number is significantly larger than that for the sample S1. In addition to almost black superconducting grains, there are extended dark gray areas. It is most likely that these regions correspond to superconducting grains, which are situated at some distances below the sample surface and for this reason provide a weaker MO contrast. Similar ‘shadows’ may also be seen in MO images of the sample S1; however, in the latter case, they are substantially weaker and more difficult to identify.

4.2. Magnetization measurements

The magnetic field dependences of the normal-state magnetization for the sample S1, as well as for the original mixture of oxides, were typically paramagnetic with $M(H) = \chi_n H$ ($\chi_n$ is the normal-state magnetic susceptibility) (see figure 5). The situation with the sample S2 was different. As may be seen in figure 5, this sample had a noticeable ferromagnetic contribution to $M$. The high field part of the $M(H)$ curve could be described by $M(H) = M_0 + \chi_n H$. The value of $M_0$ was practically independent of temperature.

Low temperature parts of the $M(T)$ curves for both samples and the original mixture are shown in figure 6. As may be seen in figures 6(a) and (b), there is a clear magnetic (antiferromagnetic) transition at temperatures a little bit above 10 K. This transition was apparently originated from Y$_2$Cu$_2$O$_5$ (blue phase) [10], which was present in a 2BaO-Y$_2$O$_3$ component. Contrary to this, the sample S2, which underwent three weeks of thermal treatment, did not show any trace of such a transition (figure 6(c)).

Zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves for the samples S1 and S2 measured in $H = 1$ Oe are shown in figures 7(a) and (b). The results for both samples are similar. Magnetization is practically reversible at temperatures very close to $T_c$ with an onset of irreversibility at lower temperatures. The critical temperature can be evaluated as a linear extrapolation of the steepest part of the $M(T)$ curve to $M = 0$. This results in $T_c = 91.6$ K and $T_c = 89.5$ K for the samples S1 and S2, respectively.

Figure 8 shows the temperature dependence of the remanent magnetization ($M_{rem}$) measured for the same conditions as the $P(T)$ curve presented in figure 3. $M_{rem}$ vanishes at $T = 91.4$ K, just a bit below $T_c = 91.6$ K. Comparing $M_{rem}(T)$ and $P(T)$ curves, one should take into account that the MO contrast is proportional to the magnetic induction $B$ in the center of a superconducting region, while $M_{rem}$ is proportional to the integral of $B$ over the sample volume. This difference between $M_{rem}$ and $P$ results in slightly different shapes of the $M_{rem}(T)$ and $P(T)$ curves, as may be seen in figures 3 and 8 (see also [11]).

![Figure 5](image-url) **Figure 5.** Magnetization as a function of magnetic field at $T = 300$ K for the samples S1 (right y-scale), S2 (left y-axis) and the mixture of oxides before reaction (left y-axis). The solid lines are the best linear fits to $M(H)$ data points for $H \geq 13$ kOe.

![Figure 6](image-url) **Figure 6.** The $M(T)$ curves measured in low applied fields. (a) A non-superconducting mixture of oxides before thermal treatment. (b) Sample S1. (c) Sample S2.

![Figure 7](image-url) **Figure 7.** ZFC and FC magnetization curves. (a) Sample S1. (b) Sample S2.
While the critical temperature for the sample S1 is close to an optimally doped YBCO (see figure 7(a)), $T_c$ for the sample S2 is about 2 K lower (figure 7(b)). Because during the reaction time the samples were held in an oxygen atmosphere, we consider it unlikely that the samples can be oxygen deficient. It is more probable that non-stoichiometry of other elements is a true reason for this effect.

6. Conclusions

The present analysis demonstrates the analytical ability of MOI for the investigation of local magnetic properties of inhomogeneous ceramic samples. Combination of MOI with magnetization measurements provides even deeper insight into the internal structure of superconducting regions and their evolution with reaction time. Application of the RNS principle to a well known system allowed us to demonstrate that local formation of superconducting material is possible and that the use of two component ($ii/j$) starting grains with sizes $\sim$80–100 $\mu$m can yield superconducting inclusions of several dozens of micrometers, which is suitable for magnetic separation and structural characterization. It was also shown that after three weeks of the reaction time, some of the initial components are completely used up, which is inconsistent with the RNS approach. Recently, we have presented optical results on local product formation when using micrometer sized starting materials [13]. The present results provide a realistic base for the application of RNS in combination with magnetic separation [4, 5] for the search for minority phases of superconducting materials featuring higher $T_c$ values than known for the bulk of a ceramic sample.

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