INTRODUCTION

Melt-processed LRE-Ba$_2$Cu$_3$O$_y$ “LRE-123” (LRE= Nd, Eu, Gd, Sm) compounds are top materials for fabrication of permanent superconducting magnets. Recent progress in their technology has significantly enhanced their electromagnetic performance [1] and brought a necessary breakthrough in mechanical performance [2]. The high-T$_c$ superconducting magnets will play an important role in a broad range of engineering applications like superconducting magnetic bearings, superconducting electric motors, magnetic separation devices for water purification, non-contact transport systems, flywheel energy storage systems etc. [1-10], some of them being, according to the latest reviews [11-14], ready for launching market in a close future. E.g., Hitachi, Ltd., Japan, recently developed and designed a mobile-type combined membrane and magnetic separator, employing long high-T$_c$ bulk superconductors, for a quick removal of phytoplankton multiplying in high amounts in eutrophic lakes and dams [15]. In a water cleaning test with kaolin as a pollution source it was found water cleaning level of more than 90 %. Another important and challenging application is HTS Maglev that is under study and development by the Southwest Jiatong University, China, and Central Japan Railways, Japan [16,17]. Material issues related to the use in the HTS Maglev system such as levitation and guidance forces, the magnetic and thermal stabilities during a high speed movement were tested and simulated. For electric power consumers superconducting flywheel storage systems are a high importance [18]. Such systems need high performance high-T$_c$ superconducting magnet bearings. An international project using three kinds of low-T$_c$ coils NbTi (6 T), Nb$_3$Sn (11.8T) and Nb$_3$Sn (13 T) but looking also for good quality, high performance high-T$_c$ analogues for both superconducting coils and/or superconducting bulk magnets in the International Thermonuclear Experimental Reactor (ITFR), started already in 1988 in cooperation of Japan, European Union, Russia and
USA. A superconducting rotating machine has been considerably improved using high temperature superconducting LRE-123 bulk materials.

All these applications require excellent vortex pinning and associated high critical current densities at 77 K. For improving electromagnetic properties, it was necessary to know well the pinning microstructure in LRE-123 materials and the vortex interaction with it. Extensive annealing experiments on clean YBa₂Cu₃O₇ “Y-123” single crystals pointed out importance of oxygen deficiency for formation of the secondary peak on the magnetization loop [19-21]. A similar effect was also observed in other RE-123 compounds. However, the positive influence of oxygen vacancies remained restricted to only a laboratory level and could not be fully employed in applications as with increasing oxygen deficiency a reduction of Tc was coupled [22]. In LRE-123 materials, the microstructure study revealed a compositional fluctuation on nm scale that had a similar positive effect on the secondary peak as oxygen deficiency [1,23]. This fluctuation originated in solid solution of LRE atoms with Ba “LRE-123ss” [1,24-26]. In order to regulate the complex melt growth process in LRE-123 compounds, leading in general also to Tc reduction and superconducting transition broadening, a melt growth in a reduced oxygen atmosphere has been introduced. In this way, melt texturing was decoupled from oxygenation process, which enabled an independent control of both. The former could be optimized with respect to the LRE-123ss cluster concentration and the associated secondary peak (fishtail effect) enhancement [1,24,27], the latter with respect to the highest Tc. Thus, the oxygen-controlled-melt-grown (OCMG) LRE-123 materials reach typically 94-96 K with superconducting transition below 1 K and exhibit a well developed secondary peak [1, 24]. Materials with a slight excess of LRE or Ba can be produced but also materials with macroscopically stoichiometric composition but a nanometer scale fluctuation of its superconducting properties, in all the cases with the same effect on electromagnetic performance.

The combination of three light rare earth elements in the elementary cell provides an additional technological freedom that enables control of a variety of physical characteristics of the final product [28-44]. The OCMG processed ternary (Nd, Eu, Gd)Ba₂Cu₃O₇ “NEG-123” system has proven to be capable of tailoring pinning performance according to the requirements of the specific use via control of the Nd:Eu:Gd ratio in the NEG-123 matrix[45, 46]. Thus materials with either a high narrow secondary peak of Jc(B) at moderate fields or with a rather broad moderate peak with maximum at fields as high as 4 T (77 K) [47-49] can be prepared. In a certain range of Nd:Eu:Gd ratio, an ordered variation in the NEG-123 matrix composition on nanometer scale appeared, which enhanced vortex pinning up to exceptionally high fields [1]. We note that similar superstructures have been recently observed also in some bulk RE-123 materials prepared by other techniques [50]. Secondary phase particles externally added to melt-textured materials enhance critical current density at low fields [51-53]. With the aim of further improving low-field pinning performance, we attempted to reduce size of the secondary phase particles, since their efficiency is inversely proportional to their size. The refinement of Gd₂BaCuO₅ “Gd-211” particles to a few tens of nanometers was performed by ball-milling the commercial powder by Y₂O₃ – ZrO₂ balls. This treatment led to creation of a new, nanometer scale, type of Zr-rich NEG-Ba-Cu-O precipitates, accompanied by an exceptional pinning enhancement not only at 77 K but also up to temperatures close to Tc. As a result, this material showed very high remanent critical current density at 90.2 K, the boiling temperature of liquid oxygen [54, 55]. In our tests of this material a permanent magnet easily levitated at 90.2 K.
In this contribution results of microstructure and magnetization analysis of LRE-123 compounds, composed of three LRE elements in the elementary cell, will be reviewed and the size effect of initially added Gd-211 secondary phase will be discuss with a special respect to applications of superconducting permanent magnets with liquid oxygen cooling.

