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Nanoscale Pinning in the LRE-123 System - the Way to Applications up to Liquid Oxygen Temperature and High Magnetic Fields

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1. Introduction

The discovery of superconductivity in oxides (Bednorz, et al., 1986), especially in the system of $\text{YBa}_2\text{Cu}_3\text{O}_y$ "Y-123" (Wu et al., 1987), having a transition temperature well above boiling point of liquid nitrogen and capable of carrying critical current densities at a level necessary for practical use, moreover in rather high magnetic fields, placed cuprate composites into center of the present material physics and technology. Liquid nitrogen cooling has promised construction of cryogenic systems greatly simplified, more realistic and economical in operation. Note that not only the critical temperatures of the new superconductors have been much higher than those of the conventional materials. The upper critical field of the order of 100 T has been estimated and also measured, making from these materials ideal candidates for high field applications (Welp et al., 1989). On the other hand, it has also been found that high- T_c materials in a polycrystalline form carry only low critical current densities, due to grain boundary weak links and crystal anisotropy (Cava et al., 1987). Attempts to improve the critical current density of the Y-123 material by texturing substrates and identifying coupling mechanisms at interface started immediately worldwide (Jin et al., 1988; Babcock et al., 1990). U.S. Pat. No. 5,061,682, issued to Aksay et al., 1991 disclosed a process for preparing conductive and superconductive ceramics composed of Y_2BaCuO_5 , $\text{YBa}_2\text{Cu}_3\text{O}_7$, and $\text{YBa}_2\text{Cu}_4\text{O}_8$. The most successful process at present is melt-texturing, which controls to a high degree lattice orientation of the crystalline material. In this way the superconducting phase ($\text{YBa}_2\text{Cu}_3\text{O}_x$) is formed by a peritectic reaction of Y_2BaCuO_5 (211) with a liquid phase. The growth process of the superconducting phase is accelerated by means of finely and homogeneously dispersed 211 phase in the liquid phase; at the same time, however, the 211 phase serves as a pinning medium dispersed in the superconducting phase. During the following slow cooling nucleation often occurs. This secondary nucleation forms parasitic grains that consume the material intended for the growth of superconducting grains. In this way high-angle grain boundaries are created that

reduce the current conducting efficiency of the polycrystalline material. The conventional procedure for fabricating a good quality 123-phase material was reported by the SRL group (Murakami et al., 1995). The material was produced by melting the raw materials for an oxide superconductor of REBaCuO, solidifying the melt, pulverizing the solidified material, and adding Pt or PtBa₄Cu₂O_y to the powder, molding the mixture to a predetermined shape, and again heating the mixture to grow a superconducting phase. The process in which the 211 phase and the platinum compound were finely dispersed in the 123 crystal was patented as U.S. Pat. No. 5,395,820 (Murakami et al., 1995).

By adding silver or silver oxide to the powder in this process, and preparing the precursor containing silver or a silver oxide finely dispersed therein (Vipulanandan & Salib, 1994) mechanical performance can be dramatically improved. Fabrication of single-grain Y-123 superconductors was reported in U.S. Pat. No. 6,046,139; Blohowiak et al., 2000. In the method, 1–25 wt % of 211 YBCO, 0.05–1.0 wt % Pt, and a balance of YBa₂Cu₃O_{7-x} (123 YBCO material) were combined. Pt is believed to limit growth of non-superconducting 211-phase crystallites. The mixed precursor powder was pressed into the form of a compact disk or other forms. A seed crystal NdBa₂Cu₃O_{7-x} or SmBa₂Cu₃O_{7-x} was placed onto the top surface, parallel to it. The compact was heated to a maximum temperature around 1050° C and held at that temperature for a time sufficient to fuse the seed crystal to the compact surface. The temperature was then lowered at the rate of approximately 0.1–1.0° C per hour. As the materials cooled, growth of the 123 YBCO grain started at the seed crystal. After nucleation, the compound was cooled at the rate of about 1–10° C per hour to a temperature of approximately 950° C. The Y-123 grain growth spread from the nucleation site until the entire pellet transformed into a single 123 YBCO grain. Using a similar approach and controlling the processing conditions and cooling rate, one can produce good-quality large single-grain YBCO pellets. In these processes the initial constitution of the starting composition resides on a "123-211 tie line" of a ternary phase diagram while keeping a sufficient but not excessive mass balance to yield a superconductive phase (123 phase) and to cause micro-dispersion of the 211 phase (in cases of Y, Sm, etc.) or the 422 phase (in cases of Nd, La, etc.), functioning as magnetic flux pinning centers in the superconductive phase. It increases critical current density, J_c , and at the same time keeps mass balance to minimize a residue of unreacted Cu, Ba, etc. As a result, such melt-grown Y-123 samples trap magnetic field much higher than that supplied by best nowadays known hard magnetics (Tomita & Murakami, 2003). The enormous effort in research and development has led to growing large single crystal grains of the 123 phase with spread the fine RE-211 phase in the matrix and significantly improved critical current density for super-magnet applications. On the other hand, it was found that the high J_c due to fine RE-211 phase appeared at low magnetic fields and decreased as the field increased (Salama et al., 1994; Cardwell et al., 1998).

In parallel to the YBCO system, the LRE-123 analogues (LRE=Nd, Sm, Eu, Gd) have been extensively studied. In these superconductors the rare earth elements partially substitute for Ba and vice versa (Yoo et al., 1994). Without control, an excess of such defects can deteriorate superconducting properties of such a compound. E.g. the early NdBa₂Cu₃O_y melt-textured blocks prepared in air exhibited a lower T_c than Y-123 bulks. It was found, however, that melt growth proceeded in a reduced partial pressure of oxygen reduced the mutual substitution of LRE and Ba ions and such materials were found to exhibit T_c even higher than that of Y-123 (Murakami et al., 1996). Moreover, the compositional fluctuation

on nm scale in such LRE-123 materials had a similar positive effect on the secondary peak of $J_c(B)$ as oxygen vacancies in YBCO (Egi et al., 1995; Ting et al., 1997). This fluctuation originated in solid solution of LRE atoms with Ba "LRE-123ss" (Osabe et al., 2000). In order to regulate the complex melt growth process in LRE-123 compounds, leading in general also to T_c reduction and superconducting transition broadening, a melt growth in a reduced oxygen atmosphere has been developed and optimized. In this process, the melt texturing process was decoupled from oxygenation, which enabled an independent control of both steps. The former could be optimized with respect to the LRE-123ss cluster concentration and the associated secondary peak (fishtail effect) enhancement (Pradhan et al., 2001), the latter with respect to the highest T_c . The oxygen-controlled-melt-grown (OCMG) LRE-123 materials reach typically 94-96 K with superconducting transition width below 1 K and exhibit a well developed secondary peak (Yoo et al., 1994). Materials with a slight excess of LRE or Ba can be produced but also materials with macroscopically stoichiometric composition but with composition fluctuation on a nanometer scale, in all the cases with the same positive effect on the electromagnetic performance.

