

Effect of TiO₂ Fibers on Properties of Single-Grain Bulk GdBCO Superconductors

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The influence of TiO₂ microfibrils doping on superconducting properties (critical temperature T_c and critical current density J_c) of single-grain bulk GdBa₂Cu₃O_{7- δ} (GdBCO) high-temperature superconductor was investigated. In this study, we prepared pure GdBCO and GdBCO+TiO₂ superconductor via the top-seeded melt growth method in air. The ceramic fibres were prepared using the electrospinning method and were added in the small quantity (0.05 wt%) for the increase of density of flux pinning centres. Magnetization measurements were performed on the specimens taken from several different locations of both studied samples. The experimental results showed that TiO₂ addition do affect the T_c along with the decrease of J_c .

DOI: [10.12693/APhysPolA.137.800](https://doi.org/10.12693/APhysPolA.137.800)

PACS/topics: high-temperature single-grain GdBCO superconductor, TiO₂ fibres, superconducting properties

1. Introduction

The single-grain bulk GdBa₂Cu₃O_{7- δ} (GdBCO) superconductor is one of the promising high-temperature superconductor materials with significant potential for development in practical applications, such as fly wheel energy storage systems, or magnetic bearings [1–3]. For these applications high critical current density J_c is the most important requirement. It is well known that size and distribution of GdBa₂CuO₅ (Gd211) particles, and addition of non-superconducting artificial pinning centres are essential to enhance flux pinning properties (J_c and trapped magnetic field). An effective way to enhance mentioned properties is introduction of elongated particles with a large surface area. Therefore, various kinds of metal oxides have been introduced already into the superconducting matrix as the second phase particles [4–6],

In this paper, we studied influence addition of ceramic TiO₂ fibres on superconducting properties (critical temperature T_c and critical current density J_c) of GdBCO bulk superconductor. We were inspired by these works, in which the influence of Ti-based addition on superconducting properties of REBa₂Cu₃O_{7- δ} (RE denotes a rare earth elements) superconductors has been investigated [7–10].

2. Materials and experimental methods

For the production of pure GdBCO and TiO₂ doped GdBCO samples, we used commercially available powders. Nominal composition of mixture powder was:

1 mol. GdBa₂Cu₃O_{7- δ} (SOLVAY, purity 99.9%, average particle size 30 μ m) + $\frac{1}{2}$ mol. Gd₂BaCuO₅ (TOSHIMA, purity 99.9%, average particle size 1–2 μ m) + 20 wt% Ag₂O (CHEMPUR, purity 99%) + 0.2 wt% PtO₂·H₂O (ACROS, purity 79–84%). Additions of Ag₂O and Pt were aimed to improve the mechanical properties, and fine dispersion of the Gd211 secondary-phase particles into the Gd123 matrix, respectively. After thorough mixing and milling of powders, the prearranged TiO₂ fibres of quantity 0.05 wt% were added to one mixture powder, and mixed with an acoustic mixer to obtain uniform doping effect in a full sample volume. The ceramic fibres [11] with average diameter of 0.49 μ m after the calcinations were prepared using the needle-less electrospinning method. Prepared mixture powders together with the thin film NdBa₂Cu₃O_{7- δ} seeds were uniaxially pressed into the 20 g cylindrical pellets of 20 mm in diameter.

The growth of samples was performed in the air atmosphere using a top-seeded melt growth (TSMG) method. The applied heating profile was as follows: the pellets were heated from room temperature to melting temperature of 1060 °C at heating rate of 100 °C/h, held for 1 h to ensure decomposition of the mixture powders, undercooled to 1020 °C by rate of 100 °C/h, and then slowly cooled down to 980 °C at cooling rate of 0.3 °C/h. Subsequently, the furnace was cooled to room temperature.

The as-grown samples were cut in halves, and then one half was prepared for measurement of magnetic properties (T_c and J_c) at liquid nitrogen temperature. Small specimens with size \approx 1.5 mm×1.5 mm×0.5 mm were carefully cut from the equivalent locations of three planes, as shown schematically in Fig. 1. Cut specimens were oxygenated in a flowing oxygen atmosphere at temperature of 410 °C for 240 h, to drive the non-superconducting tetragonal Gd123 phase to the desired superconducting orthorhombic phase.

