Fabrication and characterization of $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ (LRE: Nd, Eu, Gd, NEG) superconductors: a low oxygen partial pressure

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Abstract

We studied the effect of oxygen partial pressure reduction to 0.05% during melt processing of $\text{NdBa}_2\text{Cu}_3\text{O}_y$, $\text{EuBa}_2\text{Cu}_3\text{O}_y$, $\text{GdBa}_2\text{Cu}_3\text{O}_y$, and $(\text{Nd},\text{Eu},\text{Gd})\text{Ba}_2\text{Cu}_3\text{O}_y$ on magnetic properties and microstructure. The superconducting transition of all the optimally oxygenated samples was as narrow as in those prepared in $p\text{O}_2$ of 0.1%, the onset temperature of the present samples was slightly higher or at least same as for 0.1% $p\text{O}_2$. Optical and scanning electron microscopy showed that in the $\text{GdBa}_2\text{Cu}_3\text{O}_y$ and $\text{EuBa}_2\text{Cu}_3\text{O}_y$ clusters are formed of sub-micron sized secondary phase particles. In other two compounds the secondary phase was uniformly dispersed. Magnetic properties of the present samples were always better at low fields than those of the samples prepared in 0.1% $p\text{O}_2$. The irreversibility field data were rather controversial, in some samples improved, in others worse.

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1. Introduction

LREBa$_2$Cu$_3$O$_y$ (LRE-123, LRE = Nd, Sm, Eu, Gd) materials processed in a controlled oxygen atmosphere (OCMG) have significant potential for power applications due to the high critical current density and irreversibility field at 77 K [1]. The OCMG process substantially reduces the LRE/Ba solid solution in $\text{LRE}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ compounds [1–4]. It has been proved that both the superconducting transition temperature ($T_c$) and irreversibility field of LRE-123 materials systematically improve with lowering $p\text{O}_2$ up to 0.1% [1–5].

In this work we used a commercial gas mixture Ar/0.05% O$_2$ in the OCMG process to produce $\text{NdBa}_2\text{Cu}_3\text{O}_y$, $\text{EuBa}_2\text{Cu}_3\text{O}_y$, $\text{GdBa}_2\text{Cu}_3\text{O}_y$, and $(\text{Nd}_{0.33}\text{Eu}_{0.33}\text{Gd}_{0.33})\text{Ba}_2\text{Cu}_3\text{O}_y$ (NEG-123) samples with the aim to study the effect of the further oxygen reduction on the materials microstructure and superconducting properties.
2. Experimental

NEG-123 powders were prepared by a normal sintering process details of which were described in [4]. For fabrication of single-LRE materials, commercial Nd-123, Eu-123, and Gd-123 powders with particle size less than 10 μm were employed. The heat treatment profiles for the melt processing of Nd-123, Eu-123, Gd-123 and NEG-123 composites were scheduled on the basis of DTA measurements detected at the heating rate of 5 °C/min using high purity Al₂O₃ crucibles.

Sintered NEG-123 and commercial Nd-123, Eu-123 and Gd-123 were first pressed into pellets 2 cm in diameter and 1 cm in thickness by applying cold isostatic pressing of 200 MPa. After placing a MgO seed crystal on the top center, the pellets were subject to the OCMG process in a commercial 0.05% O₂–Ar gas mixture flowing through the furnace at the rate of 100 ml/min. No secondary phase was added. However, secondary phase (211) particles are spontaneously formed in melt-textured LRE-123 samples even when the starting composition is stoichiometric.

For oxygen-annealing, small specimens with dimensions of a × b × c = 1.5 × 1.5 × 0.4 mm³ were cut from the as-grown pellets. The specimens of Nd-123, Eu-123 and Gd-123 received a separate oxygenation process, the details of which were reported [6,7]. In the case of NEG-123 system, the samples were heated during 2 h to 600 °C and left at this temperature for 1 h, then in 12 h cooled to 500 °C, in following 48 h to 300 °C. At this temperature the samples were held for 100 h. Then the furnace was switched off to cool down to room temperature. This procedure satisfied the optimum oxygenation of the samples resulting in highest possible $T_c$.

Microstructure of the samples was observed by means of optical and scanning electron microscopes. $T_c$ was determined from the temperature scans at magnetic field of 1 mT using a commercial SQUID magnetometer (Quantum Design, model MPMS7). Magnetization hysteresis loops were measured by SQUID at 77 K in magnetic fields up to 7 T applied parallel to c-axes of the samples. The magnetic $J_c$ values were estimated by means of the extended critical state model [8].