**EXPERIMENTAL**

Microstructure control is the most complicated but at the same time the most important task in optimization of utility parameters of application materials in general. For ternary LRE-123 superconductors the following technological approaches are of primary importance for excellent electromagnetic performance of the material: (i) a proper setting of the matrix chemical ratio; (ii) doping by an appropriate, thoroughly ground secondary phase powder; (iii) formation of a point-like weak pinning disorder of LRE/Ba solid solution clusters (OCMG process); (iv) optimum oxygenation with respect to the highest Tc. These four tools enabled us to produce materials with the best so far reported parameters.

We gradually reduced the starting size of Gd2BaCuO5 “Gd-211” particles added to (Nd0.33Eu0.33Gd0.33)Ba2Cu3Oy “NEG-123”, (Sm0.33Eu0.33Gd0.33)Ba2Cu3Oy “SEG-123” and (Nd0.33Sm0.33Gd0.33)Ba2Cu3Oy “NSG-123” systems. All the the samples were produced in a routine way described e.g. in Ref. [56,57,58]. The Gd-211 powder was milled using Y2O3 – ZrO3 balls in acetone, for 0.3, 2, and 4 h. The average size of the ball-milled particles was 200 – 70 nm, in dependence of the milling time. The size was estimated by Brunauer-Emmerit-Teller (BET) specific area measurements [59]. 30 and 40 mol% of the ball-milled Gd-211 was added to the sintered NEG-123. For suppression of Gd-211 particles coarsening during melt processing, 0.5 mol% Pt and 1 mol% CeO2 were added. The pellets were grown by OCMG process in Ar with 1% partial pressure of O2. The samples of NEG-123, SEG-123 and NSG-123 reported in this work were prepared by a standard melt-growth processing described in Ref. [56,57,58]. For magnetic measurements small specimens with dimensions of about a × b × c = 2 × 2 × 0.5 mm³ were cut from the as-grown pellets and annealed in flowing O2 gas in the temperature range 300-600 °C. Microstructure of these samples was studied by scanning electron microscope (SEM) and dynamic force microscope (DFM). An atomic-resolution high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) was used to check the dispersion of nanometer-sized particles. The compositional variation in the nanoparticles was checked by bright field (BF) – STEM images. The energy dispersive X-ray analysis (EDX) associated with STEM-HAADF was employed to estimate the exact chemical composition of the nanoparticles. Magnetization hysteresis loops (M-H loops) were measured at 77 and 90 K using a commercial SQUID magnetometer (Quantum Design, model MPMS7) in field range –2 to +7 T. Jc values were estimated from the M-H loops using the extended Bean’s critical state formula for a rectangular sample [60].
MAGNETIZATION MEASUREMENTS

In Figure 1 present the \( J_c(H) \) dependencies of both NEG-123 samples, with 30 and 40 mol% Gd-211 secondary phase. 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.

![Figure 1. Field dependence of super-current density for (Nd,Eu,Gd)Ba\(_2\)Cu\(_3\)O\(_y\) 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 (≈3 \( \mu \)m). All the samples were measured at \( T = 77 \) K with \( H||c\)-axis. The current density increased in the whole field range with decreasing particle size. Record shows an remarkable super-current density still at liquid oxygen temperature, 90 K. critical current densities of 192 and 110 kA/cm\(^2\) were achieved at zero and 3 tesla, respectively. The inset shows an remarkable super-current density still at liquid oxygen temperature, 90 K](image)

