Critical Properties of Bulk-Doped $BaFe_2As_2$ Pnictides for Magnet Design

Martin Nikolo, Jeremy D. Weiss, John Singleton, Jianyi Jiang, and Eric E. Hellstrom

***Abstract*—A comprehensive study of upper critical (H_{c2}) and irreversibility magnetic fields (H_{irr}) in $(Ba_{0.6}K_{0.4})Fe_2As_2$ (critical temperature T_c = 38.3 K), $Ba(Fe_{0.95}Ni_{0.05})_2As_2$ (T_c = 19.2 K), $Ba(Fe_{0.94}Ni_{0.06})_2As_2$ (T_c = 18.5 K), $Ba(Fe_{0.92}Co_{0.08})_2As_2$ (T_c = 23.2 K), and $Ba(Fe_{0.91}Co_{0.09})_2As_2$ (T_c = 25.3 K) polycrystalline bulk pnictide superconductors with different average grain sizes was made in pulsed fields at the Los Alamos National Laboratory. The magnetic field–temperature (H_{c2}–T) phase diagrams with H_{c2} as high as 65 T at 28 K for the K-doped samples and critical current density (J_c) measurements as high as 10^5 A/cm^2 for the smallest, submicrometer grain size samples were obtained. The high H_{c2}, H_{irr}, and J_c data show the suitability of these materials for magnet design as their mechanical strength and random grain alignment show promise in the manufacturing of next-generation magnets.**

***Index Terms*—Granularity, pnictides, superconductors, upper critical magnetic fields.**

I. Introduction

IRON-BASED superconductors' high upper critical fields, low anisotropy and high critical currents, which are reduced weakly by magnetic fields at low temperatures, suggests their considerable potential in large scale applications, at high fields [1], [2]. Their cleaner nature of grain boundaries favors high critical currents at high fields without the emphasis on their crystal/grain orientation [3]. Among the different families, the 122 compounds with a chemical composition of AFe_2As_2 (A = alkaline earth metal) stand out. K-doped Ba-122 has a transition temperature of around 38 K, similar to that of MgB_2. Iron-based superconductor (122) wires and tapes are promising for magnet applications at 20–30 K, while the niobium-based magnets have much lower T_c, and their critical current densities (J_c) that rapidly decrease with increasing applied magnetic field. Pnictides wires have the potential to outperform MgB_2, Nb-Ti and Nb_3Sn conductors at a lower price point and enable operation in temperatures where cryocoolers can be used instead of expensive liquid helium [1]–[4].

Upper critical field is a critical design parameter for superconducting wires used in magnet fabrication. Magnets based on niobium conventional technology work at fields below 25 T. Improved wires with higher current densities and upper critical fields are needed for the development of the next generation of NMR, accelerator, and fusion magnets [1]–[4]. Increased current densities generating higher magnetic fields offer increased sensitivity and resolution in NMR measurements.

Granularity in polycrystalline high-T_c superconductors is known to limit the macroscopic currents and is an important problem that needs to be overcome in fabrication of wires and tapes. Secondary phases at the grain boundaries or voids reduce the cross section over which the current effectively flows and high angle grain boundaries can limit the currents in untextured polycrystalline materials [5]–[10]. Overall compositions and grain boundary segregation of oxygen atoms in K- and Co-doped Ba-122 samples were recorded. Significant variations of composition between grains and grain boundaries and significant grain boundary segregation of oxygen were observed, suggesting further processing improvements can be made to enhance J_c's [11].

In this work, we study the upper critical (H_{c2}) and irreversibility (H_{irr}) magnetic fields in a range of polycrystalline samples fabricated by the FSU group. We measure 5 different Co- and Ni-doped and 3 different K- doped Ba-122 samples. Emphasis is made on the impact of grain size within the same stoichiometric composition as H_{c2}, H_{irr}, and J_c differ. All our K-doped Ba-122 polycrystalline samples show an impressive $H_{c2} - T$ and J_c performance, showing promise in the development of next generation superconducting magnets.

II. Experimental Detail

The $(Ba_{0.6}K_{0.4})Fe_2As_2$ samples had 3 different granularities and were prepared from the same batch of starting powder, heat treated at different temperatures in hot isostatic press (HIP)[12]. The sample heat treated at 600°C had average grain diameter $<< 1$ μm. This low reaction temperature resulted in a very small grain size that yielded fewer cracks and improved the intergranular current density. Improved phase purity was responsible for the enhanced grain connectivity [13]. Second sample heat treated at 900°C had average grain diameter of about 4.8 μm,

