

## YBCO bulks for preparation of permanent magnets

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### Abstract

The magnetization of purposefully fabricated high-temperature superconductor (HTS) ceramic bulks can result in “superconductor permanent magnets” (SPMs). A pulse generator has been designed and built for this purpose. Series of HTS bulks with different compositions have been prepared by liquid phase sintering technique: the basic composition was  $\text{YBa}_{1.595}\text{Cu}_{2.405}\text{O}_y$ , which has been doped by Ca and/or Pt. The samples have been magnetized in Field Cooled (FC) and Zero Field Cooled (ZFC) modes at a maximum flux density of 0.2 T at liquid nitrogen temperature. The measurements proved that the average field trapping ability of the bulk with the composition of  $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_{1.595}\text{Cu}_{2.405}\text{O}_y$  is the highest among the tested samples.

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### 1. Introduction

There is a growing interest in the practical applications of magnetized high-temperature superconductor (HTS) ceramic bulks.<sup>1,2</sup> The reason is that the magnetization of purposefully fabricated HTS bulks can result in extremely strong “superconductor permanent magnets” (SPMs) exceeding the maximum magnetic energy product of the conventional rare-earth magnets.<sup>3,4</sup> Two kinds of magnetization for ceramic HTS bulks are used in practice: the Field Cooled (FC) mode where cooling of HTS takes place in a static magnetic field and Zero Field Cooled (ZFC) mode where the magnetization of cooled HTS is carried out by an external magnetic field having pulse form. It is known that the trapped flux is smaller in the case of ZFC magnetization of a given HTS bulk than in the FC mode.<sup>5</sup> Despite of smaller trapped flux, pulse magnetization is more advantageous from certain point of view of practical applications: building and operating the pulse magnetization equipment is economic, moreover “in

situ” magnetization of the HTS bulks is also possible, which cannot be realized by FC mode.<sup>1</sup>

The practical realization of the pulse field magnetization of HTS bulks is similar to the magnetizing process of conventional permanent magnets (PM), where the subjected material is ferrite, Alnico alloy, rare-earth magnet, etc. In the latter case, the remanent flux density nowadays can reach 1.31 T. For bulk superconductors, the maximum field to be trapped is determined by the highest possible circulating current ( $J_c$ ) and the geometry of the bulk, but it can be much higher than that in the case of PMs, especially by lowering the temperature of the HTS.<sup>6</sup>

Two relevant factors determine the value of the trapped flux in the case of ZFC magnetization: the material composition and the processing methods of the HTS bulks to be magnetized, on the one hand, and the shape of the magnetization pulse, on the other.

The general aim of our long-term research project is to find the optimal technological parameters for pulse magnetization of  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$  (YBCO) based HTS bulks. The presently reported part of the project has been focused on analyzing the flux trapping ability of the various superconducting ceramics in the case of pulse magnetization — that is how the

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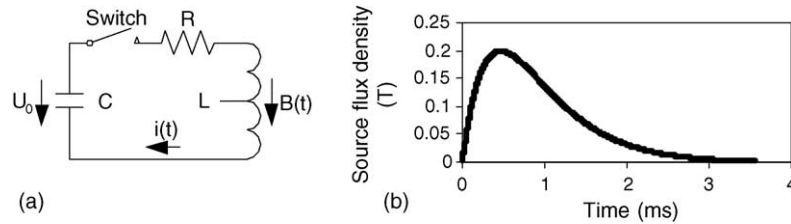


Fig. 1. (a) Principle of pulse magnetization, (b) applied magnetic pulse.

different additives influence the value of the remanent field of the SPMs.

## 2. Experimental

YBCO bulks with Ca and/or Pt additives have been prepared, as it is listed in Table 1. A pulse generator has been designed and built for supplying pulses of variable parameter to magnetize the bulks.

### 2.1. Preparation of HTS bulks for magnetization

We used additives, because it is possible to improve the long-term stability and the homogeneity of the field distribution by intentionally introducing pinning centers into HTS bulks.<sup>2</sup> Different additives have different influence on the properties of the YBCO bulks, e.g. Ag is mainly used to increase thermal conductivity and crack-resistibility,<sup>7,8</sup> Pt and Ce may act as heterogeneous nucleation centers for Y211 phase,<sup>9,10</sup> etc.

In the paper the effects of Ca and Pt additives on the morphology and magnetic flux trapping ability of YBCO samples prepared by liquid-phase sintering method are reported.

Partial substitution of  $\text{Ca}^{2+}$  ions in the Y site might enhance the superconducting coupling between grains by increasing carrier density near grain boundaries.<sup>11</sup> As a result, higher intergrain currents can be achieved. In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound it was shown, that the calcium solubility in Y123 is limited and the crystal structure of  $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  remains orthorhombic for  $x < 0.3$ .<sup>12</sup>

By addition of Pt dopant<sup>9,13</sup> advantageously can be influenced the uniform distribution of small particles of Y211 phase within Y123 domains. They act as flux pinning centers,<sup>14</sup> promising higher trapped fields.