For comparison also a sample with commercial Gd-211 powders "CP" (< 3 \( \mu \)m) 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/cm\(^2\), reached with the average starting particle size of 70 nm. The same particle size dependence was observed in the composite with and 40 mol% Gd-211 (squares in the figure) where the remnant \( J_c \) value reached for average starting particle size of 70 nm fantastic 192 kA/cm\(^2\) at remnant state and 110 kA/cm\(^2\) at 3 Tesla. This result is by more than 60% better than previous record values of NEG-123 and other RE-123 materials. This improvement represents achievement of the ISTEC internal goal in electro-magnetic properties of materials intended for large-scale bulk applications. Microstructure analysis revealed that new type of Zr/rich secondary phase nano-particles played important role in improving critical current density value. Another important consequence of the effective pinning by the new type of defects was a shift of the limiting operating temperature from liquid nitrogen (77 K) to liquid oxygen (90 K) [61-65]. For the first time the super-current density at 90 K was so high (see inset of Fig. 1) that enabled levitation experiment with liquid oxygen. Further it was verified that the nanoparticle effect was not limited to only NEG-123 but worked in all mixed LRE-123 systems as well [66,67]. The field dependence of \( J_c \) for
SEG-123 system at 77 K for H//c-axis is shown in Figure 2. Remarkable is the record value of the remnant $J_c$, 158 kA/cm$^2$, which is one order of magnitude higher than in the earlier reports on SEG-123 [68, 69]. The super-current density at higher temperatures like liquid argon (87 K) and liquid oxygen (90.2 K) were still high enough to allow for levitation (insets in Fig. 2). A considerable improvement of critical current density at 77 K and 90 K has been also confirmed in a NSG-123 system prepared in the same way [70, 71].

Further improvement of $J_c$ in a NEG-123 sample with 30 mol% Gd-211 is documented in Fig. 3. The $J_c(\mu_0H_a)$ curves were deduced from SQUID magnetometer measurements in temperature range of 70-89 K in applied field parallel to the c-axis. In this sample, both the initial matrix particles the secondary phase were ball-milled to the initial average size of 60 and 200 nm. $J_c$ values of 260 kA/cm$^2$ and 120 kA/cm$^2$ at 0 and 3 Tesla, respectively, were achieved at 77 K. The super-current density both at low and intermediate magnetic fields significantly improved as compared to earlier reports [72]. Only the irreversibility field slightly decreased. This may be due to the excessive Zr contamination of the Gd-211 and NEG-123 secondary phase. The earlier report [73] clarified that a rather low optimum Zr concentration and particle size are key factors in improving flux pinning performance at high temperatures (>77 K).
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. For understanding details of the operative pinning mechanism(s), microstructure analysis is of the key importance.

**MICROSTRUCTURE ANALYSIS**

In melt-textured RE-123 materials some portion of a superconducting phase always exists. However, for a reasonable pinning at low fields the concentration of such natural defects is not sufficient and additional LRE-211 or Nd-422 (in the case of Nd-123) have to be introduced intentionally. As these particles are normal and relatively large, they are strong pinning sites because a vortex trapping on them is associated with a high condensation energy gain. This is particularly true in the regime of individual vortex pinning and therefore these particles are most effective at low magnetic fields. Their efficiency is inversely proportional to a small power of their dimension, the actual power value depending on the particle geometry [74, 75]. In any case, size reduction of the secondary phase is an important task. In principle, each externally added 211 particle acts as a nucleation site. A slight amount of Pt is usually added to any LRE-123 composite in order to keep the LRE-211 phase dispersion in the LRE-123 superconductive parent phase fine and more stable [76,77]. SEM observations showed that morphology and distribution of secondary phase particles in NEG-123 matrix strongly depended on the kind, amount, and way of handling of the initially added secondary phase [78,79] and that additional submicron-sized 211 particles can be created in NEG system.
during the OCMG process [80,81]. Micro-structural analysis revealed that such particles were in majority Gd-211, while larger ones were mostly NEG-211. Number of spherical sub-micron Gd-211 precipitates increased in NEG-123 samples and their distribution became more uniform with introduction of additional Gd-211 powder [82].

**Scanning Electron Microscopy (SEM)**

Morphology of the final secondary phase network in the NEG-123 matrix was studied by scanning electron microscopy on several samples with various Gd-211 initial particle sizes. Figure 4 (a) shows SEM image of the NEG-123 sample with 30 mol% Gd-211 (70 nm). A notable feature is the uniformity of the secondary phase particles dispersion. A SEM image taken at a higher magnification (Fig. 4(b)) showed particles ranging between 200 to 500 nm, larger than the original size. Similar results have been reported for SEG-123 (see in Fig. 5) and NSG-123 systems [65]. However, due to limited resolution, one cannot recognize nanometer-sized particles by means of SEM. Much better chance to see such detail gives dynamic force microscopy.

![Figure 4 SEM images](image)

**Dynamic Force Microscopy (DFM)**

DFM represents in principle a tool to measure the force between the last atom on the tip and the individual atoms on the surface, yielding thus atomic resolution. Figure 6 is a 3-D
DFM image showing the particle dispersion, shape, and size. In the figure two categories of particles can be easily distinguished, one less than 50 nm and another one 100 to 200 nm in size. From the dispersion profile detected along the white stroke in the image a more precise determination of the particle diameter could be obtained as shown in Fig. 7. Diameters of the four selected nanoparticles were 44, 57, 65, and 100 nm. However, most important is chemical composition and nature of individual particles.