3. Results and discussion

Fig. 1 shows polarized light optical micrographs of Nd-123, Eu-123, Gd-123 and NEG-123 samples synthesized in the Ar/0.05% pO₂ atmosphere. Twin boundaries and spontaneously formed secondary phase particles are seen on the image of the Nd-123 sample (Fig. 1a). In the Eu-123 and Gd-123 (Fig. 1b and c, respectively) two types of RE-211 particles were found, large and sub-micron ones. Both these particles were often arranged in clusters. The number of such clusters was larger in Gd-123 than in Eu-123 and no such clusters were found in Nd-123 and NEG-123 samples. Character of these conglomerates, especially the concentric orientation of large particles with respect to the cluster centre, implies that these objects might have arose via a microscopic eruptive process. Though just in Gd-123 and Eu-123 improvement in magnetic properties in the whole irreversibility range was observed, identification of this fact with the appearance of the clusters would be too courageous. Not enough data are available at the moment.

Complementary, we prepared a NEG-123 sample with 30 mol% of Gd-211, 0.5 mol% Pt, and 1 mol% CeO₂ in the same way as the above samples. Fig. 1d shows uniformly dispersed Gd-211 particles in this sample, in accord with our earlier results obtained with Ar/0.1% pO₂ [9,10]. Fig. 1d indicates that the cluster formation is not induced by external addition of 211 particles. For verification of the origin of the particle clustering in the Gd-123 and Eu-123 systems a further study is needed.

Fig. 2 presents temperature dependencies of dc-susceptibility of the samples in zero-field-cooled and field-cooled regimes in magnetic field of 1 mT. The onset of superconducting transition, $T_{c,\text{on}}$, was found in the range 96.1–93.6 K. $T_{c,\text{on}}$ values are listed in Table 1, along with those of the samples processed in Ar/0.1% pO₂ and Ar/1% pO₂. The Gd-123 specimen melt-processed in Ar/0.1% pO₂, reported in Table 1, contained 40 mol% Gd-211 [11]. In all the samples the reduction of oxygen partial pressure during the OCMG process resulted in a slight increase of the onset $T_c$, in accord with the expected LRE/Ba substitution reduction.
Only in the NEG-123 system the values were similar.

The $J_c(H_a)$ data obtained from the $M$–$H$ loops are presented in Fig. 3. All materials had in low fields better properties than those prepared in 0.1% pO$_2$. Gd-123 sample exhibited the highest zero-field critical current density of 88 kA/cm$^2$ at 77 K for $B||c$-axis. Gd-123 and Eu-123 showed an improvement with respect to 0.1% pO$_2$ in the whole irreversibility range and irreversibility field significantly increased. The highest secondary peak position, $B_p$, and the irreversibility field, $B_{irr}$, were found in the ternary NEG-123 system but the data for 0.1% pO$_2$ were slightly better. The highest secondary peak was observed in the Nd-123 sample, $J_c(B_p)$ of 65 kA cm$^2$ at 77 K and 1.1 T but a clear secondary peak effect was observed at 77 K in all samples processed in Ar–0.05% O$_2$ atmosphere. The peak effect in the LRE-123 materials is commonly attributed to a field-induced pinning disorder due to RE/Ba chemical fluctuation or to oxygen deficiency in the superconducting RE-123 matrix. We believe that in our optimally oxygenated samples the chemical fluctuation due to RE/Ba substitution dominates [12].

The high $J_c$ value at zero-field in Gd-123 may originate from the sub-micron Gd-211 particle clustering. The same effect in Eu-123, however, did not result in such enhancement of the remanent $J_c$. Thus the role of these clusters is not yet clear. The
high overall $J_c$ and the highest irreversibility field values were obtained in the sample NEG-123. In ternary systems with different ranges of RE/Ba substitution, a competitive nucleation naturally generates scattering in this substitution. This is a probable reason for the high pinning in high magnetic fields observed in NEG-123 [13].

### Table 1

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Composition</th>
<th>$T_{c, on}$ (K)</th>
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<td>1% O$_2$</td>
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Fig. 2. Temperature dependence of magnetization for the Nd-123, Eu-123, Gd-123 and NEG-123 samples OCMG processed in 0.05% O$_2$.

4. Summary

We studied the effect of the oxygen partial pressure as low as 0.05% pO$_2$ on magnetic properties and microstructure of melt processed Nd-123, Eu-123, Gd-123, and NEG-123 samples. Microstructure observations revealed that in the Gd-123 and Eu-123 matrices the secondary phase particles formed sub-micron sized clusters. This might correlate with the highest remanent $J_c$ of 88 kA cm$^2$ achieved in the Gd-123 sample at 77 K. However, in Eu-123, where similar clusters were also found, though in a smaller amount, the remanent
$J_c$ was only about 40 kA cm$^{-2}$, similar as in both other materials. The highest second peak was observed in the Nd-123 sample, with the peak value of 65 kA cm$^{-2}$ at 77 K and $B_p = 1.1$ T. $T_c$ of the all samples prepared in 0.05% pO$_2$ was higher or at least the same as for the samples prepared in 0.1% pO$_2$. $B_{irr}$ and the superconducting performance in the whole irreversibility range clearly improved only in Gd-123 and Eu-123 while in Nd-123 and NEG-123 was slightly better for 0.1% pO$_2$.

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References