The next breakthrough came with ternary (LRE¹,LRE²,LRE³)Ba₂Cu₃O_y. Combination of three light rare earth elements in the elementary cell provides an exceptional technological freedom that enables a fine variation in the inter-atomic exchange within the elementary cell and, consequently, a control of a variety of physical characteristics of the final product (Muralidhar et al., 1998). The OCMG processed (Nd,Eu,Gd)Ba₂Cu₃O_y "NEG-123" system proved that mixture of three different elements is possible, without any deterioration of the electromagnetic performance (Muralidhar et al., 2000 patent). Moreover, a control of the Nd:Eu:Gd ratio in the NEG-123 matrix enabled tailoring the pinning performance according to the requirements of the specific use (Muralidhar & Murakami, 2000). One can produce materials with a high narrow secondary peak of $J_c(B)$ at moderate fields or with a rather broad moderate peak with maximum at fields as high as 4 T (77 K) (Muralidhar et al., 2001). In a certain range of the Nd:Eu:Gd ratio, a nano-scale variation in the NEG-123 matrix composition appeared, correlated with the ordinary twin boundary structure. It enhanced vortex pinning in exceptionally high fields, around 10 T at 77 K and lead to shifting the irreversibility field at 77 K up to 15 T (Muralidhar et al., 2002a; Muralidhar et al., 2003a). As in YBCO, also here externally added secondary phase particles enhance critical current density at low magnetic fields (Diko et al., 2000). Gd₂BaCuO₅ "Gd-211" proved to form the smallest particles of all other LRE secondary phases and became a standard addition in the LRE composites. The efficiency of the secondary phase precipitates is inversely proportional to their size. With the aim to further improve the low-field pinning performance, we reduced the initial size of the secondary phase particles. (Muralidhar et al., 2002b; Muralidhar et al., 2003b). The refinement of Gd-211 particles from the commercial size of about 3 μ m to several tens of nm was done by ball-milling with Y₂O₃ - ZrO₂ balls. With the help of these ball-milled nanoparticles a new type of nano-scale Zr-rich NEG-Ba-Cu-O precipitates appeared in the final product, accompanied by an exceptional pinning enhancement in all high temperatures, up to vicinity of T_c . As a result, this material showed very high critical current density at 90.2 K, the boiling temperature of liquid oxygen (Muralidhar et al., 2003c). With this material we could levitate a permanent magnet at 90.2 K. As a result, a remarkable flux trapping, by order of magnitude higher than the best classical hard magnets, was achieved. These new materials can be utilized as a new class of high temperature superconducting super-magnets for a wide range of commercial and industrial applications (Jirsa & Muralidhar, 2004; Muralidhar et al., 2004a).

The present review focuses on the latest development in the field of mixed ternary LRE-123 systems. We report the results of microstructure and magnetization analyses of ternary LRE-123 compounds. Flux pinning and size effect of the initially added nanometer-sized Gd-211 and Zr-, Ti-, Mo-, and Nb-based particles is reviewed and discussed, especially from the viewpoint of applications of superconducting permanent magnets usable up to vicinity of T_c (liquid oxygen refrigeration).

2. Flux pinning in ternary $\text{LREBa}_2\text{Cu}_3\text{O}_y$ materials

Critical currents in superconductors usually rapidly decrease with increasing magnetic field. This feature, expressed e.g. by the Kim's empirical formula $J_c(B) = A/(B+B_0)$, is one of the main obstacles for sharing superconducting applications. In bulk high- T_c superconductors the fishtail effect represents some sort of exception from this rule, valid in intermediate fields. However, above the fishtail peak position, the $J_c(B)$ decay is even faster than that predicted by Kim. One can thus generalize and state that in high magnetic fields critical currents in high- T_c superconductors vary rapidly decay with increasing field. There are several factors contributing to this situation: (i) high- T_c superconductors are strong type II superconductors. The Ginsburg-Landau factor $\kappa = \lambda/\xi$, where ξ is the coherence length and λ is the magnetic penetration depth, is very high, in the range of 100. Vortex core diameter, being in HTSCs in the range of a few nm, is very small. The defects interacting with such tiny vortex cores have to be of an equal or even smaller size. The corresponding pinning and activation energies are then extremely low; (ii) the high critical temperatures encountered in these materials enable operation at rather high temperatures at which thermal activation is very high. Together with the low mean activation energy it leads to a fast vortex release from the pinning sites and so called giant magnetic relaxation. This effect is manifested by the existence of an irreversibility line $B_{irr}(T)$ above which the superconductor can no more hold a reasonable internal magnetic field gradient and carry critical current associated with this gradient. In contrast to the classical metallic type-II superconductors, in HTSCs $B_{irr} \ll B_{c2}$; (iii) high- T_c superconductors are layered structures composed of superconducting and non-superconducting planes. Therefore, the materials are highly anisotropic and the flux lines are more or less stacks of freely joined pancake vortices. Such objects are very flexible and elastic, which complicates modeling of vortex-defect interaction. The activation energies, enabling a vortex release from a defect, are here very low, especially, if the pancakes correlation becomes rather weak or if the vortex matter gets liquid of individual pancakes or their short segments.

For more than 20 years it has been a major practical objective to increase efficiency of pinning centers in high- T_c superconductors by a careful control of microstructure. An important aspect was to bring the pinning defects size up to nanoscale level, close to the material's coherence length (4.5 nm in YBCO at 77 K and similar in all LRE-123 compounds). Recently, this goal was realized in the ternary NEG-123 system produced by means of the OCMG process (Muralidhar et al., 2002c; Awaji et al., 2004). A further tuning of the nanoscale secondary phase particles with Zr, Mo, Ti, Nb additives enhanced flux pinning of these materials more than 3 times compared to a single-LRE 123 materials (Muralidhar et al., 2008a; Muralidhar et al., 2008b; Muralidhar et al., 2009). These results are systematically described below in respect of microstructure and flux pinning performance.

3. Second-phase inclusions and the associated flux pinning in NEG-123

In the melt growth process the RE-123 domain growth advances with a peritectic recombination of the RE-211 particles and the liquid phase (Ba- and Cu-rich). The rare earth ions needed for the 123 phase growth are supplied from RE-211 particles dispersed in the liquid. Moreover, as an optimum, 20-40 mol% of an additional secondary phase is usually added to the 123 powders before melt processing. These extra particles are partly utilized in the liquid phase for growth of the 123 matrix, partly are trapped in the RE-123 matrix (see Fig.1).

According to some models the interface between the RE-123/RE-211 is a good pinning medium.