Figure 5 Scanning electron micrographs of SEG-123 + 40 mol% Gd-211 (average particle size is 75 nm) prepared under 1% partial pressure of O₂: (a) low magnification scanning electron micrograph, (b) high magnification scanning electron micrograph. Note that fine 211 inclusions with the size ranging from 300 to 500 nm are uniformly dispersed in the matrix.

Figure 6. 3-D Dynamic force microscope image of the (Sm₀.₃₃Eu₀.₃₃Gd₀.₃₃)Ba₂Cu₃O_y sample with 40 mol% Gd-211 (average particle size is 75 nm) prepared under 1% partial pressure of O₂: (left figure) low magnification DFM, (right figure) high magnification DFM. Note the uniform dispersion of nanometer size particles in the SEG-123 matrix (left figure).
Figure 7. Dynamic force microscope image of the (Sm_{0.33}Eu_{0.33}Gd_{0.33})Ba_{2}Cu_{3}O_{y} sample with 40 mol% Gd-211 (average particle size is 75 nm). Bottom panel presents dispersion profile of nanoparticles along the white line in the top figure.

**Transmission Electron Microscopy (TEM)**

To acquire better insight, resolution, and composition, TEM study is appropriate. Figure 8 present the typical picture of a NEG-123 sample with 30 mol% of 70 nm initial size Gd-211 particles, melt processed in Ar-1% O$_2$. Two types of defects can be seen: large irregular inclusions of about 200 to 500 nm in size as observed in scanning electron microscopy and round particles of 20-50 nm size. Chemical analysis of the nanoparticles with different sizes and shapes was made by energy dispersive spectroscopy (EDS) in scanning transmission electron microscopy (STEM) mode. The analyzed spot had diameter of 2-3 nm. More then 65 nanoparticles were analyzed. We found that particles of size below 50 nm contain a significant amount of Zr (Figure 9). The four nanoparticles (A1 - A4) possessed different elemental ratios always with a significant amount of Zr atoms. A similar feature was observed in different parts of the sample. As no Zr was intentionally introduced into the system, we concluded that the Gd-211 powder was contaminated with Zr from the balls used in milling. To estimate 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 detailed analysis of which will be discussed below.
Figure 8. Transmission electron micrograph of NEG-123 sample with 30 mol% Gd-211 (average particle size is 70 nm); the black arrows show some nanometer size Zr-rich particles.

Figure 9. The elemental content in the new-type nanoparticles in the material from Fig. 8. Note the significant amount of Zr in all nanoparticles.

Atomic–Resolution High-Angle Annular Dark Field (HAADF) Scanning Transmission Electron Microscopy (STEM)

HAADF STEM exhibits a strong atomic number (Z-) contrast, thus the phase-shift problem can be omitted and the HAADF STEM images can be directly inverted into the object level without any image simulation and give directly an exact structural and compositional information, especially on the nanoparticle size and phase. In Fig. 10 (left) Z-contrast image from a 200 kV scanning transmission electron microscope (STEM) equipped with a HAADF detector indicates size of the nanoparticles in the range 20 – 50 nm, some of the nanoparticles being marked with white arrows.
Figure 10. The atomic-resolution high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) image of the (Sm$_{0.33}$Eu$_{0.33}$Gd$_{0.33}$)Ba$_2$Cu$_3$O$_y$ sample with 40 mol% Gd-211 (average particle size is 75 nm) (left). The bright-field image of the same area (right).

Chemical composition of the particles was found from bright field STEM image of the same micrograph plotted in the right figure 10. Large particles between 100 and 300 nm in size, marked by block arrows, were of a similar composition, Gd-211 and Gd-rich SEG-211. This is an important result with respect to the general believe that Ostwald ripening [83] prevents in formation of secondary phase nanoparticles. Here we have an evidence that nanoparticles of secondary phases can be realized in mixed LRE-123 systems and participate thus on the strong vortex pinning. Size reduction further enhances flux pinning efficiency of the normally conducting paramagnetic 211 phase particles in the 123 matrix, especially at low and moderate magnetic fields. Such particles can pin simultaneously several vortices. While the number of pinned vortices per one pinning site decreases with decreasing particle size, the global pinning efficiency is inversely proportional to (a power of) the particle size as the number of particles grows and vortex matter adaption to the pinning landscape improves [84].

Table I. The STEM-EDXHAADF results for SEG-123 sample with addition of 40 mol% Gd-211 (average particle size is 75 nm) + 0.5 mol% Pt + 1 mol% CeO$_2$. The diameter of the analyzed spot was 1 nm.

