Production of Sharp-Edged and Surface-Damaged Y$_2$BaCuO$_5$ by Ultrasound: Significant Improvement of Superconducting Performance of Infiltration Growth-Processed YBa$_2$Cu$_3$O$_{7−δ}$ Bulk Superconductors

Sugali Pavan Kumar Naik,* Muralidhar Miryala, Michael Rudolf Koblischka, Anjela Koblischka-Veneva, Tetsuo Oka, and Masato Murakami

ABSTRACT: Growth and physical properties of bulk REBa$_2$Cu$_3$O$_{7−δ}$ (REBCO) superconductors fabricated by the infiltration growth (IG) method strongly depend on the initial size and morphology of the RE$_2$BaCuO$_5$ (211) particles. The present work details the novel method we developed for producing sharp-edged and surface-damaged 211 particles to be added to the REBCO bulks. We employed high-energy ultrasonic irradiation for pretreating the 211 particles and fabricated high-performance bulk single-grain YBa$_2$Cu$_3$O$_{7−δ}$ (YBCO) superconductors via the top-seeded IG process. Increasing the ultrasound irradiation power and time duration mechanically damaged the surface of the 211 particles, producing more fine and sharp edges. Systematic investigations of the microstructural properties of the final YBCO bulks indicated that the size and content of the 211 particles gradually decreased without any additional chemical doping. The effective grain refinement and improved interfacial defect densities enhanced the critical current density by a factor of two at 77 K and self-field as compared to a YBCO sample fabricated without any pretreatment. A maximum trapped field of 0.48 T at 77 K was obtained for a sample (20 mm diameter) with 211 particles treated for 60 min and 300 W ultrasound radiation. The effectiveness of the novel method is demonstrated by the superior performance of the YBCO bulk samples prepared as compared to bulk samples fabricated with the addition of Pt and CeO$_2$. This method is novel, cost effective, and very convenient, maintaining high sample homogeneity, and is free of chemical contaminants as compared to other methods which significantly affect the properties of all REBCO bulk products grown by sintering, melt growth, and IG methods.

1. INTRODUCTION

Bulk (Y/RE)Ba$_2$Cu$_3$O$_{7−δ}$ [(Y/RE)BCO, RE-123 or 123; RE = light rare-earth elements, Sm, Nd, Eu, and Gd] superconductors are prominent applied materials and have drawn much attention in the literature. This is mainly due to their relatively high superconducting transition temperature ($T_c$), critical current density ($J_c$), low flux creep, and low anisotropy. Many applications can be realized because $T_c$ of REBCO materials is well above 77 K. Trapping of high magnetic fields by bulk (Y/RE)BCO superconductors enables the fabrication of superconducting quasi-permanent magnets for magnetic resonance imaging, NMR, friction-free flywheels for energy storage, motors, and others.\textsuperscript{1−3} One of the important criteria in the evaluation of the quality of a high-$T_c$ superconductor is the $J_c$ and its temperature and field dependence. Therefore, improving the trapped fields (TFs) and $J_c$ which stands up to high fields and high temperatures, is the recent topic of research.

$J_c$ is not an intrinsic property of a superconductor and depends strongly on the final microstructure achieved. Several parameters such as the homogenous distribution of non-superconducting phases, oxygen content, cracks, and the coupling at grain boundaries may affect the $J_c$ of the bulk REBCO materials. One of the most attempted approaches for improving $J_c$ in these materials is the introduction of secondary phase inclusions.\textsuperscript{4,5} The defects generated at the interface of...
non-superconducting and insulating (Y/RE)\(_2\)BaCuO\(_5\) (hereafter abbreviated as Y-211/RE-211, 211) particles within the 123 matrix and those associated with nano-inclusions, dislocations, twins, and stacking faults have been proven to act as efficient flux pinning centers. For optimum performance, the size of these flux pinning sites should be comparable to \(2\xi\), the superconducting coherence length. Several methods such as sintering, melt growth (MG), and infiltration growth (IG) techniques have been developed for synthesizing various REBCO bulks. The IG process is found to be superior because of its advantageous merits such as the near-net-shape formation, minute amount of macrodefects such as pores, high dense microstructure embedded with fine-sized RE-211 inclusions, and so forth. In our recent work, we compared all these methods comprehensively.\(^6\) In the IG method, it is well known that the initial size of the RE-211 particles is considered to be dominant in the growth of REBCO.\(^7\) \(^9\) Therefore, the production and utilization of smaller-sized RE-211 particles is essential for the fabrication of high-quality REBCO bulk materials which support high \(J_c\) and trap large magnetic fields.

It is also well known that during the peritectic reaction between RE-211 and liquid phases, the smaller RE-211 particles will be consumed first to form the continuous 123 matrix. Employment of finer particles thus results in a continuous matrix with finer RE-211 particles left back. Much effort has been put through to the embedding of large fractions of fine-sized, non-superconducting inclusions and their homogeneous dispersion, which improves the interfacial defect density in the superconducting bulk samples. Conventional solid-state reaction and chemical routes and the combination of these with ball milling, coprecipitation, and spray-drying produce spherical RE-211 phase particles in the powder form with grain sizes ranging from submicron to several microns. To refine the RE-211 particles in the final products, many methods such as the addition of grain refiners (Pt, CeO\(_2\), Ba\(\rightarrow\)Ce\(\rightarrow\)O, etc.) have been tried.\(^10\) \(^11\) \(^12\) \(^13\) However, these additives are economically costly and with chemical addition, there always exist problems in maintaining the chemical composition throughout the bulk, and the achieved homogeneity is questionable. Ball milling is also limited to produce particles with \(\sim\)100 nm size, but milling for several hours results in the introduction of impurities, which is not desirable. Hence, it is necessary to look for new and advanced methods of producing nanometer-sized RE-211 phase particles within the 123 matrix without using any chemical dopants.