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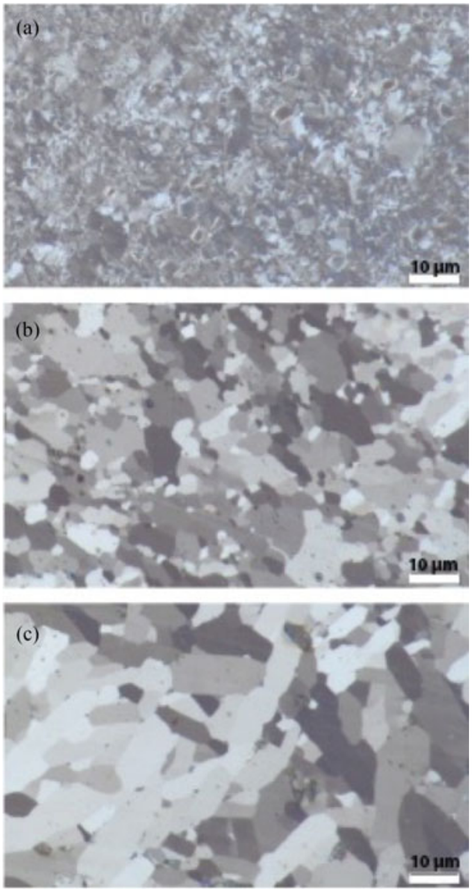

Fig. 1. Optical microscopy of K-doped 122. Image (a) shows grain diameter much less than 1 μm when reacted at 600°C. Image (b) shows average grain size 4.8 μm after reaction at 900°C. Image (c) shows average grain size of 8.2 μm after reaction at 1000°C. 10 μm bar is shown for size comparison.

and a third sample heat treated at 1000°C had average grain diameter of about 8.2 μm. Fig. 1 shows photos of grain sizes obtained via optical microscopy where light was polarized to show granular contrast.

The Co-doped samples we measured were $Ba(Fe_{0.92}Co_{0.08})_2As_2$, ($T_c = 23.2$ K), labeled Co8, and $Ba(Fe_{0.91}Co_{0.09})_2As_2$ ($T_c = 25.3$ K), labeled Co9 [14]. They were cut into parallelepipeds with dimensions of 0.7 × 0.7 × 4.9 mm^3 and 0.6 × 0.7 × 2.0 mm^3, respectively. We also measured two $Ba(Fe_{0.95}Ni_{0.05})_2As_2$ (Ni5) polycrystalline samples [15]. The average grain size of one was about 17 μm and its T_c was 19.2 K. The average grain size of the other was larger and its T_c was 20.4 K. We distinguish between those two Ni5 samples as follows: the larger grain and higher T_c sample is labelled Ni5(LG), and the smaller grain and lower T_c sample is labeled Ni5(SG). Some FeAs impurities were observed between most grains in Ni5(LG). The parallelepiped dimensions of the samples were: Ni5(LG) – 0.7 × 0.7 × 2 mm^3 and Ni5(SG) – 0.6 × 0.75 × 3.9 mm^3. Furthermore, we measured $Ba(Fe_{0.94}Ni_{0.06})_2As_2$ (Ni6) polycrystalline sample whose T_c and dimensions were 18.5 K and –0.7 × 0.7 × 2 mm^3, respectively. The K-doped samples had dimensions of 0.7 × 0.7 × 3.5 mm^3.

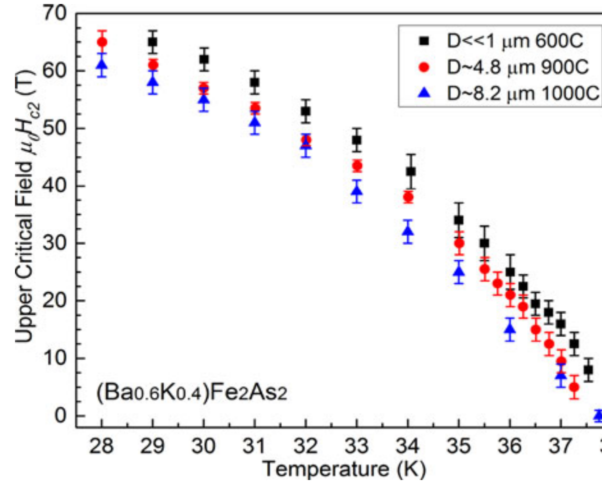

Fig. 2. Upper critical field of K-doped samples for different average grain sizes. The sub-micron grain size sample reacted at 600°C gives us the highest critical field. The largest grain size (8.2 μm) sample has the lowest critical field.