<table>
<thead>
<tr>
<th>Area</th>
<th>Sm (at%)</th>
<th>Eu (at%)</th>
<th>Gd (at%)</th>
<th>Ba (at%)</th>
<th>Cu (at%)</th>
<th>Zr (at%)</th>
<th>Expected phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>8</td>
<td>8</td>
<td>41</td>
<td>22</td>
<td>21</td>
<td>-</td>
<td>LRE$_2$BaCuO$_4$</td>
</tr>
<tr>
<td>P2</td>
<td>4</td>
<td>7</td>
<td>43</td>
<td>23</td>
<td>23</td>
<td>-</td>
<td>LRE$_2$BaCuO$_4$</td>
</tr>
<tr>
<td>P3</td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>21</td>
<td>27</td>
<td>-</td>
<td>LRE$_2$BaCuO$_4$</td>
</tr>
<tr>
<td>P4</td>
<td>5</td>
<td>3</td>
<td>7</td>
<td>40</td>
<td>23</td>
<td>22</td>
<td>LREBa$_2$CuZrO$_4$</td>
</tr>
<tr>
<td>P5</td>
<td>4</td>
<td>4</td>
<td>9</td>
<td>33</td>
<td>39</td>
<td>10</td>
<td>(LRE,Zr)BaCuO$_4$</td>
</tr>
<tr>
<td>P6</td>
<td>4</td>
<td>4</td>
<td>14</td>
<td>36</td>
<td>35</td>
<td>8</td>
<td>(LRE,Zr)BaCuO$_y$</td>
</tr>
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</table>
It follows from the STEM-EDXHAADF analysis that most of the nanoparticles in the size of around 40-60 nm are a new phase LRE-Ba$_2$CuZrO$_y$ (LRE=Sm,Eu,Gd) (the light dark particles marked in the top figure 10). The particles smaller than 30 nm were of (LRE,Zr)BaCuO$_y$ (the black particles in the top figure 10), very similar to those reported in Ref. [85]. We note again that Zr contaminated the secondary phase powders during the ball-milling process. Data on chemical composition of some nanoparticles (P1-P6), obtained from the STEM – EDXHAADF results, are summarized in Table 1. Note that the STEM-EDXHAADF analysis brought evidence of coexistence of some (RE,Zr)BaCuO$_y$ nanoparticles with larger pure secondary phase corpuscles (Figure 11).

**LEVITATION EXPERIMENTS AT LIQUID NITROGEN TEMPERATURE (77.3 K)**

Levitation of objects is fascinating. It allows enormous masses to move with elegance, without any friction and noise. Just bulk high-temperature superconductors give to the levitation effect a new dimension as levitation applications can be realized with relatively cheap coolant, in a wide range of dimensions.
The development of large size good quality pellets of melt-textured RE-123 compounds brought the realization of big projects close to reality. Except electro-magnetic performance also the mechanical properties were successfully mastered. Fascinating levitation of people was for the first time demonstrated in ISTEC, Japan (1997) and recently also in IPHT, Jena (Fig. 12). However, the most challenging is the potential replacement of conventional superconducting coils by bulk superconducting high-\( T_c \) magnets in MagLev trains or design of superconducting motors.

LEVITATION EXPERIMENTS AT LIQUID OXYGEN TEMPERATURE (90.2K)

The old dream to utilize bulk high-\( T_c \) superconducting magnets at very high temperatures became more realistic with the recent achievement in levitation using liquid oxygen (boiling point 90.2 K) as a coolant. It was enabled by the recent progress in fabrication of NEG-123 materials [85]. Although \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) “Y-123”, commonly used for levitation at 77 K, has critical temperature (91-93 K) [86], lying only slightly below that of NEG-123, the pinning performance of Y-123 rapidly drops at high temperatures and therefore is insufficient for levitation at 90.2 K. Even worse situation is met in the superconductors with \( T_c \) above 100 K [87, 88], like Bi-Sr-Ca-Cu-O, Tl-Ba-Cu-O and others. These compounds 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 samples, but they possess an exceptionally good pinning at high temperatures, super-current density being in the range of several tens of kA/cm\(^2\) at 90 K (Fig. 1 & 2, insets). The trapped field associated with this exceptional pinning performance [62] enabled levitation experiments with liquid oxygen cooling. Superconducting permanent magnets 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, with potential use in medicine, rocket technology etc.