Employing novel methods for producing the fine-sized RE-211 particles and the successful incorporation into final IG-processed REBCO bulks is still challenging.\(^16\) \(^17\) \(^18\) To address the above-mentioned problems and to improve the properties of bulk REBCO, sharp-edged, surface-damaged, and nanometer-sized RE-211 particles were produced employing the method of high-energy ultrasonic irradiation. The manipulated RE-211 particles were then utilized for fabricating single-grain YBCO bulk superconductors via the top-seeded IG (TS-IG) method. Therefore, the present work reports the systematic development of a novel method for the production of surface-modified and nanometer-sized Y-211 particles, controlling the content and size in the final bulk microstructures of bulk YBCO samples, which significantly improves the field-dependence properties and T\(c\)s. For comparison, we additionally fabricated a bulk YBCO sample with the addition of Pt and CeO\(_2\) to demonstrate the effectiveness of the present method.

### 2. RESULTS AND DISCUSSION

#### 2.1. Working Mechanism

The strength of the superconductivity of REBCO materials largely depends on the crystal imperfections developed in the samples during the growth. According to various models available on the growth mechanism of REBCO superconductors, the peritectic reaction progresses by consuming the RE reservoirs, mainly the RE-211 phase, as given in eq 1. Recently, the utilization of nanotechnology in all scientific fields has been increased because of the fact that the properties of the material dramatically changes when the size changes to the nanometer scale. At the initial stages of the peritectic reaction, smaller-sized RE-211 particles (nanometer-sized) will be utilized for the peritectic 123 phase formations followed by larger-sized RE-211 grains.\(^19\) \(^22\) However, the growth reaction/rate could be further improved by geometrical modifications of precursor RE-211 particles.\(^23\) \(^25\) This can be achieved by employing RE-211 particles with very sharp edges and damaged surfaces. The nanometer-sized, sharp-edged, and surface-damaged RE-211 particles will be consumed during peritectic reaction and so contribute to improve the growth rate and allow fabricating larger-sized single domains in shorter times. By this technique, one can produce highly dense and superior quality final bulk products with embedded and homogeneously distributed fine-sized (nanometer) RE-211 particles in the bulk matrix. The working mechanism of manipulating the initial RE-211 particle size and morphology, employing the high-energy ultrasonication method, is illustrated in Figure 1.

\[
\text{RE}_2\text{BaCuO}_5 + \text{Ba}_2\text{Cu}_3\text{O}_8 \rightarrow \text{REBa}_2\text{CuO}_7 + \text{RE}_2\text{BaCuO}_5 \quad (\text{left back})
\]

#### 2.2. Microstructural Properties of Precursor Y-211 Powders

The Y-211 particles prepared by the solid-state sintering method will be of nearly spherical shape and are agglomerated because of which their size is effectively larger. The micrographs recorded by field emission scanning electron microscopy (FE-SEM) on the Y-211 precursor powders are displayed in Figure 2a,b. The effective size range of the 211 particles was determined to be large as \(~3\)–6 \(\mu\)m because of agglomeration, which is commonly observed in any sintered powder particles. For demonstrating the effectiveness of the proposed method of applying ultrasonic energy and producing sharp-edged and surface-damaged particles, we have chosen the YBCO system. We manipulated the initial Y-211 particle...
size and morphology, employing high-energy ultrasonication. In order to investigate the effect of power and time duration on the breaking of the Y-211 particles, different conditions such as variation of power, duration (Δt), amount of power and liquid mediums, and so forth were tested.

During the irradiation of low-energy ultrasonic waves and smaller Δt, sintering bonds between the 211 particles were broken and became individual. In Figure 2c,d, the FE-SEM images were recorded at magnifications of 5000× and 20,000×, respectively, illustrating the damage after irradiation of ultrasonic waves with 300 W power for 15 min. During this stage, the sintering bonds between the agglomerated Y-211 grains were broken and became individual ones with sizes in the submicron range. These fine-sized Y-211 particles are believed to participate and to improve the crystal growth, and remaining fine-sized Y-211 particles will be acting as superior flux pinning centers. A detailed microstructural analysis of the Y-211 precursor powders pretreated by the high-energy ultrasonic irradiation was discussed in our recent work.25

When an ultrasonic power of 300 W was irradiated, the average size range of the Y-211 phase particle was reduced to about 700 nm. Controlling the size of the initial additives and the homogenous distribution are the most prominent issues to achieve flux pinning centers within the 123 matrix, which is the key for enhancing the $J_c$ up to large applied magnetic fields.

To create more sharp-edged grains and to further modify the surface morphology, we employed an energy of 300 W at different time intervals of 15, 30, 45, and 60 min. We found that allowing 300 W for 45 min was the optimum condition for breaking the Y-211 phase particles while maintaining high homogeneity. Figure 3 shows the FE-SEM micrographs of (a) 30, (b) 45, and (c) 60 min ultrasonically pretreated Y-211 particles. All the sample microstructures reveal that the Y-211 particles are individual, in which the sintering bonds between the agglomerated Y-211 particles were successfully divided. However, the morphology of sample Y-211-30 is nearly spherical, and the broken bonds are marked by the blue box (see Figure 3a), whereas, the Y-211-45 particles can be found to be differently shaped, that is, partially eradicating and sharp-edged. It was observed that the Y-211 phase particles show sharp edges because of bombarding a high energy of 300 W. The sharp edges produced because of ultrasonic irradiation were marked with arrows in Figure 3b. The ultrasonic waves were eradicating some part of the surfaces of Y-211 grains. In some cases, the Y-211 particles could break up in the middle. The eradication could be achieved in shorter times if higher ultrasonic powers could be employed. More importantly, the nanometer Y-211 particles of different morphologies made by ultrasonic irradiation were expected to participate in a new type of growth as compared to conventional spherical shape and larger-sized Y-211 precursor particles. This method also can be employed for creating such sharp-edged and surface-damaged particles for other types of materials, by which their reaction or physical properties could be engineered. As evinced in Figure 3c, when an ultrasonication power of 300 W was employed for 60 min, the Y-211 particles were damaged immensely because of which very small-sized flakes can be observed, as marked by the circles.