Upper critical fields were measured in pulsed magnetic fields of up to 65 T at the National High Magnetic Field Laboratory (NHMFL) in Los Alamos, NM. A radio-frequency proximity detector oscillator (PDO) induction technique was used, in which the sample is placed inside a coil that forms part of a tank circuit whose resonance frequency is monitored as a function of field and temperature [16], [17]. The exclusion of flux by the sample from the coil decreases the inductance of the circuit and the resonant frequency increases. We observe the superconducting-normal state phase transition as a large change in resonant frequency. The details of the measurement are described elsewhere. Furthermore, we measured the magnetization in pulsed fields of up to 65 T, using a compensated, inductive extraction magnetometer probe [18] to determine the irreversibility fields of our samples.

An Oxford vibrating sample magnetometer (VSM) was used to measure magnetic moment in fields up to 14 T and global J_c was calculated from the width of the magnetization loops ΔM where ΔM is the difference between the magnetic moment in increasing and decreasing field [19].

III. Results and Analysis

Fig. 2 plots the upper critical fields for the K-doped 122 samples of different granularities. The critical fields reach very impressive 65 T at 29 K. Even at 35 K, the critical fields are about 30 T. The highest H_{c2} was obtained for the smallest sub-micron average grain size while the lowest H_{c2} was obtained for the sample with the largest average grain size of 8.2 μm.

The upper critical magnetic field measurements show that bulk shielding currents and inter-grain connectivity are improved for the smallest grain size in the K-doped 122 materials. The global critical current density ($J_{cglobal}$) obtained from the magnetization measurements was found to be over 100 kA/cm^2 at 5 K and 0 T for the smallest sub-micron average grain size. See Fig. 3.

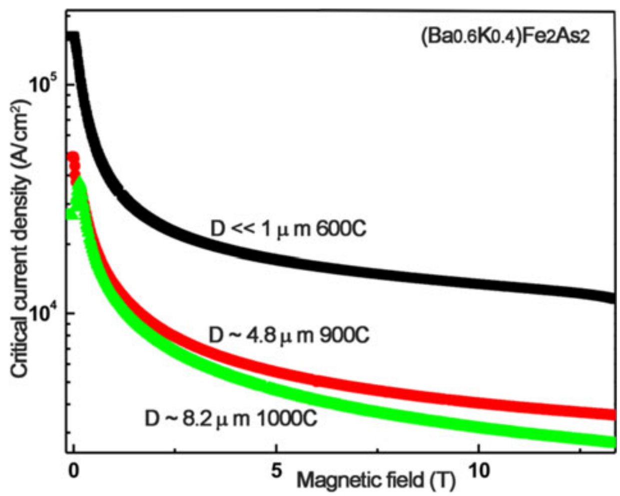

Fig. 3. Global critical current density of K-doped 122 samples. The smallest grain size sample gives current density of over 100 kA/cm^2 at 5 K and 0 T.

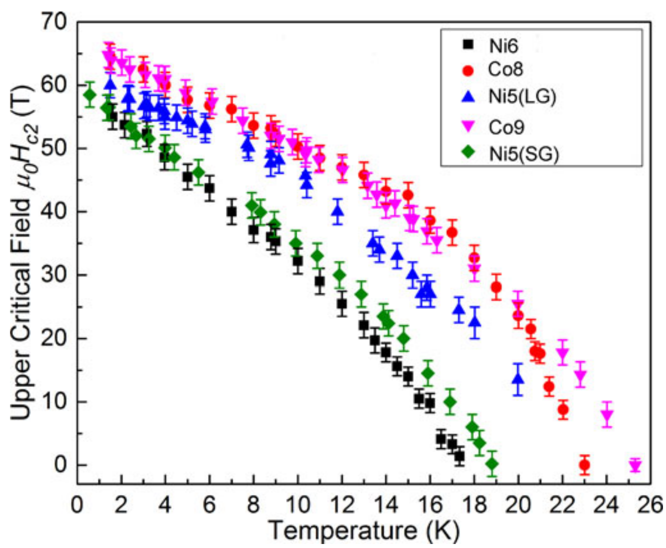

Fig. 4. Upper critical field of Co- and Ni-doped samples.

Furthermore, $J_{cglobal}$ was found to be inversely proportional to grain radius (r) [5]. This $1/r$ dependence suggests that decreasing grain size further while maintaining bulk homogeneity and granular connectivity may be a viable route to improving critical current density in K-doped $BaFe_2As_2$.

Results on similar samples from the FSU group show that the grain size is a key parameter for increasing the maximum operable field range of polycrystalline HTS materials that are governed by Josephson tunneling [19]. For the examined iron-based superconductors the grain size can be changed by milling the starting materials and by varying the heat treatment of the bulks [5], [19], [20].