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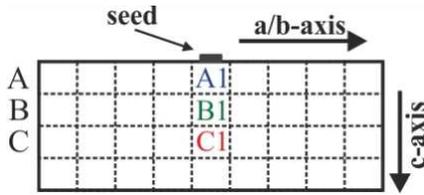


Fig. 1. Schematic illustration of the single-grain cross-section and the specimen positions along *c*-axis of single GdBCO grain cut for measurement of T_c and J_c .

The magnetic measurements of oxygen-annealed specimens were conducted in a vibrating sample magnetometer from Cryogenic Limited. The temperature dependent of magnetization were measured in zero field cooled regime at external constant magnetic field 2 mT which was applied parallel to the *c*-axis of each specimen. The middle critical transition temperatures $T_{c,m}$ were determined as the $T_c(50\%)$ of the magnetic transition curves. In turn, J_c were calculated from the magnetic hysteresis loops at 77 K using the extended Bean model [12].

3. Results and discussion

Transition curves for pure single-grain GdBCO sample (Fig. 2) and for GdBCO sample with the addition of 0.05 wt% TiO₂ microfibrils (Fig. 3) show that the addition of microfibrils caused small decrease of transition temperature T_c to superconducting state. This effect is caused by some change in the charge carrier density, similarly as it was demonstrated with DyBa₂Cu₃O_{7- δ} [13]. The charge carrier density can be changed either by differences in substitution of Ba²⁺ ions with Gd³⁺ ions in the Gd123 crystal lattice, or by substitution of Ti⁴⁺ ions in the Gd123 crystal lattice. Ti can be accommodated at Cu sites due to the similar ionic radius with Cu [13]. The substitution of Gd/Ba ions depends on Ba activity (concentration) during the growth of Gd123 crystal [14].

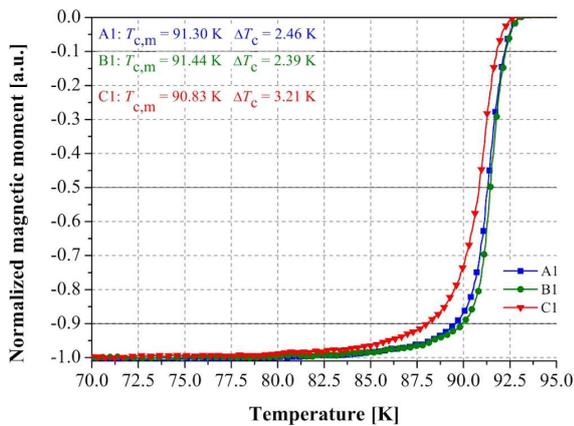


Fig. 2. Temperature dependences of the magnetization of the pure GdBCO specimens.

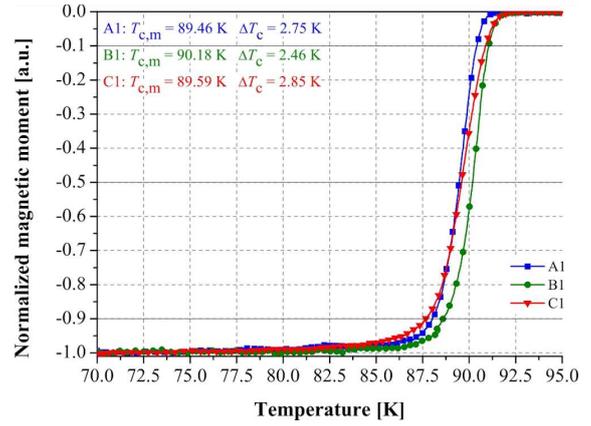


Fig. 3. Temperature dependences of the magnetization of the GdBCO+TiO₂ specimens.

