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MICROSTRUCTURAL CHARACTERIZATION OF Ag-SHEATHED Tl-Ba-Ca-Cu-O AND Bi-Sr-Ca-Cu-O SUPERCONDUCTING TAPES BY ANALYTICAL ELECTRON MICROSCOPY*

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1992 Applied Superconductivity Conference, August 24-28, 1992, Chicago, IL

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*Work supported by the U.S. Department of Energy, Division of Basic Energy Sciences-Materials Sciences and Superconductivity Pilot Center under contract #W-31-109-ENG-38 (DJM, KCG, RBP) and the National Science Fondation Office of Science and Technology Center for Superconductivity contract #DMR-8809854 (JG).

Microstructural Characterization of Ag-Sheathed Tl-Ba-Ca-Cu-O and Bi-Sr-Ca-Cu-O Superconducting Tapes by Analytical Electron Microscopy

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Abstract -- The microstructures of Tl(1223) and Pb-doped Bi(2223) silver tapes produced by the powder-in-tube (PIT) method have been examined by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive spectrometry (EDS). The Tl tapes annealed below the melting point exhibited fine grains and a high density of pores while tapes subjected to partial melting prior to solid state annealing were fully dense with large grains. However, these tapes also showed an increase in the size and density of impurity particles, particularly CaO and a Ba-Cu rich phase. Silver powders added to the precursors tended to promote the growth of Tl(1223) at lower temperatures but also interfered with the development of texture by providing nucleation sites of random orientations. In contrast, the Bi(2223) tape exhibited a high degree of texture and alignment. The incorporation of silver within the superconducting phase was found to be negligible for both the Tl(1223) and Bi(2223) tapes.

I. INTRODUCTION

Significant efforts have been directed towards the development of silver-sheathed high temperature superconductor tapes and wires for a variety of practical applications.. Due to the relatively poor mechanical properties of Y-based superconductors, more recent efforts have concentrated on wires and tapes of Bi- and Tl-based superconductors. However, both the Bi- and Tl-based superconductors are highly anisotropic, with highest critical currents along the *a-b* planes. [1,2] In addition, these superconductors suffer from weak coupling across grain boundaries which severely limits current flow in polycrystalline materials.[3,4,5,6] Therefore, it is highly desirable to have well aligned grains whose *a-b* planes lie parallel to the tape surface, i.e. parallel to the direction current flow. Another factor which may limit current flow is the presence of non-superconducting impurity phases and voids. The presence of these defects may serve to limit current flow in two ways. Firstly, they may interfere with grain growth, offsetting efforts to achieve grain alignment or texture. Secondly, they may limit the critical current carried by a wire as a result of a decreased cross-sectional area of superconductor. Therefore it is also of significant benefit to minimize the volume fraction of these defects.

The Tl(1223) superconductor has a higher transition temperature than Bi-based superconductors. In addition, due to a higher irreversibility line, Tl(1223) is more suitable to high magnetic field applications at temperatures above 20K due to stronger coupling between Cu-O layers.[7] To date, however, although considerable attention has been focused on Ag-sheathed Bi-Sr-Ca-Cu-O superconducting tapes, little has been published on Tl-based superconducting tapes in spite of these potential advantages. In this work, Ag has been added to the superconducting powders to lower the melting point and yield a micro-composite in an effort to improve mechanical properties of the tapes.[8,9] In this paper we report on studies of the microstructures of Tl(1223) tapes processed with and without partial melting prior to solid state sintering. The role of Ag in the development of microstructure of the Tl(1223) tapes has also been investigated, and the results are compared with those obtained from the Bi(2223) tape.

II. EXPERIMENTAL PROCEDURE

The Tl and Bi tapes were fabricated by a powder-in-tube technique which has been described in more detail elsewhere.[10,11] In brief, powders of the appropriate superconducting phase were loaded into 6.35 mm outer diameter closed-end tubes and packed by vibration and ramming to increase the packing density. The loaded tubes were evacuated, sealed, and then drawn at ≈15% reduction per pass with an intermediate anneal at 260°C for 20 minutes every third pass to a diameter of 1.8 mm. The tubes were then rolled at ≈10% reduction per pass to a final thickness of ≈450μm. The Tl(1223) tapes were annealed in oxygen according to two schedules. One set of tapes was annealed at 850°C for 36 hours while the other was heat treated at 895°C for 6 minutes to achieve partial melting and then held at 845°C for 2 hours. The Bi tape was first annealed at 890°C for one and a half hours to achieve partial melting followed by annealing at 840°C for 100 hours, both treatments in air.