As the irradiation time interval Δt increased, more Y-211 grain surfaces were damaged and the sizes reduced along with increasing homogeneity. The created sharp edge and surface damages are believed to improve the peritectic reaction which enhances the growth rate and distribute the fine-sized nanometer-sized Y-211 particles homogeneously throughout the bulks. This is supported by reports available in the literature on other composites.24 The experiments related to investigating the influence of ultrasonically irradiated Y-211 particles on the growth of various REBCO bulks are under way.

2.3. Structural Properties of Ultrasonicated Y-211 Powders and YBCO Bulk Samples. The as-processed Y-211 particles are agglomerated and are effectively large-sized (~6 μm) grains. In order to evince the reduction of the Y-211 particle sizes with ultrasound irradiation time, X-ray diffraction (XRD) patterns of each pretreated powder were recorded (see Figure 4a). The expanded version of the characteristic Bragg peak (2θ = 29.6–30°) of Y-211 for all powder samples is shown in Figure 4b. It can be observed that as Δt increases, the Bragg peak is widened and the corresponding fwhm value (determined by fitting with the peak function) increased. The details of the Y-211 size, fwhm, dispersion, and so forth are given in Table 1. This clearly evinces that the Y-211 particle size decreases with increasing Δt. This result is consistent and gets further support from the microstructural observations made on the pretreated Y-211 powders.23

The as-processed bulk sample photographs of Y−U−0 to Y−U−60 and Y−Pt−CeO₂ are shown in Figure 5a,b respectively. The fourfold facets for the samples clearly indicate that they grew in single-grain nature.
The crystal structure of all bulk YBCO samples produced by the pretreated Y-211 and Pt−CeO$_2$ was analyzed from the XRD patterns and is shown in Figure 6. It can be seen that all the Bragg peaks of samples are highly oriented in the (00l) direction, which indicates that the bulks are grown in c-axis orientation. Strong (00l) peaks along with no other (hkl) peaks suggest a high degree of texturing, indicating that all bulks are entirely a single grain. The prominent reflections show that all the XRD patterns can be well indexed to a YBCO superconducting phase with an orthorhombic unit cell. Some of the additional Bragg lines found in the Y−U-0 sample represent Y-211 as the minor phase and are marked with the symbol *. No other phases such as Ba−Cu−O were observed in any of the samples.

2.4. Critical Temperature. The in-phase component (real part) of DC magnetic susceptibility ($\chi$) with a function of temperature for all oxygenated YBCO samples produced by the ultrasonically pretreated Y-211 and Pt−CeO$_2$ is depicted in Figure 7. A small magnetic field of 1 mT was applied parallel to the c-axis. To clearly see the onset transition of each sample, the curves are magnified in the inset of Figure 7. The onset of the superconducting transition for Y−U-0, Y−U-15, Y−U-30, Y−U-45, Y−U-60, and Y−Pt−CeO$_2$ samples occurs at 90.8, 90.8, 90.2, 90.3, and 90.5 K, respectively. This clearly evidences that all the samples are exhibiting superconducting nature. The superconducting transitions in all samples are very sharp, and their transition widths “$\Delta T_c$” of $\leq 1.1$ K indicate the high-quality nature of the samples without any secondary phases. This result supports the observation of pure phases without any low-$T_c$ phases in the XRD studies, as shown in Figure 6. A minor amount of distribution in $T_c$ mainly at the tail of the curves represents the presence of small amounts of low-$T_c$ phases of oxygen-deficient phases in the samples which may aid flux pinning. The values of the $T_c$ and $\Delta T_c$ are given in Table 2.

2.5. Microstructural Properties of Bulk YBCO Samples. The fundamental criterion in achieving high $J_c$ in REBCO superconducting materials is engineering of the bulk
Table 2. Effect of Ultrasonic Irradiation on the Y-211 Particle Size and the Superconducting Properties

| Sample | Yttrium (µm) | Average 211 size (µm) | V_{911} (%) | Onset Tc (K) | Delta Tc (K) | J_c (0) (kA/cm²) | J_c at 2 T (kA/cm²) | TF_{surface} | TF_{norm} |
|--------|--------------|------------------------|-------------|--------------|--------------|-----------------|-------------------|---------------|-----------|
| Y-U-0  | 0            | 4                      | 41          | 90.8         | 0.3          | 45.1            | 13.6              | 0.25          | 0.21      |
| Y-U-15 | 15           | 3                      | 39          | 90.8         | 0.4          | 57.4            | 14.1              | 0.28          | 0.23      |
| Y-U-30 | 30           | 1.5                    | 34          | 90.2         | 0.5          | 68.1            | 21.3              | 0.30          | 0.24      |
| Y-U-45 | 45           | 0.9                    | 32          | 90.3         | 0.3          | 80.8            | 40.4              | 0.31          | 0.24      |
| Y-U-60 | 60           | ~0.9                   | 21          | 90.5         | 0.8          | 88.5            | 11.4              | 0.48          | 0.41      |
| Pt-211C | 1            | 1.1                    | 34          | 62.5         | 1.1          | 68.5            | 11.4              | 0.33          | 0.27      |

matrix with fine-sized non-superconducting inclusions. It was predicted that the effective surface area of these particles is proportional to the flux pinning of the bulk samples. Among non-superconducting and non-interacting inclusions such as the 211 phase, particles are considered as effective pinning centers. The defect density due to the left back 211/123 interfaces will be of coherence length size and effectively pins the fluxons and aids in improving the J_c performance of the single-grain REBCO bulk products.7,26

However, even in the IG process, great care needs to be taken in dispersing the non-superconducting particles homogeneously throughout the bulk matrix. The incorporation of fine-sized Y-211 into the bulk samples depends greatly on the initial Y-211 conditions. If two differently sized Y-211 phase particles are employed, it is well known that the smaller-sized particles participate in the peritectic reactions as the surface energy is large and form a 123 matrix. The FE-SEM images of Y−U-0, Y−U-15, Y−U-30, Y−U-45, and Y−U-60, and Y−Pt−CeO_2 are displayed in Figure 8a−f, respectively. One important observation that can be made immediately from the microstructural features of all samples is that the Y-211 particle boundaries are spherical, even though the initial particles have sharp edges and surface damages. Indeed, this clearly demonstrates that during peritectic reaction, the sharp-edged particles were consumed and the Y-211 particles become spherical of nanometer-size and homogeneously distributed throughout the matrix.