Fig. 1. Scanning electron micrographs of the NEG-123 + 30 mol% (left figure) & 40 mol% (right figure) Gd-211 composite prepared under 1% partial pressure of O_2 . Note the uniform dispersion of fine 211 inclusions in the NEG-123 matrix.

In such models the critical current density increases with the V_{211}/d_{211} ratio, where V_{211} is the RE-211 volume fraction and d_{211} is the average size of the RE-211 particles (Murakami 1991), Sandiumenge et al., 1997). According to another model, this dependence is $V_{211}/\sqrt{d_{211}}$. (Zablotskii 2002). In both cases, the particle size decrease leads to a J_c enhancement.

In the mixed LRE-123 systems one can control the size, homogeneity, and dispersion of the Gd-211 particles (see Fig. 2). As the formation temperature of Gd-123 is lowest among the four LRE-123, the small Gd-211 particles cannot be consumed for the growth of Gd-123 and thus have a chance to survive (see Fig. 2). As a result, the critical current density of the samples with Gd-211 shows a remarkable J_c -B performance as compared to the “classical” melt-processed Y-123 or LRE-123 (LRE: Nd, Sm, Eu, Gd) systems without additional secondary phase. The OCMG-processed Nd-123 presents a well-developed peak effect. However, an extremely good pinning performance can be seen in the melt-processed (Nd, Eu, Gd)-123 “NEG-123” with 40 mol% NEG-211 or 30 mol% Gd-211 (see Fig. 3). The microstructure observations along with a compositional analysis showed that the extremely fine NEG-211 particles contain only Gd on the rare earth site. These particles therefore represent the effective flux pinning centers. The samples exhibit a pronounced secondary peak effect in the magnetization loops. A further improvement of the NEG-123 flux pinning was possible by an intentional size reduction of the initial Gd-211 particles to nanometer scale.

Fig. 2. Transmission electron micrograph of NEG123 with 30 mol% NEG-211 and 0.5 mol% Pt. Note the fine 211 inclusions dispersed in the matrix, which mainly comprise Gd in the rare earth site.

Fig. 3. Comparison of the field dependences of critical current density ($T = 77\text{ K}$, H_a parallel to the c axis) for melt-processed YBCO, OCMG-processed Nd-123, (Nd,Eu,Gd)-123 with 0 mol%, 10 mol%, and 40 mol% additions of NEG-211, and 30 mol% addition of Gd-211.

4. Nanometer-sized second-phase inclusions in NEG-123

Further improvement in flux pinning was obtained in NEG-123 system with a gradually reduced starting size of the $\text{Gd}_2\text{BaCuO}_5$ particles. The Gd- 211 powder was milled using $\text{Y}_2\text{O}_3 - \text{ZrO}_3$ balls in acetone, for 0.3, 2, and 4 h. The size was estimated by Brunauer-Emmerit-Teller (BET) specific area measurements (Brunauer et al., 1938). 30 and 40 mol% of the ball-milled Gd-211 were added to the sintered NEG-123. For coarsening suppression of the Gd-

211 particles during melt processing, 0.5 mol% Pt and 1 mol% CeO₂ were added. The pellets were grown by OCMG process in Ar with 1% O₂. The starting average particle size was 200 nm, 100 nm, and 70 nm, in dependence of ball-milling time 0.3 h, 2 h, and 4 h, respectively. The $J_c(H)$ dependencies of both types of NEG-123 samples with 30 and 40 mol% of differently sized Gd-211 particles are shown in Fig. 4. For comparison also a sample with commercial Gd-211 powders "CP" (< 3 μm) was measured. All measurements were performed at 77.3 K and $H//c$ -axis. A clear increase of remnant J_c with decreasing size of the particles is visible. Remarkable is the record value of the remnant J_c , 140 kA/cm², reached in the sample with 30 mol% of Gd-211, with the average starting particle size of 70 nm. The same particle size dependence was observed in the composite with 40 mol% Gd-211 (squares in the figure), where the remnant J_c value for the average starting particle size of 70 nm reached even 192 kA/cm² and 110 kA/cm² at remnant state and 3 Tesla, respectively. This result is by more than 60% better than the previous record values of NEG-123 and other RE-123 materials. Simultaneously with the enhancement of the low-field pinning also the super-current density at intermediate fields significantly increased in both materials with decreasing secondary phase particle size. This might be an indication of an overlapping of the "large" particle pinning mechanism with the individual vortex pinning regime on point-like defects. However, the 70 nm particles seem to be rather large to significantly contribute to single-vortex pinning regime. Microstructure and chemical analyses enlightened the problem. DFM test of the sample with 30 mol% Gd-211 (starting size 70 nm) brought an evidence of the final particle size dispersion between 20 and 50 nm. Such small secondary phase particles have not been observed before in any RE-123 material. Figure 5 shows the TEM micrographs of this sample. Two types of nanoparticles can be seen: large irregular inclusions of about 300 to 500 nm in size and round particles of 20-50 nm in diameter. The quantitative analysis by TEM-EDX clarified that the former ones were Gd-211 and Gd-rich NEG-211 particles. Both types were evidently created or at least strongly modified during the melting process. The small 211 inclusions had a clear link to a long-term ball-milling.

Fig. 4. Field dependence of super-current density for (Nd,Eu,Gd)Ba₂Cu₃O_y samples with 30 mol% and 40 mol% Gd-211 (squares) refined by ball-milling for 0.3, 2, and 4 h (200 nm, 100 nm, and 70 nm). "CP" represents the commercial Gd-211 powders ($\approx 3\mu\text{m}$). All the samples were measured at $T = 77\text{ K}$ with $H//c$ -axis. The current density increased in the whole field range with decreasing particle size. Record critical current densities of 192 and 110 kA/cm² were achieved at 0 and 3 Tesla, respectively.

Fig. 5. Transmission electron micrographs of (Nd,Eu,Gd)Ba₂Cu₃O_y samples with 30 mol% Gd-211 (average particle size was 70 nm); Insets show the new Zr-rich pinning medium in a higher magnification.

These defects, denoted as A1 - A4, are marked in figure 5 by arrows. Chemical analysis of nanoparticles with different sizes and shapes was made by energy dispersive spectroscopy (EDS) in scanning transmission electron microscopy (STEM) mode. Each analyzed spot had diameter of 2-3 nm. More than 65 nanoparticles were analyzed. We found that particles of size below 50 nm contained a significant amount of Zr. The four nanoparticles (A1 - A4) possessed different elemental ratios, always with a significant amount of Zr. A similar feature was observed in different parts of the sample. As no Zr was intentionally introduced into the system, we learned that the Gd-211 powder was contaminated with Zr from the balls used for milling. To estimate the Zr content in the Gd-211 particles, we made very precise quantitative analysis by inductively coupled plasma spectroscopy (ICP model: SPS-1700HVR). An average content of Zr was found to be 0.23 wt% for 4 hours ball-milled Gd-211 powders. Chemical composition of the particles represents a new, Zr-rich compound close to Gd-211, with yet not fully clear chemical structure.