Figure 13. A permanent Fe-Nd-B magnet stably levitates over an NEG-123 + 40 mol% Gd-211 (average particle size is 70 nm) superconductor at liquid oxygen temperature (90.2 K), after the superconductor had been magnetized by stray field of the permanent magnet and cooled down to One can see the Fe-Nd-B magnet stably levitating above the NEG-123 90.2 K (right figure); the same experiment with a Y-123 superconductor (left figure). Note that we cannot perform levitation at 90.2 K using the Y-123 superconductor.
Figure 13 shows simple levitation experiments performed with liquid oxygen and Y-123 and NEG-123 bulks. In the case of Y-123 the levitation experiment at 90.2 K was not possible (left figure). The main reason for this failure was close vicinity of transition temperature to 90.2 K. In the newly developed NEG-123 with 30 and 40 mol% Gd-211 (initial size of 70 nm) both $T_c$ was well above 90 K and a sufficiently good pinning efficiency at this temperature made the levitation experiment successful (right figure). Prove of the oxygen use in the experiment can be recognized in Figure 14, where liquid oxygen, due to its paramagnetism, is attracted to the tilted levitating permanent magnet. superconductor at 90.2 K, similarly as a Y-123 pellet cooled to 77 K [86]. The newly developed secondary phase, together with the Zr-rich nanoparticles enhance pinning efficiency also in SEG-123 and NSG-123 bulk superconductors grown by oxygen-controlled-melt-growth process [89]. In both cases vortex pinning was high enough for levitation at liquid oxygen temperature (90.2 K) (see Fig. 15). These results make evidence that the pinning enhancement at low fields is due to the size reduction of the secondary phase particles and that this effect works irrespective of the chemical composition of the ternary melt-processed superconductor. An effective potential well works effectively also with another NEG-123 superconducting magnet either levitating above or being suspended below the first NEG-123 block (Fig. 16). Comparison with a Y-123 superconductor cooled to 77 K and suspended below a permanent Fe-Nd-B magnet (Fig. 17) clearly demonstrates the superiority of ternary LRE-123 compounds with respect to Y-123. One of the recent reports demonstrated more than 0.5 kg weight loaded on the levitating permanent magnet at liquid oxygen temperature [62]. Two blocks of the superconductor were used as a support. In the case of two levitating superconducting blocks one superconductor is first magnetized by external field and placed afterwards in a close vicinity of the lower one.

![Image](image-url)

**Figure 14.** A tilted permanent Fe-Nd-B magnet levitating over an NEG-123 + 40 mol% Gd-211 superconductor at liquid oxygen temperature (90.2 K), after the superconductor had been magnetized by stray field of the permanent magnet and cooled down to 90 K. Liquid oxygen, due to its paramagnetism, is attracted to the magnet. This is a clear mark that the coolant is neither liquid He, nor liquid N$_2$ but liquid oxygen.
Stray field of the first one is then trapped in the another one during field cooling process, similarly as in the case of a conventional permanent magnet. In this context very important message is the successful solution of the basic problem of the proper mechanical material reinforcement. During magnetization, enormous mechanical forces are developed that can easily destroy the pellet, especially during the external field reduction period. Such forces use the weakest points, which are numerous pores and other imperfections in this brittle material. Therefore, the achievement of Tomita and Murakami [2] in a successful reinforcement of an Y-123 pellet and its magnetization up to 18 Tesla, with the final trapped field of 17 Tesla at 29 K, was a big step to utilization of superconducting magnets in practice. This experiment showed the potential of bulk RE-123 materials as new class of permanent magnets, by order of magnitude stronger than conventional ones. These properties present quite new dimensions in permanent magnet applications. We note that the pellet used in Ref. [2] was of Y-123 and only about 2 cm in diameter. As above-described ternary LRE-123 compounds possess by order of magnitude better electromagnetic properties than Y-123 and trapped field is proportional to the pellet size, use of LRE-123 and a properly sized and fabricated pellet has to bring further enormous improvement to the above mentioned fantastic results.

Two main factors affecting the superior electromagnetic properties of ternary LRE-123 compounds in temperatures above 80 K and leading to levitation at liquid oxygen temperature are (i) a uniform dispersion of initial Gd-211 secondary phase particles 100 - 200 nm in size (slightly more than the mean size of the initial long-milled powder) and (ii) particles reduced
in size during melt-texturing process to less then 50 nm, composed of LRE-Ba$_2$CuZrO$_y$ and/or (LRE, Zr)BaCuO$_y$. Now we will look at the interaction mechanism of these defects with vortices and the associated shape of the magnetization loop.

Figure 16. NEG-123 "permanent" magnet field-cooled in a uniform field of 0.5 Tesla to 90 K, suspended below another NEG-123 superconductor in the same temperature. This is a test of quality of the potential well formed between the two superconducting magnets.