Even though we added differently sized Y-211 particles to the samples Y−U-15, Y−U-30, Y−U-45, and Y−U-60, we did not observe any traces of solidified liquid phases in the samples as evinced from the XRD and Tc analysis. Therefore, it can be stated here that the sharp-edged and surface-damaged Y-211 particles were completely utilized together with the supplied LPs for the peritectic growth of the Y-123 matrix.

The Y-211 particles which are of different sizes are employed for the IG process to enhance the superconducting properties of the final YBCO bulks. In our previous studies, it was observed that employing two differently sized Y-211 (micron and nanometer) particles in the IG process is not suitable.31−33 This is mainly due to the fact that the nanometer-sized particles of spherical morphology were observed to close the open gaps (porosity) available between the Y-211 particles in the preformed pellets. The amount of open porosity in the preformed pellets is crucial in infiltration of the liquid phases which will be further utilized during the peritectic reaction. If the open porosity is abundant, a large amount of liquid will infiltrate; thus, the preformed pellet will collapse and an inhomogeneous reaction will occur with left back non-superconducting Ba−Cu−O-rich phases in the final samples.34

These unwanted phases will be detrimental to the superconducting properties of the samples. If, in contrast, the open porosity is too less, then a sufficient amount of liquids cannot be homogeneously supplied to the preformed pellets. Therefore, the open porosity available in the preformed pellets is determined by the applied pressure, and the preformed particle size is crucial in the growth of the bulk REBCO superconductors.

Another important and different observation made from our previous work of adding nanometer-sized inclusions in Y-211 for IG processing is the absence of the enlargement of Y-211 particles in the final samples. In all our previous studies, we added different nanometer-sized and spherical-shaped RE sources in the preformed Y-211. The spherical inclusions were observed to sinter and fuse the gaps between the Y-211 particles in the preformed pellets and limited the infiltration of the liquid phases. In the present case, even though we added nanometer- and micron-sized Y-211 phases in the preformed pellets because of sharp-edged particles sufficient amount of liquid phases were infiltrated for effective peritectic reaction. Another factor which caused enlargement of the 211 phase particles in the mixed YBCO/REBCO bulk superconductors is the growth of mixed RE-211 during the peritectic reaction, which was grown up to several micron sizes. As discussed in our recent work of mixed REBCO bulk superconductors, these larger-sized mixed RE-211 particles will be consumed during the peritectic reaction and form mixed RE-123 unit cells in the final samples.35 However, this case is not valid in the present case of pure YBCO samples where no other RE elements are involved. Therefore, the sharp-edged particles were consumed for continuous growth of the matrix leaving very fine-sized Y-211 particles within the bulk samples.

The histograms presented in Figure 9a−f give the distribution of the Y-211 particle size of samples Y−U-0, Y−U-15, Y−U-30, Y−U-45, Y−U-60, and Y−Pt−CeO_2, respectively. The average sizes and volume fractions (V_{121}) of the left
back Y-211 particles within the Y-123 matrix for samples Y−U-0, Y−U-15, Y−U-30, Y−U-45, Y−U-60, and Y−Pt−CeO₂ are estimated to be 4 μm (41%), 3 μm (39%), 1.6 μm (34%), 0.9 μm (32%), ~0.9 μm (21%), and 1.8 μm (34%), respectively. The systematic difference in V₂₁₁ and sizes of Y-211 particles within the different samples clearly shows the difference between the pretreated ones and the ones without any ultrasonication. Obviously, the Y−U-0 sample contains coarser Y-211 particles because of the larger-sized and agglomerated precursors. Because of pretreating by increasing the irradiation time of ultrasonication, the 211 sizes are becoming finer. This implies that the sharp-edged and surface-damaged Y-211 particles have participated and were consumed effectively in the peritectic reaction.

The Y−U-45 sample exhibits a higher density of uniformly dispersed and fine-sized 211 particles within the bulk 123 matrix. The Y-211 particles left back in Y−U-45 are found to be finer, and their average is centered on 0.9 μm, whereas those in Y−U-0 are larger, falling in the 4 μm range. The size distribution of Y-211 precipitates in the case of Y−U-0 is observed to be much wider in the range 1–8 μm. As the irradiation time increased, the average size of the Y-211 particles is decreasing with increasing density of submicron-sized Y-211 particles. The density of smaller-sized particles ≤200 nm is observed to be more in sample Y−U-45 as compared to other samples, thus indicating the optimal condition. The Y-211 content is largely decreased in the case of the Y−U-60 bulk sample because of the increased Y-211 particle dissolving rate in the melt at the growth front. The preformed Y-211 particles were finer and sharp (see Figure 3c) in the case of sample Y−U-60, which was mostly utilized in forming the 123 matrix. Therefore, irradiating an ultrasonic energy of 300 W for 45 min was observed to be optimum to achieve high homogeneity in dispersion of fine-sized Y-211 particles. The decrease in the size of the flux pinning inclusions for maintaining the same optimal volume fraction of Y-211 will increase the flux pinning strength. The systematic decrease of the Y-211 particle sizes and content in the final bulks shows the efficiency of the proposed method in tuning the microstructural properties without any addition of chemical dopants. As argued from the microstructural features of pretreated Y-211, the reason for fine-sized left back Y-211 particles in Y−U-45 is attributed to present a sufficient amount of sharp edges with surface-damaged Y-211 precursor powders.

2.6. Superconducting Properties. 2.6.1. Critical Current Density. To evaluate the effect of irradiation of ultrasonic energy for different time intervals on the field dependence of J_c [i.e., J_c(H)] performance at 77 K, M−H loops were recorded up to 5 T field applied normal to the c-axis of each bulk specimen. The J_c values of all bulk samples were determined using the extended Bean critical state model. Figure 10 shows the field dependence of J_c for all the bulk, YBCO single-grain samples.