The average size 20 – 70 nm sets these pins between point-like and “large” particles. This implies a potential of these defects to enhance material pinning in both low and intermediate fields. In comparison with another method capable of producing comparably sized artificial defects, namely fast neutron irradiation (Umezawa et al., 1997), the present technology is quite simple and can be easily adapted for mass production. Therefore, the new type of pins represents a unique economically feasible way how to enhance pinning in low and intermediate fields. This is particularly important for the applications using liquid nitrogen cooling. Note that J_c at 77 K and 3 Tesla is by about one order of magnitude higher than in high quality Nd-123 samples.

Another important consequence of the effective pinning by the new type of defects is the shift of the operating temperature from liquid nitrogen (77.2 K) to liquid oxygen (90.3 K).

For the first time the super-current density at 90 K was high enough to successfully levitate permanent magnet under liquid oxygen cooling (Muralidhar et al., 2003c).

5. Trapped magnetic field in RE-123 bulk superconductors

A strong electromagnetic suspension force can be generated by interaction of the melt-processed ternary RE-123 bulk superconductor with the stray magnetic field of a strong permanent magnet. This effect is applicable e.g. to construction of a practically lossless magnetic bearing, a contact-less liquid pump or a superconducting flywheel. The latter system has a wide range of applications, like position stabilizer, electric power storage, a high capacity, high current “fast” electric “battery”, unit absorbing and compensating voltage fluctuations at solar-cell or wind power plants etc.

When the superconducting pellet is magnetized to a high magnetic field, part of this field is trapped in the pellet and we get a superconducting permanent magnet or, shortly, super-magnet. Such a name is fully justified as high- T_c superconductors can trap magnetic field by order of magnitude higher than the best hard ferromagnets nowadays known. The major problem to solve is that the material is a ceramic, though in the state of pseudo single crystal. It is difficult in practice to prevent generation of micro-cracks and micro-pores during the melt processing. The micro-cracks are formed especially during the oxygenation process when a transformation from tetragonal to orthorhombic phase takes place, accompanied by significant atom displacements and stresses. As a result, the c-axis shrinks and b-axis is prolonged with respect to the a-axis. As the main atom displacement takes place within the a-b plane, most cracks lie just in the plane. Some, however, are also transversal to the current flow and hinder its flow. In any case, the mechanical properties are rather poor. To improve the mechanical performance of the materials, (i) addition of 20-30 wt% silver can help, when silver atoms prevent cracks proliferation, as well as (ii) reinforcement of the sample with metal ring, (iii) resin impregnation in vacuum when resin fills the pores and cracks, or (iv) resin impregnation with wrapping the material in carbon fiber. All these procedures greatly improve mechanical performance of the material. As a result, a trapped field of 14.35 T was recorded at 22.5 K (Fuchs et al., 2009). However, the samples are cracked also during the experiment, from a strong mechanical impact, thermal impact due to sudden temperature variation, a large electromagnetic force. The stress is then concentrated just in the aforesaid micro-cracks, which become a starting point of a progressive cracking of the whole sample. To overcome this problem, Tomita et al. 2003 impregnated the melt processed YBCO sample with Bi-Pb-Sn-Cd alloy along with the epoxy resin impregnation. The alloy has a high thermal conductivity at low temperatures (at 29 K) and its thermal expansion coefficient is close to the YBCO disk. To improve the thermal conductivity of the interior region of the disk, 1 mm in diameter bores were mechanically drilled in the center of the sample and filled with 0.9 mm diameter Al wires fixed by the Bi-Pb-Sn-Cd alloy. As a result, the trapped field of 9.5 T at 46 K, and 1.2 T for 78K was recorded. Until now valid record of 17.24 T was achieved at 29K, that all between two 2.65 cm in diameter discs, all without fracturing. These results opened the way to a new class of compact super magnets for various industrial applications. Note that the above experiment was done with a specially treated YBCO bulk. In the case of NEG-123 the pinning effect is considerably higher than in YBCO, both due to the LRE/Ba substitution and the capability of these materials to incorporate a rich network of various types of nanoparticles. According to recent reports, these bulk superconductors can trap magnetic field of about 1T at liquid nitrogen temperature (77 K) and several tens of Tesla even at liquid oxygen temperature

(90.2 K). The present refrigeration technique enables, however, operation at considerably lower temperatures, where the critical current and thus also the trapped field rapidly grow. Thus, in comparison to YBCO, the LRE super-magnets can trap comparable fields at much higher temperatures or at the same temperatures in pellets of much smaller diameter (the trapped field magnitude is also proportional to the pellet diameter). This opens a new class of applications, especially for space programs and medicine.

6. Flux pinning in NEG-123 due to TiO_2 nanoparticles

One should note that in these early NEG-123 materials with high pinning at high temperatures (in the range above 80 K) only the remnant critical current density was high but rather rapidly decayed with increasing magnetic field. It was desirable to extend the range of high critical current densities at high temperatures to higher magnetic fields. As the nanoparticles contaminated by Zr during ball milling appeared so effective, we also tried to introduce and to study the pinning effect of ZrO_2 (Muralidhar et al., 2004c) and other oxides of refractory metals from vicinity of Zr in the periodic table of elements. First, we tried to dope the material with TiO_2 nanoparticles. In accord with our expectations, nanometer-sized defects appeared in the final product of this kind, correlated with a significantly improved flux pinning at low and medium magnetic fields. This effect was particularly significant at high temperatures. To characterize the superconducting transition of the NEG-123 samples with various contents of Ti, the temperature dependence of the dc magnetic moment was first measured (Fig. 6). The zero-field-cooled (ZFC) and field-cooled (FC) curves were measured in magnetic field of 1 mT. All studied compositions exhibited a sharp superconducting transition (around 1 K wide) with the onset T_c around 93 K. The onset T_c slightly decreased from 93.2 K to 92 K with increasing Ti content. This showed that the small quantities of Ti studied in this work only slightly affected the superconducting performance of the NEG-123 material. Several previous reports have dealt with the TiO_2 doping. It was found that the increasing content of TiO_2 from 1% to 5% in a flame-quench-melt-grown (FQMG) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ bulk caused a decrease of superconducting transition temperature, while in the range from 7 to 10 wt.% T_c slightly recovered again (Yanmaz et al., 2002). In the $\text{YBa}_2(\text{Cu}_{3-x}\text{Ti}_x)\text{O}_y$ specimens, T_c of about 80 K was observed for $0 \leq x \leq 0.9$ (Okura et al., 1988).

Fig. 6. Temperature dependence of the normalized DC susceptibility of the OCMG-processed NEG-123 + 35 mol% Gd-211 (70 nm) with varying content of TiO_2 .