Figure 17. An MPMG processed Y-123 pellet is cooled to 77.2 K and suspended below Fe-Nd-B magnet, using the attractive force between the superconductor and the magnet.
ROLE OF NANOPARTICLES IN $J_c(B)$ DEPENDENCE

The field dependence of critical current density at 77 K with $B//c$-axis is shown in Figure 18. A clear increase of the remnant $J_c$ with decreasing particle size was observed. Remarkable is the record value of the remnant $J_c$, 157 kA/cm$^2$, reached with the average starting particle size of 75 nm, which is also presented in Fig. 2 (only 75nm size sample). We analyzed the experimental curves of Fig. 18 (a) by means of two additive contributions originating from vortex pinning on large normal particles (central peak) and point-like disorder (secondary peak) [90].

$$J_c = J_{c1} \exp\left(-\frac{B}{B_L}\right) + J_{c2} \frac{B}{B_{\text{max}}} \exp\left[\frac{1}{n}\left(1 - \left(\frac{B}{B_{\text{max}}}\right)^n\right)\right],$$

where $J_{c1}$ and $J_{c2}$ are heights of the central and secondary peaks in Figure 18. (a), respectively; $B$, $B_L$, and $B_{\text{max}}$ are the applied field, characteristic field scale [91], and position of the secondary peak, respectively; $n$ is the effective exponential decay rate of the second term. $J_{c1}$ was directly determined from experiment, $J_{c2}$, $B_L$, $B_{\text{max}}$, and $n$ were used as free fitting parameters. Note that the first estimate of $B_{\text{max}}$ and $J_{c2}$ values can be in most cases (especially in the case of well separated peaks) obtained directly from the experimental $J_c(B)$ plot and fit gives then only their small corrections. Parameter $n$ is closely bound with the shape of the $J_c(B)$ dependence. Its value is given by the logarithmic derivative $\partial \ln J_c / \partial \ln B$ at the high-field inflexion point [91]. It can be obtained graphically as a crosssection of the $J_c(B)$ curve normalized to the coordinates of the secondary peak with straight line going from coordinate origin with the slope 1/e [92]. So, in the fitting formula (1) only $B_L$ is the only really free parameter, the other ones are close to the values directly accessible from the experimental curve. The fits are in Fig. 18 represented by the full lines practically coinciding with the experimental data (symbols). The fitting parameters are summarized in Table 2.

The $J_{c1}$ data can be compared to theoretical formula

$$J_{c1} = \frac{3\Phi_0 V_f}{2\mu_0 \lambda^2(T) \sqrt{2R \xi(T)}},$$

following from the model of pinning by large normal particles [91]. Here $V_f$ is the volume fraction of ‘large’ particles and $R$ is their average effective radius, $\Phi_0$ is the flux quantum, $\mu_0$ is the permeability of vacuum, $\lambda$ and $\xi$ are the penetration depth and coherence length, respectively. For the sample with particles 75 nm in size, $J_{c1}$ value according to Eq. (2) is about 20-times higher than the experimental one. This discrepancy is simply due to the fact that the model in Ref. [91] did not take into account relaxation effects. Bearing this in mind, the theoretical value seems to be quite reasonable.
Figure 18. Field dependence of super-current density of (Sm,Eu,Gd)Ba$_2$Cu$_3$O$_y$ samples with 40 mol% Gd-211 refined by ball-milling for 0.3, to 4 h (200 nm, 150nm, 100 nm, and 75 nm). All the samples were measured at T = 77 K for H$_{||}$c-axis (a). The experimental data (symbols) were fitted by Eq. (2) (full lines falling together with the symbols. The decomposition into two contributions is shown in the inset. The current density increased in the whole field range with decreasing particle size. Record critical current density of 157 kA/cm$^2$ was achieved at 0 Tesla. A remarkable super-current density was observed also at higher temperatures, 86 K (b) and liquid oxygen temperature (90.2 K), (c).

Table 2. The fitting parameters for J(B) dependence of SEG-123 sample with addition of 40 mol% Gd-211 of various average particle sizes + 0.5 mol% Pt + 1 mol% CeO$_2$ measured at 77 K and 90 K. The theoretical data of $J_c$ were calculated according to Eq. (2). $^*$J$_c$(R) data were related to the experimental value for 75 nm particle size (the first row of each table part). J$_c$(T) dependence for 90 K calculated as a $\{(1-(90/93.5)^2)\}/[1-(77/93.5)^2]\}$1.25-multiple of the experimental data at 77 K were 24.8, 20.8, 17.0, and 14.6 kA/cm$^2$ for 75, 100, 150, and 200 nm, respectively, in a good correspondence with the experimental data in column 2.