The zero field J_c [i.e., J_c(0)] for Y−U-0 is found to be 45.1 kA/cm². As the irradiation time of ultrasonic waves is increased, the J_c values are increased. The Y−U-45 sample is exhibiting superior J_c performance with 80.8 kA/cm² at the self-field. The details of J_c(0) and J_c at 2 T field for all samples are given in Table 2. If the J_c performance is compared with Y−Pt−CeO₂ (62.5 kA/cm² at 77 K and self-field) also, the Y−U-45 sample is superior, indicating the effectiveness of the present method. The analysis of the J_c(H) curves at a lower field may shed light on the effect of different grain refiners on the strength of the pinning performances. Therefore, having a larger number of non-superconducting particles with fine size is suitable for supporting larger currents. Among all samples studied here, the density of fine-sized Y-211 particles (≤200 nm) was higher in sample Y−U-45 and supported larger currents as compared to the other samples. The magnitude of the J_c in the REBCO is determined by the ability of the microstructure which pins the magnetic flux. This result gets support from the fine-sized 211 phase particles as observed in the superior microstructure of the Y−U-45 sample.
2.6.2. Trapped Field. The oxygenated bulk samples are field-cooled by a permanent magnet for 15 min. The 3-D TF profiles recorded at 1 mm distance (sample surface—Hall probe) for Y−U−0, Y−U−15, Y−U−30, Y−U−45, Y−U−60, and Y−Pt−CeO$_2$ single-grain samples are shown in Figure 11a−f, respectively. The single conical curves without any distortion for all the samples indicate that all the samples are grown as single grains and the complete bulk is oxygenated. The observed TF values at 0.3 mm (TF$_{\text{surface}}$) and 1 mm (TF$_{\text{normal}}$) for all the samples are given in Table 2. It is obvious from Table 2 that the TF performance is gradually improved with irradiation of ultrasound energy duration, and a maximum TF$_{\text{surface}}$ value of 0.48 T was recorded for the sample Y−U−60. This value is nearly twice that of sample Y−U−0. The gradual increase in the TF performance can be attributed to the improved pinning performance because of the employment of fine-sized 211 phase particles.

The $J_c$ performance of sample Y−U−45 is superior compared to sample Y−U−60. As demonstrated from microstructural features of both samples, it relates to the density and the size of the Y−211 particles left back in the samples. The density of nanometer-sized Y−211 particles ($<200−500$ nm) is high in the case of the Y−U−45 sample, and the dispersion of the Y−211 grains is also uniform which supports the higher magnitude of $J_c$ values (Figure 12). From microstructural observations, it is evident that even though the Y−211 particle sizes are smaller for Y−U−60, the lower $V_{\text{211}}$ limits the $J_c$ performance. However, here, we point out that the TF reflects the global $J_c$ of the complete bulk sample. However, the $J_c$ determined on a small subspecimen with a limited micro-

structure is sensitive to many parameters such as defects or fluctuations. Therefore, the $J_c$ of Y−U−60 might be inferior to that of Y−U−45. To make a conclusive statement, however, we need a detailed growth and microstructure-related investigation which we will be carried out subsequently. The present results may be even improved by employing higher ultrasonic powers, which will also lead to reduction of the time interval, thus efficiently producing the sharp-edged 211 preformed particles and without chemically doping.

In order to further validate the results obtained from sample Y−U−60, we synthesized a new single-grain YBCO bulk sample (Y−U−60-Rpt) with 60 min ultrasonicated Y-211 powders by the TS-IG method. The microstructures of Y−U−45, Y−U−60, and Y−U−60-Rpt samples are displayed in Figure 13a−c, respectively. The comparison of the microstructures of samples Y−U−60 and Y−U−60-Rpt clearly depicts that both the samples show similar features with the low 211 content and dispersion. The microstructural features indicating that a large amount of fine-sized and sharp-edged Y−211 powders produced by ultrasonication for 60 min were utilized for fabricating the bulk single-grain YBCO sample. Because of this, the field dependence $J_c$ curves determined at 77 K of Y−U−60 and Y−U−60-Rpt, as shown in Figure 14, exhibit a similar trend. The TF at 77 K for Y−U−60-Rpt was measured to be 0.38 and 0.45 T at the 1 and 0.3 mm distance from the sample surface, respectively, whereas these values for the Y−U−60 sample are 0.41 and 0.48 T, respectively. The 3-D TF profiles of Y−U−60 and Y−U−60-Rpt are given in (a,b), respectively, of Figure 14 as insets. These results clearly imply that the produced samples have similar properties which strongly support the novel approach as the samples could be successfully reproduced. Also, this further supports the different reactivity of the ultrasonicated Y−211 in the bulk REBCO growth, which needs to be studied further.

2.7. Future Perspectives. As demonstrated, the proposed novel method is advantageous and superior to any of the available methods. More importantly, this method is general by which the sharp-edged rough surface 211 particles could be employed for any methods such as MG and IG. The effectivity of the present method can be further improved to develop the REBCO material as a candidate for various practical applications. The future perspectives for further investigation of the effect of ultrasonication on the REBCO superconductors are discussed below.

1. Precursor powders of different 123 and 211 phase powders synthesized via different methods such as solid state and chemical routes and test the ultrasonic effect. Utilizing the 123 and 211 phase particles with sharp-edged and damaged surfaces, synthesize the bulk samples via MG and IG processes. Ultrasonically
pretreated 123/211 powders could be employed in fabricating other forms of superconducting materials such as thin films, tapes, thick films, cables, foams, and so forth.

2. Testing of high ultrasonic powers (≥300 W) for quickly producing the pretreated various 211/123 phases for constructing high-performance REBCO bulk products.

3. Producing different sized 211/123 phases and mixing them as micron-sized particles, and studying the effects on the growth of the bulks and their final physical properties.

4. Using the pretreated initial 211 particles to study the growth and reaction in IG/MG processing of REBCO superconductors. This study may help in growing larger-sized bulk single grains in shorter durations.