Venkataramani et al., 1988 found T_c significantly dropping with increasing x in $Y_{1-x}Ti_xBa_2Cu_3O_{7-\delta}$ ($x=0.05$ and 0.1), which they attributed to a site preference (Venkataramani et al., 1988). In the $DyBa_2(Cu_{1-x}Ti_x)_3O_{7-z}$ system the observed decrease of T_c with increasing Ti doping was attributed to the hole-filling mechanism (Mavani et al., 2004). In all above-mentioned cases the Ti doping was high compared to the present work. It is clear that the optimum content of Ti cannot depress T_c of the investigated RE-123 system.

In the present case small amounts of nanometer-sized TiO_2 (≤ 0.35 mol%) were added to the NEG-123 samples in order to improve the current-carrying capacity of the material, in particular around liquid nitrogen boiling point or at higher temperatures. Figure 7 presents the critical current densities at 77 K of the 0-0.35 mol% TiO_2 -added NEG-123 composites magnetized parallel to the c -axis. It is evident that the self-field critical current increased for 0.1 mol% of TiO_2 as compared to the pure NEG-123 and reached at 77 K 320 kA/cm². The high-field critical current density, J_c , and the irreversibility field, H_{irr} , decreased with further increase of TiO_2 content (≥ 0.2 mol% of TiO_2). These results proved that the optimum amount of TiO_2 in the NEG-123 system was around 0.1 mol%.

Ti is a 3d transition metal that can be accommodated at Cu sites in the RE-123 system due to the similar ionic radius with Cu. The drop of T_c in the Dy-123 system doped by Ti was in one previous study interpreted so that Ti ions maintain their +4 normal valence state as in the starting TiO_2 (Mavani et al., 2004). Venkataramani et al., 1988 found only a slight effect of Ti-substitution. They argued that the T_c dependence on Ti substitution is slower than that arising from oxygen vacancies in the Cu(1)-O chains. The behavior of the system up to 10% of Ti did not change much and correlated much more with the concentration of the second phase when Ti was substituted for yttrium. It could mean that Ti actually did not occupy the Y-sites but the Cu- ones. On the other hand, a low Zn substitution for Cu in the Y-123 system (Krabbes et al., 2000) or Fe, Co, or Ni substitutions for Cu in Bi-2212 single crystals were found to enhance J_c (Shigemori et al., 2004). These results showed that a direct doping in superconducting CuO_2 planes is an effective method for introducing point-like pinning sites in cuprate

Fig. 7. Field dependence of the super-current density in NEG-123 samples with the same, 35 mol% content of Gd-211 (70 nm) but various contents of TiO_2 . All the samples were measured at $T = 77$ K with $H||c$ -axis. The current density increased in the whole field range up to the 0.1 mol% content of TiO_2 and decreased thereafter. Note the relatively high critical current density of 320 kA/cm² at self-field and 77 K, achieved with 0.1 mol% TiO_2 .

superconductors provided the doping levels stay low. Such a dilute doping technique is particularly effective when the mean distance between the impurity ions is much longer than the coherence length in the *a-b* plane (Shimoyama et al., 2005). The present results indicate that an optimum “dilute” content of Ti enhances flux pinning of the NEG-123 material.

To find more about the pinning effect of Ti nanoparticles in NEG-123, we examined the microstructure of the samples in detail using the high resolution transmission electron microscopy (HRTEM). Figure 8 shows the typical TEM images of 0.1 mol% of TiO₂-added NEG-123 viewed from the <001> direction. In the images, two types of defects could be distinguished: large irregular inclusions of about 200 to 500 nm in size, and round particles of 20-50 nm size. The energy-dispersive x-ray (EDX) spectra of the larger particles identified them as a Gd-rich NEG-211 secondary phase, spontaneously created by peritectic decomposition of LRE-123 in the partial-melted region during the melt-texturing process. On the other hand, the small round particles of 20-50 nm size contained a significant amount of Ti, similar to the samples with a Zr addition. The critical current densities of the samples with various contents of TiO₂ are presented in Figure 9 for temperatures between 65 K and 90 K. Magnetic field was applied parallel to the *c*-axis and J_c was calculated from *M-H* curves using the extended Bean model. In all samples, the remnant critical current density dramatically increased in the whole range of investigated temperatures. At 65 K the critical current density of the sample with 0.1 mol% TiO₂ reached 550 kA/cm² at 0 and 4.5 Tesla and exceeded 450 kA/cm² over the whole range up to 5 Tesla. In the case of 0.2 mol% TiO₂ doping the super-current density at 65 K reached 275 kA/cm² at 0 and 4.5 Tesla and exceeded 250 kA/cm² over the whole range up to 5 Tesla, while the sample with 0.35 mol% of TiO₂ showed J_c of only 150 kA/cm² at 0 Tesla and 100 kA/cm² over the whole range up to 5 Tesla. At 90.2 K the remnant super-current density of the sample with 0.1 mol% TiO₂ reached 50 kA/cm² and the value decreased with further increasing the TiO₂ (≥ 0.2 mol%) content. All these data indicate that the optimum pinning was reached for 0.1 mol% of TiO₂. The J_c values presented here are significantly higher than those of a pure NEG-123 (without TiO₂) (Fig. 8). TiO₂ addition makes the NEG-123 composite a further member of the group

Fig. 8. Transmission electron micrograph of the NEG-123 + 35 mol% Gd-211 (70 nm) with 0.1 mol% TiO₂. Besides the rather large precipitate of NEG-211 seen in the right figure, two types of nanoparticles appear in the product, one within the size range 200-500 nm and another one of 20-50 nm size. The 200-500 nm particles are Gd-rich NEG-211 and Gd-211 secondary phase. The smallest particles are (LRE,Ti)BaCuO and LRE-Ba₂CuZrO_y. The arrows point to some of the nanometer sized Ti-based nanoparticles.

Fig. 9. Field dependence of the super-current density of the NEG-123 samples with the same, 35 mol%, content of Gd-211 (70 nm) but various contents of TiO_2 , measured from 65 K to 90 K with $H \parallel c$ -axis. Note the critical current densities of 550 kA/cm² at self-field and 4.5T at 65 K and 50 kA/cm² at self-field at 90 K, achieved with 0.1 mol% TiO_2 .

capable of permanent magnet levitation at 90.2 K, with liquid oxygen cooling (Muralidhar et al., 2003b).

The normalized volume pinning force density, $f_p = F_p/F_{p\max}$, as a function of the reduced field, $h = H_a/H_{\text{irr}}$, is frequently used as a measure of the pinning structure effectiveness. H_{irr} was determined from magnetization loops using the criterion of 100 A/cm². The $f_p(h)$ curves for a pure and Ti-doped NEG-123 are presented in Fig. 10. For the pure and 0.1 mol% of Ti NEG-123 samples, the $f_p(h)$ dependence peaked close to 0.42. Note that 0.5 was in classical theories associated with δT_c pinning. While even a slightly increased TiO_2 content over 0.1 mol% shifted the peak of $f_p(h)$ down to 0.36, the optimum quantity of 0.1 mol% of Ti did not affect the pinning mechanism much.