In the second part of of our work we studied the upper critical and irreversibility magnetic fields of 5 different Co- and Ni-doped samples which were synthesized using different starting powders and processing techniques [14], [15] than the K-doped samples. Fig. 4 shows the upper critical fields. These materials reached H_{c2}'s as high as 65 T at 1.5 K. The Co- doped samples reached higher critical fields than the Ni-doped materials, yet well below H_{c2} of the K-doped 122 materials which have $H_{c2} > 70$ T at $T < 28$ K. Overall, this makes the use of the Co- and Ni-doped samples in magnets for helium free operation questionable.

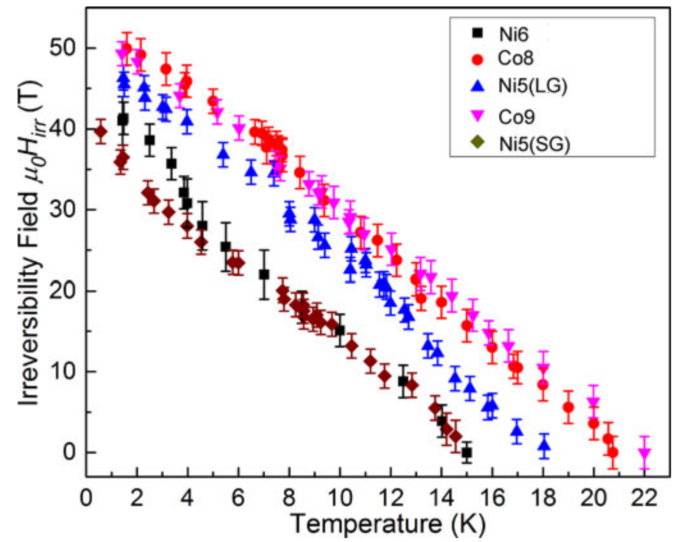

Fig. 5. Irreversibility fields of Co- and Ni-doped samples.

Fig. 5 shows the irreversibility fields for the same 5 Ni- and Co-doped samples. The irreversibility field defines the onset of ac losses and is an important parameter for ac applications. The irreversibility lines look more linear and have comparable slopes as the H_{c2} lines but are about 15–20 T below. The Co-doped samples have higher irreversibility fields while Ni-doped samples with larger average grain size have higher H_{c2} and H_{irr}. This suggests that the grain size dependence of upper critical and irreversibility fields may not be universal property and stoichiometry and processing methods need to be taken in consideration when making generalizations about optimal grain size.

Another factor in favor of the use of K-doped Ba122 pnictides is that they have a relatively broad superconducting doping phase space while the Co-doped Ba122 materials, just as YBCO systems, have a very narrow superconducting doping phase space. This may cause practical problems as small deviations from ideal stoichiometry result in strongly suppressed superconductivity.

We see sharper T_c transitions in ac susceptibility measurements and higher $J_{cglobal}$ currents for K-doped Ba122 samples than for Co-, Ni-doped Ba122, and YBCO polycrystalline materials [5]. Due to their brittle failure mechanics, superconductors with high fracture toughness (K_C) are desired for high field applications. The K-doped Ba122 materials have a K_C of ~2.35 (± 0.14) MPa m$^{0.5}$ [5], [21]. This fracture toughness exceeds HIPped MgB_2, bulk top-seeded melt-grown YBCO, and is comparable to polycrystalline Al_2O_3 [21].

The fracture toughness material properties also make K-doped Ba122 materials suitable for making larger bulk magnets that can be magnetized to trap strong magnetic fields higher than 10 T. Persistent currents induced by external fields can be trapped inside a superconductor to produce trapped magnetic fields which scale with the size of the current loops flowing in the bulk. This field trapping ability is limited by the ability of the material to develop high $J_c(H)$ at high fields. Weiss *et al.* [21] reported the first iron pnictide superconducting magnet capable of trapping over 1 T at 5 K. Bulk Ba122 magnets can be fabricated by a scalable, versatile, and low-cost technique using ball milling, CIPping, and HIPping, common industrial ceramic processing techniques [5].

IV. Conclusion

The Fe-based superconductor, $(\mathrm{Ba}_{0.6}\mathrm{K}_{0.4})\mathrm{Fe}_2\mathrm{As}_2$, can generate tesla-scale fields with a polycrystalline bulk form. Its T_c is comparable to MgB_2 but its H_{c2} is higher (>70 T versus <30 T), making it a good candidate for magnet operation in helium free environment. The grain size is a key parameter for increasing the maximum operable field range of polycrystalline K-doped Ba122 superconducting materials where connectivity of grains improves for smaller grains (diameter $<< 1$ μm). This in turn improves magnetic properties and global $J_{cglobal}$. The K-doped Ba122 materials show superior magnetic and transport properties compared to the Ni- and Co-doped samples, they show higher fracture toughness and are in many respects better candidates than YBCO or MgB_2 for magnet design.

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