5. Pretreat different REBCO phases and construct mixed REBCO bulk superconductors.

6. Batch processing of various YBCO/REBCO superconductors with ultrasonicated 211/123 phase particles.

3. CONCLUSIONS

We propose a novel, reliable, and cost-effective method, which controls and reduces the 211 particles size in precursor powder and then subsequently produces nanometer-sized 211 precipitates. The initial Y-211 particle size and morphology were manipulated employing high-energy ultrasonication for producing sharp-edged and surface-damaged Y-211 preformed powders. To demonstrate the effectiveness of the method, bulk single-grain YBCO superconductors of high quality were fabricated by the TS-IG method and compared with the addition of grain refining agents of Pt−CeO₂. As the time duration was increased, the Y-211 size was decreased and sharp-edged and different-shaped Y-211 particles were created. The effectiveness of the present method lies in the tuning of the initial Y-211 particle size, morphologies, and the grain boundary volume fraction in the final bulk YBCO samples. With increasing irradiation time, the 211 particle size and $J_c$ in the final bulk samples were decreased. The TF performance of bulk single-grain YBCO samples exhibited a systematic improvement with the increase of irradiation time. The YBCO sample fabricated using Y-211 particles with ultrasonic irradiation for 60 min was able to trap a magnetic field of ~0.48 T at 77 K. $J_c$ (at 77 K) was increased monotonically for ultrasonic irradiation time of up to 45 min. A further increase of $\Delta T_{lc}$ led to a decrease of $J_c$ because of lower interfacial defect density. The method presented will enable even in MG-processed composites to homogeneously disperse the 211 secondary phase particles in the bulk REBCO body.

4. EXPERIMENTAL DETAILS

Precursor powders of the Y-211 and liquid phase (LP = Er-123 and Ba₃Cu₄O₉) were synthesized employing highly pure Y₂O₃, BaO₂, and CuO raw materials via the solid-state sintering method. To assure single-phase formation of Y-211 and Er-123, the sintering process was carried out at 860, 880, and 900 °C for 4 h at each temperature. After each sintering, the powder was mechanically ground for 2 h for mixing the compounds employing an auto mortar grinder (Nitto Kagaku, model ANM-1000). For reducing the size and damaging the surface of the Y-211 particles, we employed a high-energy ultrasonic processor (MITSUI, model UX-300). This ultrasonic processor allows operation in two modes: (i) continuous and (ii) pulse. We employed both modes to compare the effect on reducing the size of the Y-211 particles. We observed that the Y-211 particles were effectively reducing their size operating the “pulse” mode. For this reason, we experimented by changing the energy of the ultrasonic probe from 100 to 300 W. It was observed that applying the ultrasound radiation with 300 W was effective. Then, to further optimize and control the Y-211 particle size and morphology, the irradiation time intervals ($\Delta t$) of 15, 30, 45, and 60 min were employed. Ethanol was used as an aqueous medium for all present ultrasonication experiments. Ultrasonically treated Y-211 powders were heat-treated at 400–600 °C for 12 h to eliminate the carbon-related compounds in the Y-211 powders. Utilizing the 15, 30, 45, and 60 min ultrasonically treated Y-211 precursor powders, we successfully grew YBCO bulk single grains via the TS-IG method. The Y-211 powders pretreated with 0, 15, 30, 45, and 60 min of ultrasonication are referred to as Y-211-0, Y-211-15, Y-211-30, Y-211-45, and Y-211-60, respectively.

The preformed pellets of Y-211 and LP sources of 20 mm diameter were made by applying a uniaxial pressure of 420 MPa. A box furnace calibrated over a wide range of temperatures was employed for the YBCO bulk sample growth. The temperature profile recorded over the calibrated
temperature range indicated a uniform thermal gradient. To fabricate a well-defined orientation of the single-grain YBCO bulk superconductors, a single crystalline NdBCO bulk was used as a seed. The time–temperature schedule followed for fabricating the YBCO bulks was designed as follows: The sample assembly was heated to 820 °C in 5 h and for improving the strength of the Y-211, a 1 h dwell was allowed. Then, the temperature was increased to 1060 °C (T_f) with a heating rate of 4 °C/min, and for homogeneous infiltration of liquid phases, a 1 h dwell was given. The temperature from T_f was cooled to 1005 °C (peritectic temperature T_p) in 30 min. To initiate the crystal growth and for growing the single grain of YBCO, a slow cooling of 100 h (0.25 °C/h) was facilitated from the T_p to 980 °C. Then, the furnace was allowed to cool naturally.

The YBCO bulk single grains fabricated with different time intervals (∆t) of the Y-211 ultrasound treatment of 0, 15, 30, 45, and 60 min are referred to as Y−U-0, Y−U-15, Y−U-30, Y−U-45, and Y−U-60, respectively. To corroborate the developed ultrasonic method, one more YBCO bulk single grain was fabricated with the addition of 0.25 wt % of Pt and 0.25 wt % of CeO_2 and is referred to as Y−Pt−CeO_2. Finally, all the samples were oxygenated at 450 °C (400 °C for 250 h with a constant oxygen flow of 0.3 L/min and an additional 100 h for M−H measurements. It is also interesting to mention here that recently, Takanori Motoki and Jun-ichi Shiomiya group have proposed a novel method for reducing the prolonged oxygenation annealing process employing the oxygen-containing water vapor. The YBCO bulks exhibit the typical spatial inhomogeneities and hence, their physical properties vary with position in the sample. Keeping this in mind, in order to overcome the spatial dependence, the specimen (~0.5 × 1.5 × 2 mm³) intended for the magnetic measurements from each sample was collected ~2 mm below the seed.

Investigation of the microstructural properties was carried out by FE-SEM, JEOL model JSM-7100F. The structural properties of the pretreated Y-211 particles and of the final bulk YBCO samples were examined by the XRD technique. TF measurements were performed in liquid nitrogen (77 K) with a Hall probe and field cooling in a 0.5 T field provided by a permanent magnet. The superconducting transition temperature and field-dependence critical current densities of the samples were characterized with the superconducting quantum interference device (SQUID, Quantum design, model MPMS-XL5). Characterization details of various physical properties of the samples can be found in our previous studies.