Whatever the pinning mechanism really is, a higher position of the $f_p(h)$ peak is associated with a better flux pinning. Moreover, the normalized peak position 0.5 is the highest met in literature. In this sense the $f_p(h)$ dependence confirms the conclusion that the 0.1 mol% Ti concentration is optimum. Magnetic data combined with microstructure analysis proved that TiO_2 nanoparticles belong to the agents capable to significantly improve pinning performance of the LRE-123 materials so that NEG-123 could be utilized for fabrication of superconducting super-magnets working at liquid argon and/or liquid oxygen temperatures.

Fig. 10. Normalized pinning force density $f=F_p/F_{p,max}$ as a function of reduced field $h=B/B_{irr}$ of NEG-123 samples with the same, 35 mol%, content of Gd-211 (70 nm) but various contents of TiO_2 , for temperatures from 65 to 90 K.

7. Flux pinning in NEG-123 with MoO_3 nanoparticles

The size reduction of non-superconducting pinning centers significantly below 100 nanometer range proved that mesoscopic precipitates (size of a few tens of nanometers) were able to exceptionally enhance flux pinning up to very high temperatures. Although levitation experiments at 90.2 K have already been realized with NEG-123 superconductors doped by Zr-based or TiO_2 based nanoparticles, the safety margins needed for practical applications require a further improvement in flux pinning in these materials. Recent experiments clarified that this task could be realized with MoO_3 nanoparticles.

Figure 11 shows the temperature dependence of the dc magnetic susceptibility in the ZFC and FC modes in magnetic field of 1 mT for NEG-123 + 35 mol% Gd-211, 1 mol% CeO_2 , and 0.5 mol% Pt samples with varying contents of MoO_3 . All the samples exhibited a sharp superconducting transition (around 1 K wide) with a high onset T_c . The onset T_c systematically decreased from 93.2 to 92 K with increasing MoO_3 content.

The critical current density at 77 K of the MoO_3 added NEG-123 composites with 35 mol% Gd-211 secondary phase is presented in Fig. 12 (left). The remnant critical current density dramatically increased for 0.1 mol% MoO_3 but decreased thereafter. The J_c - B curves of the 0.1 mol% MoO_3 sample deduced from SQUID magnetometer measurements in the temperature range around 77 K in magnetic field applied parallel to the c -axis are shown in Fig. 12. At 65 K tremendous super-currents were obtained, exceeding 700 kA/cm² at 0 and 4.5 Tesla and 610 kA/cm² over the whole range, up to 5 Tesla. These values approach the range typical for thin films. It might be promising to combine this technology with that used for fabrication of thick coated conductors. At liquid argon (87 K) and liquid oxygen (90.2 K), the super-current densities at zero field reached 175 kA/cm² and 50 kA/cm², respectively.

Fig. 11. Temperature dependence of the normalized susceptibility of the OCMG-processed NEG-123 + 35 mol% Gd-211 (70 nm) with varying contents of MoO₃.

Fig. 12. Left: $J_c(B_a)$ plots for NEG-123 samples with 35 mol% Gd-211 (70 nm), 1 mol% CeO₂, 0.5 mol% Pt, and various contents of MoO₃ at 77 K and $B_a \parallel c$ -axis. Note the relatively high critical current density of 390 kA/cm² at self-field at 77 K achieved with 0.1 mol% MoO₃. Right: The $J_c(H)$ curves of the sample with 0.1 mol% MoO₃ under liquid nitrogen pumping (65 K), at liquid nitrogen (77 K), liquid argon (87 K), and liquid oxygen (90.2 K) ($H \parallel c$ -axis). Note the very high critical current density of 700 kA/cm² at self-field and 4.5T at 65 K (right figure).

The MoO₃-based nanoparticles thus represent an effective pinning medium, appropriate for moderate magnetic fields and high temperatures, going up to boiling point of liquid oxygen. In order to evaluate the nanoparticle dispersion and its chemical analysis in the NEG-123 sample with 0.1 mol% MoO₃, TEM-EDX observations were performed on it. Figure 13 shows the TEM viewed from the <001> direction. Three types of defects can be seen: large irregular inclusions of about 150 to 500 nm in size, round particles of 20-50 nm size, and clouds of spots less than 10 nm in diameter. We note that in the partial-melted region there are two different kinds of LRE-211 inclusions: one (ball-milled) added to the initial powders and another one being created by peritectic decomposition of LRE-123. The large particles (over 150 nm in size) are Gd-rich NEG-211 or NEG-211 ones of the latter origin.

The chemical composition of the precipitates was studied by scanning TEM-EDX analysis. The quantitative analysis clarified that the large particles were Gd-211/Gd-rich-NEG-211, in agreement with our earlier studies of the NEG-123 system. In contrast, the defects with size below 50 nm always contained a significant amount of Mo. For the particles less than 10 nm, marked by the white arrows, it was difficult to estimate the exact composition. Anyway, just these particles are considered to be responsible for the high J_c observed at high temperatures. We succeeded in finding the appropriate processing parameters for their creation. The pinning enhancement due to the new type of defects is so profound that it extends up to temperatures above 90 K. This means that the limiting operating temperature for levitation experiments and other applications shifts from liquid nitrogen (77.3 K) to liquid oxygen (90.2 K) temperature.

Fig. 13. Transmission electron micrograph of NEG-123 sample with 35 mol% Gd-211 (the initial average particle size 70 nm) and 0.1 mol% MoO_3 the arrows point to some of the smallest nanoparticles, of size below 10 nm.

8. Flux pinning in NEG-123 due to Nb_2O_5 nanoparticles

An optimum content, size, and dispersion of the nanoparticles play the crucial role in improving vortex pinning in the melt-textured LRE-123 materials. Different physical/chemical properties are certainly equally important. This conclusion follows from the fact that the refractory metals of the same group as Zr give so different results, even if added in the same amount and same size. The best results in this direction were so far achieved with Nb_2O_5 nanoparticles added to the NEG-123 material. The critical current densities at 77 K of the NEG-123 composites with 35mol% Gd-211 doped by various contents of Nb_2O_5 are presented in Fig. 14. The low-field super-current density in the sample with 0.1 mol% of Nb_2O_5 was more than factor three higher than that of the standard NEG-123. The remnant J_c values of 640 kA/cm^2 and 400 kA/cm^2 were achieved at zero and 2 Tesla, respectively. This result was by more than 50% better than the previous record values of NEG-123 and by more than order of magnitude better than in other RE-123 materials. With further increase of Nb content the super-current density and irreversibility already dropped. The super-currents in the sample with 0.1 mol% of Nb_2O_5 in temperatures around 77 K are presented in the in Fig. 15. The remnant J_c value reached 925 kA/cm^2 at 65K. In liquid argon (87 K) and liquid oxygen (90.2 K) the super-current densities at zero field reached 300 kA/cm^2 and 100 kA/cm^2 , respectively. These J_c values are the highest reported so far for bulk RE-123 materials at the respective temperatures, approaching nearly the thin film limit.