The compositions of the samples were chosen in order to form about 10 wt%  $\text{Y}_2\text{BaCuO}_5$  (Y211) phase beside the superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_y$  (Y123) grains. High purity (99.9%)  $\text{Y}_2\text{O}_3$  (BET specific surface area  $18.1 \text{ m}^2/\text{g}$ ),  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{CuO}$  (BET specific surface area  $18.4 \text{ m}^2/\text{g}$ , obtained from  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot n\text{H}_2\text{O}$  by heat treating at  $500^\circ\text{C}$  for 1 h),  $\text{CaCO}_3$  and  $\text{PtCl}_4$  were used. The starting powders with nominal compositions were homogenized with alcohol and pressed into pellets at 60 MPa. The pellets presintered at  $920^\circ\text{C}$  for 5 h were powdered and the  $\text{PtCl}_4$  was added. These powders were pelletized at a pressure of 60 MPa

Table 1  
Samples

Code	Composition	$J_{c \text{ intra max}}$ ( $\text{kA}/\text{cm}^2$ )	$J_{c \text{ inter}}$ ( $\text{kA}/\text{cm}^2$ )
S1	$\text{YBa}_{1.595}\text{Cu}_{2.405}\text{O}_y$	8.7	0.16
S2	$\text{YBa}_{1.595}\text{Cu}_{2.405}\text{O}_y + 0.5\% \text{ Pt}$	13	0.18
S3	$\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_{1.595}\text{Cu}_{2.405}\text{O}_y$	4.3	0.13
S4	$\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_{1.595}\text{Cu}_{2.405}\text{O}_y + 0.5\% \text{ Pt}$	10.5	0.22

and then heat treated according to a melt textured-growth method. During the heat treatment the pellets were partially melted at  $1030^\circ\text{C}$  for 20 min, where the following peritectic reaction took place (1):



The samples were quickly ( $300^\circ\text{C}/\text{h}$ ) cooled down to the Y123 peritectic temperature ( $1000^\circ\text{C}$ ) and then cooled slowly ( $2^\circ\text{C}/\text{h}$ ) down to  $950^\circ\text{C}$  and held at this temperature for 2 h. Subsequent cooling was performed in an oxygen atmosphere at a rate of  $300^\circ\text{C}/\text{h}$ .

The shape of all the samples is cylindrical, 22 mm in diameter and 2 mm in height. The microstructure have been characterized by Philips XL30-ESEM type scanning electron microscope.

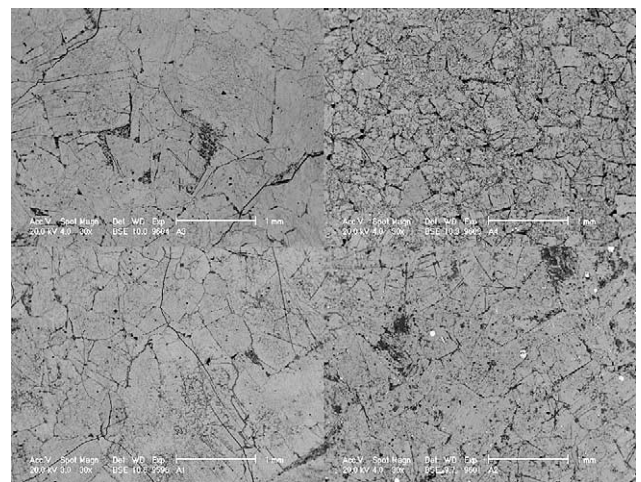


Fig. 2. SEM images of S1(A3), S2(A4), S3(A1), S4(A2) samples.

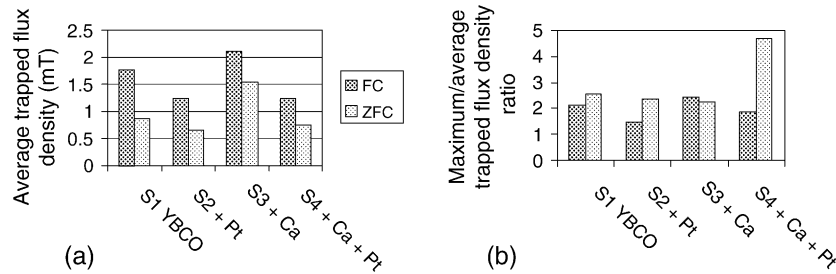


Fig. 3. (a) Average trapped flux densities, (b) inhomogeneity of the trapped flux.