Michael Rudolf Koblishcha — Superconducting Materials Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan
Anjela Koblishcha-Veneva — Superconducting Materials Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan
Tetsuo Oka — Superconducting Materials Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan
Masato Murakami — Superconducting Materials Laboratory, Graduate School of Science and Engineering, Shibaura Institute of Technology, Tokyo 135-8548, Japan

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b02816

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This work was partly supported by Shibaura Institute of Technology (SIT), Japan Research Center for Green Innovation and Grant-in-Aid FD research budget code: 112704. S.P.K.N. wishes to thank SIT and JSPS (grant no. P19354) for the support. The kind support from Dr. Hiraku Oguno, Superconducting Electronics group, AIST, Tsukuba, Japan, is gratefully acknowledged for allowing utilization of the facilities procured in JSPS KAKENHI, grant number JP16H16439.

REFERENCES
(1) Cardwell, D. A. Processing and properties of large grain (RE)BCO. Mater. Sci. Eng., B 1998, 53, 1–10.
(2) Tomita, M.; Murakami, M. High-temperature superconductor bulk magnets that can trap magnetic fields of over 17 tesla at 29 K. Nature 2003, 421, S17–S20.
(3) Muralidhar, M.; Sakai, N.; Jirsa, M.; Murakami, M.; Hirabayashi, I. Record flux pinning in melt-textured NEG-123 doped by Mo and Nb nanoparticles. Appl. Phys. Lett. 2008, 92, 162512.
(4) Koblishcha-Veneva, A.; Mücklich, F.; Koblishcha, M. R.; Hari Babu, N.; Cardwell, D. A. Crystallographic Orientation of Y_{1-x}Ba_xCu_3O_y (M=Nb, Zr, Ag) Nanoparticles Embedded in Bulk, Melt-Textured YBCO Studied by EBSD. J. Am. Ceram. Soc. 2007, 90, 2582–2588.
(5) Koblishcha-Veneva, A.; Koblishcha, M. R.; Ogawara, K.; Murakami, M.; Murakami, M. Interactions of Y_{1-x}Ba_xCu_3O_y particles and the YBCO matrix within melt-textured YBCO samples studied by means of electron backscatter diffraction. Supercond. Sci. Technol. 2005, 18, S158–S163.
(6) Pavan Kumar Naik, S.; Nagaveni, K. Infiltration growth processing of bulk mixed REBa_2Cu_3O_x superconductors: Nano metal oxides and rare earth elements effects on microstructural properties. Proc. SPIE 2019, 11054, 110540H.
(7) Cloots, R.; Koutzarova, T.; Mathieu, J.-P.; Ausloos, M. From RE-211 to RE-123. How to control the final microstructure of superconducting single-domains. Supercond. Sci. Technol. 2005, 18, R9–R23.
(8) Devendra Kumar, N.; Shi, Y.; Zhai, W.; Dennis, A. R.; Durrell, J. H.; Cardwell, D. A.; Cardwell, D. A. Buffer Pellets for High-Yield, Top-Seeded Melt Growth of Large Grain Y_{1-x}Ba_2-xCu_3O_y Superconductors. Cryst. Growth Des. 2015, 15, 1472–1480.
(9) Pavan Kumar Naik, S.; Raju, P. M. R.; Rajasekharan, T.; Seshubai, V. Growth Mechanism in Infiltration Growth Processed YBCO Composites through Quench Studies. J. Supercond. Novel Magn. 2014, 27, 1211–1215.
(10) Shi, Y.; Hasan, T.; Babu, N. H.; Torrisi, F.; Milana, S.; Ferrari, A. C.; Cardwell, D. A. Synthesis of $YBa_2Cu_3O_7-x$ and $YBa_2CuO_4$ nanocrystalline powders for YBCO superconductors using carbon nanotube templates. ACS Nano 2012, 6, 5395–5403.

(11) Yang, W. M.; Zhou, L.; Feng, Y.; Zhang, P. X.; Wu, M. Z.; Zhang, C. P.; Wang, J. R.; Du, Z. H.; Wang, F. Y.; Yu, Z. M.; Wu, X. Z.; Gawalek, W.; Gornert, P. The effect of excess $Y_2O_3$ addition on the levitation force of melt processed YBCO bulk superconductors. Phys. C Supercond. 1998, 305, 269–274.

(12) Monot, I.; Verbist, K.; Hervieu, M.; Lafez, P.; Delamar, M. P.; Wang, J.; Desgardin, G.; Van Tendeloo, G. Microstructure and flux pinning properties of melt textured grown doped $YBa_2Cu_3O_7$–$x$. Phys. C Supercond. 1997, 274, 253–266.

(13) Kim, C. J.; Kim, K. B.; Kwon, S. C.; Chang, I. S.; Won, D. Y. Phase transition induced by addition of CeO$_2$ in $Y_1_{1-x}Ba_xCu_3O_7$ $\delta$ superconductor. J. Mater. Lett. 1992, 11, 346–348.

(14) Raju, P. M. S.; Seshubai, V.; Rajasekharan, T. A generic process to introduce nanoparticles into powder preforms and its application to Infiltration Growth processing of REBa$_2$Cu$_3$O$_{6.6}$-superconductor. Mater. Chem. Phys. 2015, 161, 59–64.

(15) Swarup Raju, P. M.; Kumar, N. D.; Pavan Kumar Naik, S.; Rajasekharan, T.; Seshubai, V. Introduction of Nano Ceria into Critical Currents by $CeO_2$ additions in directionally solidified YBa$_2$Cu$_3$O$_7$-superconductor. J. Mater. Chem. 2015, 25, 3948–3953.

(16) Ogawa, N.; Hirabayashi, I.; Tanaka, S. Breakthrough in reduction of oxygen-annealing time of Nb on the preform optimized infiltration growth processed YBCO superconductors. J. Phys. Chem. Solids 1991, 52, 105.−110.