Fig. 14. Field dependence of the super-current density in NEG-123 samples with the same, 35 mol% content of Gd-211 (70 nm) but various contents of Nb₂O₃. All the samples were measured at $T = 77\text{ K}$ with $H\parallel c\text{-axis}$. The current density increased in the whole field range up to the 0.1 mol% content of Nb₂O₅ and decreased thereafter. Note the critical current density of 640 kA/cm² at self-field and 77 K, achieved with 0.1 mol% Nb₂O₅.

In Fig. 16 we show the TEM images of the sample with 0.1 mol% Nb₂O₅, viewed from the $\langle 001 \rangle$ direction. Three types of defects can be seen: large irregular inclusions of about 150 to 500 nm in size, round particles of 20-50 nm size, and clouds of spots less than 10 nm in diameter. We note that in the partial-melted region there are two different kinds of LRE-211 inclusions: one (ball-milled) added to the initial powders and another one being created by peritectic decomposition of LRE-123. The large particles (over 150 nm in size) are Gd-rich NEG-211 or NEG-211 ones.

Fig. 15. The $J_c(H)$ curves of the sample with 0.1 mol% Nb₂O₅ under liquid nitrogen pumping (65 K), at liquid nitrogen (77 K), liquid argon (87 K), and liquid oxygen (90.2 K) ($H\parallel c\text{-axis}$). Note the record critical current density of 925 kA/cm² at self-field and 4.5T at 77 K.

Fig. 16. Transmission electron micrograph of NEG-123 sample with 35 mol% Gd-211 (the initial average particle size 70 nm) and 0.1 mol% Nb_2O_5 the arrows point to some of the smallest, Nb-based, nanoparticles.

The small Gd-211 nanoparticles (≈ 20 nm) were found to be those contaminated by Zr during the ball milling process. As Nb and Mo just follow Zr in the periodic table of elements, they possess similar properties as Zr, in particular chemical inactivity with respect to the constituents of the perovskites under study.

The chemical structure identification of the precipitates was made by scanning TEM-EDX analysis. The analyzed spot of 2-3 nm in diameter enabled to unambiguously analyze even the smallest clusters. The quantitative analysis clarified that the large particles were Gd-211/Gd-rich-NEG-211, while the defects with size below 50 nm always contained a significant amount of Zr, in agreement with our earlier studies of the NEG-123 and SEG-123 systems (Muralidhar et al., 2003c; Muralidhar et al., 2004a). Recently, the exact chemical composition of these particles was determined as $\text{LREBa}_2\text{CuZrO}_y$ (Muralidhar et al., 2003). The new class of precipitates of less than 10 nm in size contained a detectable amount of Nb incorporated in the NEG secondary phase. Some of these defects are marked in Fig. 16 by white arrows but these defects were distributed over the whole sample. Four such defects are denoted as B1 - B4 in figure 16. The four nanoparticles possessed different elemental ratios but always a significant amount of Nb atoms (see Fig. 17). The appearance of such small defects correlates with the super-current enhancement in a wide temperature range, spread up to liquid oxygen temperature.

The decreasing average particle size resulted in a critical current density enhancement at low and intermediate magnetic fields. Although the size of the smallest particles came close to the vortex core size, 2ξ , (in YBCO $2\xi_{ab}(77\text{ K}) \approx 4.5$ nm) and thus the limit of single-vortex interaction has been approached for these particles, no sign of a crossover to the secondary peak enhancement was observed. Note that a similar behavior was observed in the studies of [Werner et al., 2000] and [Sauerzopf et al., 1995; Sauerzopf et al., 1998] done on various RE-123 and Y-124 single crystals irradiated by fast neutrons. The explanation might be still a broad distribution of defect sizes, the largest ones having the strongest pinning energy, governing thus the overall behavior of the sample. Another possibility is that the crossover

between multiple- and single-vortex pinning is rather sharp and we are still not close enough. Or, the present defects are in some sense different from the typical point-like defects (oxygen vacancies and/or the LRE-123 matrix chemical fluctuation (Werner et al., 2000; Ting et al., 1997; Osabe et al., 2000)).

Fig. 17. The elemental content in the new nanoparticles in the material from Fig. 16. Note the significant amount of Nb in all nanoparticles.

The last NEG-123 material features the highest flux pinning performance of all bulk RE-123 compounds developed in SRL-ISTEC and to our knowledge in the world. To control pinning performance of the NEG material in a broad low-field range, various second phase precipitates have been tested in various contents. Gd-211 was found to produce always the highest flux pinning. Its optimum content was established to be around 35mol%. In each further step we have used the optimum composition obtained in the previous step. Thus, the Gd-211 content was also here just 35 mol%. Also the oxygen partial pressure has been chosen in accord with the best previous experience. The only variable in the present work was the varying content of the nanometer-sized TiO_2 , MoO_3 , and Nb_2O_5 . As a result, critical current density was enhanced by factor 2, 3, and 4, respectively, in comparison with the best our previous results, in all cases extended up to high temperatures. This record electromagnetic performance was always accompanied by appearance of clouds of exceptionally small precipitates (10 nm in size) in the NEG-123 matrix. Although this cannot be taken as a direct proof of causality, a similar coincidence observed previously in the case of Zr-contaminated 20 nm in size particles and the previous significant enhancement of the low- and medium-field critical currents (Muralidhar et al., 2005) supports this conclusion. In fact, it correlates with predictions of various models of vortex interaction with “large” normal particles (Campbell et al., 1991; Dew-Hughes et al., 1974; Zablotskii et al., 2002) suggesting $j_c \propto d^{-n}$, where d is the average particle diameter and $n=1$ [2] or $1/2$. These facts are strong indications that the enhanced pinning is due to a collaborative pinning by the operative pinning assemble, the result being exceptionally sensitive to the smallest nanoparticles, in our work especially those containing Mo and Nb, 10 nm in size.

9. Trapped-field distribution in the NEG-123 samples calculated using the J_c - B data at 77 K and 90 K.

In the NEG system, we can now for the first time create a particles distribution of the size less than 10 nm. As a result, the critical current density is very high, even at the boiling point of liquid oxygen. Trapped field measurements at 90.2 K for sample with Zr-contaminated nanoparticles (Muralidhar et al., 2004b) showed two peaks the higher of which reached 0.16 T. It indicated a crack in the sample created during magnetization process. Evidently, the mechanical performance was not good enough and a reinforcement was needed by adding silver oxide, resin impregnation (Tomita & Murakami, 2003), and/or an external metal ring (Kita et al., 2006).