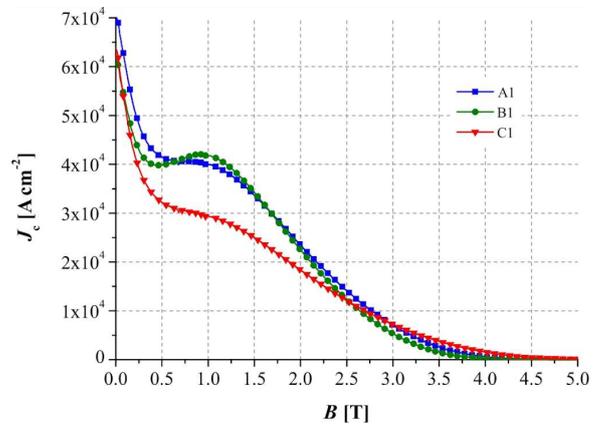
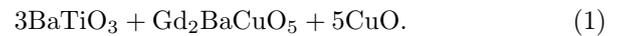
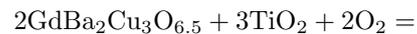


Fig. 4. Critical current density for the pure GdBCO specimens at 77 K.

From thermal and X-ray analyses we know that added TiO₃ fibres react with a part of Gd123, according to reaction:



At the peritectic reaction Gd123 phase decomposes, according to reaction:



Melt L will have deficit of barium due to formation of BaTiO₃ phase. This will result in higher substitution of Ba²⁺ ions by Gd³⁺ ions in Gd123 crystal lattice, and consequently, in lower charge carrier density and lower T_c . Some substitution of Ti⁴⁺ ions in to Gd123 crystal lattice has not been reported so far, but we cannot exclude it.

The field dependencies of critical current density at 77 K calculated from magnetization measurements are presented in Fig. 4 and 5. The peak effect is observed for all specimens. The most significant effect is decrease

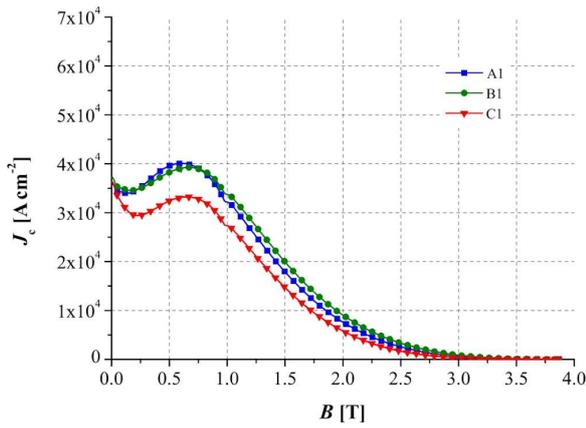


Fig. 5. Critical current density for the GdBCO+TiO₂ specimens at 77 K.

of J_c at zero field for the sample with TiO₂ fibre addition. At the zero field, however, it is expected that J_c is mostly influenced by the size and volume fraction of Gd211 non-superconducting particles. Therefore, we can suppose that some coarsening of Gd211 particles was caused by presence of Ti⁴⁺ ions in the partially melted system. Moreover, this effect was not compensated by TiO₂ fibres transformed to BaTiO₃ phase.

The addition of TiO₂ fibres leads to more pronounced secondary peak in the field dependence of J_c and to lower irreversibility field (Fig. 5). Both these effects are influenced by pinning centres formed by substitutions in Gd123 crystal lattice [14]. Lower peak at the higher distance from the beginning of solidification is caused by lower concentration of chemical pinning centres what suggest lower Gd/Ba substitution in the Gd123 lattice.

4. Conclusions

The single-grain GdBCO bulk sample with TiO₂ fibres was successfully prepared by the top-seeded melt growth method in air. The experimentally obtained results showed the following:

1. Formation of BaTiO₃ phase leads to deficit of barium in the melt during Gd123 crystal growth and to higher substitution of Ba²⁺ ions by Gd³⁺ ions in Gd123 crystal lattice. As a consequence, the lower charge carrier density and lower transition temperature to superconducting state appear.
2. More pronounced secondary peak effect in the field dependence of critical current density in the sample with the addition of TiO₂ fibres can be explained by higher concentration of chemical pinning centres. These latter inform of Gd/Ba substitutions due to lower activity of barium in the melt.

3. The lower secondary peaks closer to the seed may be caused by a decrease of Ba concentration in the melt with the distance from the seed.

Acknowledgments

This work was realised within the framework of the projects: Research Centre of Advanced Materials and Technologies for Recent and Future Applications “PROMATECH” (ITMS 26220220186), APVV-17-0625, VEGA No. 2/0044/19.

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