(17) Antal, V.; Zmorayova, K.; Rajnak, M.; Vojtkova, L.; Hlasek, T.; Plechacek, J.; Diko, P. Relationship between local microstructure and superconducting properties of commercial YB$_2$Cu$_3$O$_{6.6}$-superconductors. Supercond. Sci. Technol. 2020, 33, 044004.

(18) Endo, A.; Chauhan, H. S.; Egi, T.; Shiohara, Y. Macro-segregation of $YBa_2Cu_3O_7$ particles in $YBa_2Cu_3O_{6.8}$, crystals grown by an undercooling method. J. Mater. Res. 1996, 11, 795–803.

(19) Cardwell, D. A.; Shi, Y.; Numburi, D. K. Reliable single grain growth of (RE)BCO bulk superconductors with enhanced superconducting properties. Supercond. Sci. Technol. 2020, 33, 024004.

(20) Guo, X. Y.; Yang, W. M.; Li, J. W.; Guo, L. P.; Chen, L. P.; Li, Q. Effects of Vertical Temperature Gradient on the Growth Morphology and Properties of Single Domain YBCO Bulks Fabricated by a New Modified TSIG Technique. Cryogenics Growth Des. 2015, 15, 1771–1775.

(21) Xu, H.; Abe, H.; Naito, M.; Fukumori, Y.; Ichikawa, H.; Endoh, S.; Hata, K.; Hata, K. Efficient dispersing and shortening of supergrowth carbon nanotubes by ultrasonic treatment with ceramic balls and surfactants. Adv. Powder Technol. 2010, 21, 551–555.

(22) Elwell, D.; Scheel, H. J. Crystal Growth from High-Temperature Solutions; Academic press: London, 1975.

(23) Pavan Kumar Naik, S.; Murakami, M.; Koblischka, M. R.; Koblischka-Veneva, A.; Oka, T.; Murakami, M. Novel method of tuning the RE$_2$BaCuO$_5$ phase and bulk REBa$_2$Cu$_3$O$_{6.6}$ superconductors physical properties. Appl. Phys. Express 2019, 12, 063002.

(24) Murakami, M.; Fujimoto, H.; Yamaguchi, K.; Nakamura, N.; Koshizuka, N.; Tanaka, S. Is Y$_2$BaCuO$_5$ inclusion effective pinning site in YBa$_2$Cu$_3$O$_7$? Adv. Sci. 1992, 4, 75–80.

(25) Murakami, M.; Gotoh, S.; Koshizuka, N.; Tanaka, S.; Matsushita, T.; Kambe, S.; Kitazawa, K. Critical currents and flux creep in melt processed high T$_c$ oxide superconductors. Cryogenics 1990, 30, 390–396.

(26) Yang, W. M.; Zhou, L.; Feng, Y.; Zhang, P. X.; Zhang, C. P. The effect of temperature gradient on the morphology of YBCO bulk superconductors by melt texture growth processing. J. Alloys Compd. 2006, 415, 276–279.

(27) Shi, Y.; Dennis, A. R.; Zhou, D.; Namburi, D. K.; Huang, K.; Durrell, J. H.; Cardwell, D. A. Factors Affecting the Growth of Multiseeded Superconducting Single Grains. Cryst. Growth Des. 2016, 16, 5110–5117.

(28) Pavan Kumar Naik, S.; Raju, P. M. S.; Seshubai, V. Role of Sm and Nb on the preform optimized infiltration growth processed YBCO superconductors. Mater. Chem. Phys. 2016, 182, 503–507.

(29) Pavan Kumar Naik, S.; Raju, P. M. S.; Rajasekharan, T.; Seshu Bai, V. Limited infiltration due to reactive sintering of nano-Sm$_2$O$_3$ with preforms - its effect on (Y, Sm)Ba$_2$Cu$_3$O$_{6.6}$ superconductors. Supercond. Sci. Technol. 2016, 29, 115001.

(30) Pavan Kumar Naik, S.; Bai, V. S. Role of nano and micron sized inclusions on the oxygen controlled POIG processed YBCO superconductors. J. Phys. Chem. Solids 2017, 101, 65–73.

(31) Devendra Kumar, N.; Rajasekharan, T.; Muraleedharan, K.; Banerjee, A.; Seshubai, V. Unprecedented current density to high fields in YBa$_2$Cu$_3$O$_{7-\delta}$ superconductor through nano-defects generated by preform optimization in infiltration growth process. Supercond. Sci. Technol. 2010, 23, 105020.

(32) Pavan Kumar Naik, S.; Muralidhar, M.; Jirsa, M.; Murakami, M. Investigations of (Gd, Dy) BCO bulk superconductors processed by cold-top-seeded infiltration growth method. Adv. Powder Technol. 2020, 551, 981–105.

(33) Pavan Kumar Naik, S.; Muralidhar, M.; Jirsa, M.; Murakami, M. Optimization of the Dy content in single crystalline (Gd, Dy)BCO bulk superconductors processed by melt growth method. Adv. Powder Technol. 2020, 551, 981–105.

(34) Pavan Kumar Naik, S.; Muralidhar, M.; Jirsa, M.; Murakami, M. Investigation of (Gd, Dy) BCO bulk superconductors processed by cold-top-seeded infiltration growth method. Mater. Sci. Eng. B 2020, 253, 114494.

(35) Pavan Kumar Naik, S.; Murakami, M.; Takemura, K.; Jirsa, M.; Murakami, M. Infiltration growth processing of single grain (Gd,Dy)BCO bulk superconductors: Optimization of liquid phase mass and characterization of physical properties. J. Appl. Phys. 2019, 125, 093907.

(36) Pavan Kumar Naik, S.; Murakami, M.; Murakami, M. Optimization of the Dy content in single crystalline GdBCO bulk superconductors fabricated in air via top-seeded Infiltration growth process. J. Supercond. Novum. Magn. 2018, 31, 981–987.

(37) Pavan Kumar Naik, S.; Murakami, M.; Nakanishi, Y.; Murakami, M. Investigations of (Gd, Dy) BCO bulk superconductors fabricated via top-seeded infiltration growth process. IEEE Trans. Appl. Supercond. 2018, 28, 6801104.