<table>
<thead>
<tr>
<th>Gd-211 initial size (nm)</th>
<th>77 K</th>
<th>90 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$J_c$ exp. (kA/cm$^2$)</td>
<td>$J_c$(R) theory$^*$</td>
</tr>
<tr>
<td>75</td>
<td>157</td>
<td>157</td>
</tr>
<tr>
<td>100</td>
<td>132</td>
<td>136</td>
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<tr>
<td>150</td>
<td>108</td>
<td>111</td>
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<tr>
<td>200</td>
<td>93</td>
<td>96</td>
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<tr>
<td>75</td>
<td>25</td>
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<tr>
<td>100</td>
<td>22</td>
<td>21.65</td>
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<tr>
<td>150</td>
<td>15.5</td>
<td>17.7</td>
</tr>
<tr>
<td>200</td>
<td>13</td>
<td>15.3</td>
</tr>
</tbody>
</table>
We used the experimental data as a test of dependencies on temperature and particle size of Eq. (2), namely $J_{c1}(R,T) \propto R^{-0.5}[1-(T/T_c)^2]^{1.25}$, considering $\lambda(T) \propto \xi(T) \propto [1-(T/T_c)^2]^{-0.5}$. The theoretical $J_{c1}(R)$ dependence related to the particle size of 75 nm is in column 3. The experiment at 77 K reproduces the $J_{c1}(R) \propto R^{-0.5}$ dependence nearly perfectly, at 90 K reasonably well. The temperature dependence, calculated as $J_{c1}(R,90K)=J_{c1}(R,77K)\times[1-(90/93.5)^2]/[1-(77/93.5)^2]^{1.25}$ with $T_c=93.5$ K, gives 24.8, 20.8, 17.0, and 14.6 kA/cm$^2$ for 75, 100, 150, and 200 nm, respectively, again in a reasonable correspondence with the experimental $J_{c1}(R,90K)$ data. The $B_L$ values in all three temperatures seem to relate much more to the irreversibility field value, $B_{irr}$, than to the actual size of particles, similarly as $B_{max}$: while at 77 K $B_{irr}$, $B_L$, and $B_{max}$ are nearly constant, at 86 K and especially 90 K, where $B_{irr}$ increases with decreasing $R$, $B_L$ and $B_{max}$ increase, too, with approximately same rate. At 77 K parameter n was nearly constant, slightly above 2, which is a commonly observed value. $J_{c2}$ increased with decreasing particle size in a similar manner as $J_{c1}$. At 90 K, a weak but clear secondary peak contribution was identified only for the sample with the smallest particles, the other curves were successfully fitted by the single first term in Eq. (2). This itself indicates the qualitatively same dependence on $R$ as at 77 K. Similar conclusions follow also from analysis of the 86 K data.

In general, the present analysis indicates that we probably reached the crossover region between large particle (multi-vortex pinning) and point-like (single vortex pinning) mechanisms. The observed increase of both central and secondary peak with the reduced size of defects clearly support this conclusion. A further progress in Zr-rich secondary phase particle size reduction in LRE-Ba$_2$CuZrO$_y$ compounds promises not only a verification of the above model but also a further improvement of the performance of bulk melt-textured superconductors above 80 K.

Today’s hospital requires comprehensive and safe 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 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 gas pumps. Technology presented in this contribution has a great potential for production of high-quality superconducting magnets for industrial applications at temperatures above 80 K, which however means that these materials offer at the same time a better contingency fund for operation at liquid nitrogen temperature.

**Conclusions**

In this contribution a new class of RE-123 materials is presented, namely ternary (Nd,Eu,Gd)-123, (Nd,Sm,Gd)-123, and (Sm, Eu, Gd)-123 composites. These materials offer an exceptionally strong flux pinning at liquid nitrogen temperature (77.3 K), as well as an excellent performance even at liquid oxygen temperature (90.2 K). HADDF-STEM analysis revealed various types of nanometer sized particles in the 123 matrix, with a rather homogeneous distribution. The STEM-EDXHAADF analysis identified two types of new nanoparticle compositions, namely LRE-Ba$_2$CuZrO$_y$ and (RE,Zr)BaCuO$_y$. Besides these two
Zr-rich defect types, pure LRE-211 secondary phase particles with an average diameter above 100 nm co-existed in the 123 matrix. This complex pinning medium produced an excellent electromagnetic performance. The enhanced pinning enabled the supercurrent density in the order of $10^4$ A/cm² even above 86 K. As a result, we could levitate a permanent magnet over and below the ternary LREBa₂Cu₃O₇ superconductor cooled by liquid oxygen. This is a path to non-contact pumps of liquid oxygen for different fields of practice.

The analysis of the experimental data in terms of additive pinning by ‘large’ particles and point-like pins indicated that in the present samples both mechanisms were enhanced with decreasing particle size. This implied a potential crossover between these two pinning mechanisms. The recently derived $J_{c1}(R,T)\propto R^{-0.5}[1-(T/T_c)^2]^{1.25}$ dependencies were well reproduced. The new nanometer-scale pinning medium has a big potential in improving the melt-processed LRE-123 materials for superconducting permanent magnets and design of non-contact pumps for liquid oxygen. But still a space for further development is open.

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REFERENCES

Levitation at 90.2 K and its Applications