We calculated TF values using experimental J_c - B data and with help of a numerical simulation. NEG-123 with 30 mol% Gd-211 (70 nm particles) was selected for this purpose, the J_c - B data from Fig. 4. Based on these data we calculated trapped field profile for disks of 40 mm and 50 mm diameters and thicknesses of 10 mm and 20 mm, respectively. Figure 18 shows the result for the disk of 50 mm in diameter and 20 mm thick, giving 0.45 T at 90 K. So far a standard NEG-123 sample of 32 mm diameter was able to trap in remnant state at 77 K maximum of 1.4 T (Yamada et al., 2003). Using the same J_c - B data, trapped field profiles for 77 K and samples of 50 mm in size and 10 and 20 mm thick were calculated in the same manner as above. The results are presented in Fig. 19. The trapped field reached more than 4 T in remnant state at 77 K. A summary of the calculated TF values at 77 K and 90 K is presented in the right Fig. 19. It is clear that the NEG-123 samples can generate more than 5T at 77 K with increasing the sample size to 60 mm diameter. The simulation results proved that the new material enables construction of non-contact pumps for transport of liquid gases including liquid oxygen. Thus, these results represent a significant step forward in the technology of bulk high- T_c superconductors towards novel engineering applications.

10. Levitation experiments at liquid oxygen temperature (90.2 K) and its new application potential

When speaking about applications of bulk high-temperature superconductors, superconducting levitation should be mentioned in the first place. Several years after the discovery of high temperature superconductivity, we developed a NEG-123 disk capable of levitation with liquid oxygen cooling. Although Y-123 has also critical temperature above boiling point of oxygen (90.2 K), levitation with this coolant has not yet been possible. The reason is that the pinning performance of Y-123 rapidly drops when coming close to the critical temperature. Thus, Y-123 can be used so far only for levitation at 77.3 K. The superconductors with T_c higher than 100 K, like $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{9+\delta}$ and others, exhibit a poor pinning performance already at intermediate temperatures and thus they cannot be used for levitation even with liquid nitrogen cooling. The new LRE-123 materials reach critical temperatures 93-96 K, not significantly above those typical for Y-123, but the best of them possess an exceptionally good pinning at high temperatures, super-current density being in the range of several tens of kA/cm² at 90 K (Fig. 15). This enabled levitation experiments with liquid oxygen cooling. Superconducting materials working at 90.2 K might have an important impact in industrial applications as magnet levitation at this temperature is a direct link to construction of non-contact pumps for liquid oxygen. Note that the industrial use of liquid oxygen is quite broad. It is commonly used in hospitals or as an oxidizer for liquid hydrogen fuel for launching rockets.

Fig. 18. The calculated trapped field distribution in the sample NEG-123 + 30 mol% Gd-211 (70 nm in size), melt processed in Ar-1% O₂, at liquid oxygen temperature (90.2 K). Dimensions and thicknesses of the sample were assumed 40&50 mm and 10&20 mm, respectively. The high trapped field of 0.45 T was achieved in the remnant state at 90.2 K.

Fig. 19. The calculated trapped field distribution in the sample NEG-123 + 30 mol% Gd-211 (70 nm in size), melt processed in Ar-1% O₂, calculated for the liquid nitrogen temperature. Dimensions and thicknesses of the sample were assumed 50 mm and 10&20 mm, respectively. Trapped field as high as 4.5 T was achieved in the remnant state at 77.3 K. The summary for the sample size vs trapped field at 77 K and 90 K in the remnant state is in the right figure.

Fig. 20. (left) NEG-123 + 40 mol% Gd-211 superconductor suspended below another NEG-123 + 40 mol% Gd-211 superconducting magnet. Both NEG super-magnets were before cooled by liquid oxygen; (right) Levitation of a tilted Fe-Nd-B magnet over the NEG-123 + 40 mol% Gd-211 superconductor cooled by liquid oxygen. Note that liquid oxygen is attracted to the magnet due to its paramagnetism.

Fig. 20 (left) is a proof, how effective is the potential well created in this way: a NEG-123 magnet can be suspended *below* another NEG-123 magnet when both are kept cool enough. That liquid oxygen is really used as a coolant, it is seen in figure 20 (right): since liquid oxygen is paramagnetic (in contrast to the diamagnetic liquid nitrogen), it is attracted to a tilted Fe-Nd-B magnet hanging over the superconductor immersed in liquid oxygen. Hospitals need comprehensive medical gas distribution systems to meet increasing demands of the life support technologies and emergency help. Medical gases have to be distributed in a clean, safe, and reliable manner. Gases in liquid form can be transported in a sophisticated network, which would supply either medical air and/or oxygen for patient breathing support or nitrous oxide for anesthesia. For such systems, the new superconductors represent a basic construction material for design of non-contact liquid oxygen pumps.

11. Summary

Over the past 20 years, remarkable progress in the area of melt-grown LRE-123 systems processing has been made. Improved processing techniques like oxygen controlled melt growth (OCMG) have been used for $\text{LREBa}_2\text{Cu}_3\text{O}_y$ bulks processing and then ternary $\text{LREBa}_2\text{Cu}_3\text{O}_y$ systems have been developed. Ternary $\text{LREBa}_2\text{Cu}_3\text{O}_y$ composites feature typical T_c onset around 94 K, critical current density at 65 K in the self-field and 5 T at the level of 10^5 A/cm^2 ($H//c$ -axis), and irreversibility field at 77 K ($H//c$ -axis) up to 15 T. This performance, highly exceeding that of YBCO, makes from these materials an excellent option for utilization in practical applications. A very important aspect is the possibility to control the pinning defects size up to nanoscale level and to bring it close to the material's coherence length (4.5 nm in YBCO at 77 K and similar in the LRE-123 compounds). A further tuning of the nanoscale secondary phase particles and Zn, Mo, Ti, Nb etc. additives enhance flux pinning of these materials up to 3 times compared to a single-LRE 123 material. As a result, pinning in these materials is very strong up to liquid oxygen temperature (90.2 K), leading to impressive levitation forces and extending thus the

application range of 123 compounds by about 13 K. In another direction, these materials can be utilized as a new type of bulk superconducting magnets, in particular for liquid oxygen pumps for various purposes.

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This book contains a collection of works intended to study theoretical and experimental aspects of superconductivity. Here you will find interesting reports on low- T_c superconductors (materials with $T_c < 30$ K), as well as a great number of researches on high- T_c superconductors (materials with $T_c > 30$ K). Certainly this book will be useful to encourage further experimental and theoretical researches in superconducting materials.

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