## 2.2. Pulse generator

For the generation of high field magnetizing pulses a pulse generator has been designed and built (Fig. 1a) equipped with a magnetizing coil (L). The electrical energy stored in the capacitor bank (C) is discharged by the switch (Switch) through a damping resistance (R). The shape and the amplitude of the pulse can be varied to optimize the value of the trapped field. In these experiments a “critically damped” pulse has been used (see Fig. 1b).

## 2.3. Magnetization of the bulks

The bulks have been fixed in a liquid nitrogen (LN) container and the whole set have been positioned in the centre of the magnetizing coil. The HTS bulks have been cooled down to 77 K before activation of the coil (ZFC mode). The coil was energized by discharging the capacitor bank, creating fields up to 0.2 T in the useful cylindrical space of the coil. The pulse generator is able to create up to 2 T, but we emphasize that in the present work we analyze not the reachable maximum value of the trapped fields but the influence of the different additives on the field trapping ability of the YBCO compositions. It is known, that in the case of pulse magnetization, there is an optimum magnetization flux density amplitude, beyond which there is a decay of the trapped flux attributed to the critical current decrease due to local heating.<sup>15,16</sup> For our material compositions and geometries, this amplitude of source field have been found to be 0.2 T.

## 3. Results and discussion

The superconducting onset temperature has been measured using the magnetic susceptibility method on powdered samples: it has not been showed difference between samples ( $T_{\text{onset}} = 93 \pm 1$  K). The morphology of the YBCO bulks have been analyzed by SEM. The trapped magnetic flux of the bulks have been measured by field mapping.

### 3.1. Morphology

In SEM micrographs of the surface (see Fig. 2) it can be seen, that the samples without Pt have higher density and

larger textured domain sizes, but the texture of the doped samples are more uniform and homogenous, although Pt inclusions have been appeared.

### 3.2. Field mapping

For the analysis of the efficiency of the pulse magnetization (ZFC mode) and FC mode, trapped flux density mapping have been carried out on all samples. Usually the levitation force measurement is very informative, but may be insufficient to qualify the superconductors, and it is recommended to complement it with field mapping.<sup>17</sup> We built a three-dimensional robot arm equipped with a Hall-sensor for this purpose, positioned over  $1 \pm 0.1$  mm above the surface of the bulk, and having horizontally  $2 \text{ mm} \times 2 \text{ mm}$  resolution.

We calculated a simple average from the mapped values (Fig. 3a). The average trapped flux density is smaller in the case of ZFC magnetization of a given HTS bulk than that with FC mode. We observed that in our polycrystalline samples it was not as much different as in single crystals.<sup>5</sup> We defined the maximum-to-average ratio as the “inhomogeneity” of the flux distribution (Fig. 3b).  $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_{1.595}\text{Cu}_{2.405}\text{O}_y$  produced more uniform flux distribution on the surface than the basic other compositions, while the maximum inhomogeneity and maximum peak value of the ZFC trapped flux density was measured for the  $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_{1.595}\text{Cu}_{2.405}\text{O}_y + 0.5\% \text{ Pt}$  composition.

The intergrain and intragrain currents were calculated from the FC trapped flux map according to the method described in ref.18: the highest small-sized peak on each scan was considered as a result of a currents circulating in a grain of 1 mm diameter detected from a height of 1 mm. For the intragrain value, the calculation is based on a single-peak approximation of a homogenously distributed current density. For the resulted  $J_c$  values see Table 1.

## 4. Conclusion

Analysing the measurements, the results can be summarized as follows.

Pulse magnetization of ceramic superconducting bulks in ZFC mode can be carried out under controlled technical conditions using high power pulse generator.

The Ca and Pt additives have significant roles in the texture formation and determine the microstructure. As a result, they influence the critical current density and so the field trapping ability of YBCO ceramic superconductors both in the case of ZFC and FC modes. The results in Table 1 showed us, that Pt additive positively influenced both intragrain and intergrain critical currents. Together with the Ca additive they increased intergrain currents. From the point of view of the pulse magnetization process (ZFC mode), the  $Y_{0.95}Ca_{0.05}Ba_{1.595}Cu_{2.405}O_y$  material composition is the most suitable for modeling among the tested HTS samples because of the “smoothest” and higher average trapped flux. From the point of view of future applications (in ZFC mode), the  $Y_{0.95}Ca_{0.05}Ba_{1.595}Cu_{2.405}O_y + 0.5\%$  Pt material composition should be selected out of the tested HTS samples because of the highest peak trapped flux.

Considering that the trapped flux depends on the geometry of the HTS bulks, further R&D work will be carried out with bigger samples.

Taking into account that the trapped flux depends on the form of the magnetizing pulse, more investigations have to be done to optimize the form of the pulse applied for magnetization of Ca doped YBCO bulks, for example increasing the pulse rise time.

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