Samples were prepared for SEM observation using standard metallographic techniques. Isopropyl alcohol was used for cleaning in between steps to avoid any possible reaction with water. In the SEM, backscattered electron imaging was used extensively for enhanced sensitivity to composition. Cross-sectional samples were prepared for TEM by grinding flat the outer surface of the tape and then sandwiching the cleaned tape between Al_2O_3 using M-bond 610 epoxy. After encapsulating the sandwich in a 3 mm O.D. tube, TEM samples were prepared using standard techniques involving slicing, grinding, and dimpling. Final thinning to perforation was carried out by ion milling using 4 kV Ar ions while maintaining the sample at liquid nitrogen temperature. TEM and EDS were carried out using Philips EM420 and CM30 microscopes operated at 100kV and 300kV respectively.

Research supported by the U.S.D.O.E., Divisions of Basic Energy Sciences-Materials Sciences and Superconductivity Pilot Center under contract #W-31-109-ENG-38, and the NSF-Office of Science and Technology Centers under contract #STC8809854. Manuscript received August 24, 1992.

III RESULTS AND DISCUSSION

The microstructure of the Tl(1223) tape annealed at 850°C without partial melting is shown in the backscattered electron micrograph of Fig. 1. The micrograph, which shows the interior of the tape, shows several different impurity phases, which appear dark gray or black, together with the Tl(1223) phase, which is gray, and silver particles, which are light. In addition, the tape has a high density of pores, which appear black, indicating incomplete sintering and densification. A higher temperature and/or longer annealing period is needed to eliminate the pores. The dominant impurity phases observed are CaO and a Ba-Cu rich phase. A lesser amount of a Ca-Cu phase was observed. Perhaps most significant is the small grain size and poor connectivity of the Tl(1223) grains.

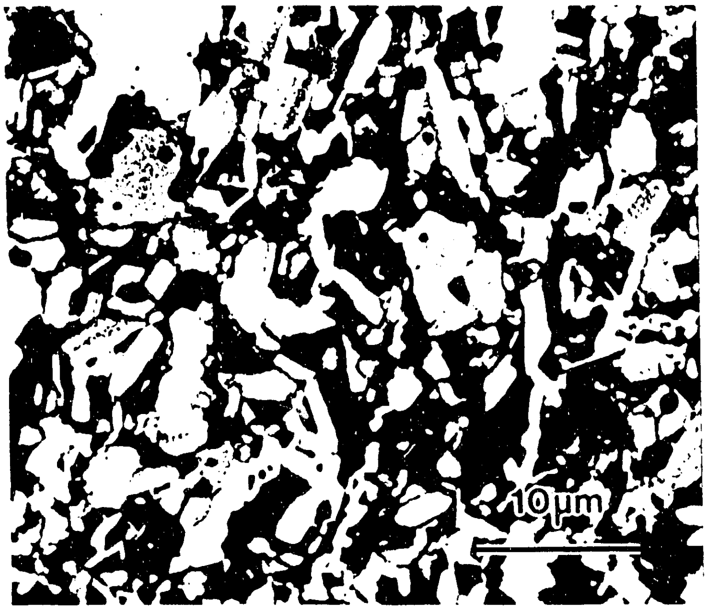

Fig. 1 SEM backscattered electron micrograph of the Tl(1223) tape annealed in the solid state at 850°C for 36 hours.

In contrast, the Tl (1223) tape that had been subjected to partial melting by heating to 895°C prior to solid state sintering appeared to be fully dense with large, well-connected Tl(1223) grains, as shown in Fig. 2. It seems likely that partial melting during the initial high temperature anneal allows liquid to fill void space and enhance sintering kinetics. However, a high fraction of CaO phase (black) and a Ba-Cu rich phase (dark gray) were also observed. In addition very small amount of CuO and a Ca-Cu rich phase were also observed. The impurity phases typically exist as discrete particles and are more or less uniformly distributed throughout the sample, including along the Ag interface. In addition, all of the impurity phases observed were found to be much larger than in the tape processed without partial melting. Thus, although the effect of partial melting appears to be beneficial in terms of increasing density and promoting the growth of large, connected Tl(1223) grains, there are some potential drawbacks related to the precipitation and growth of impurity phases.

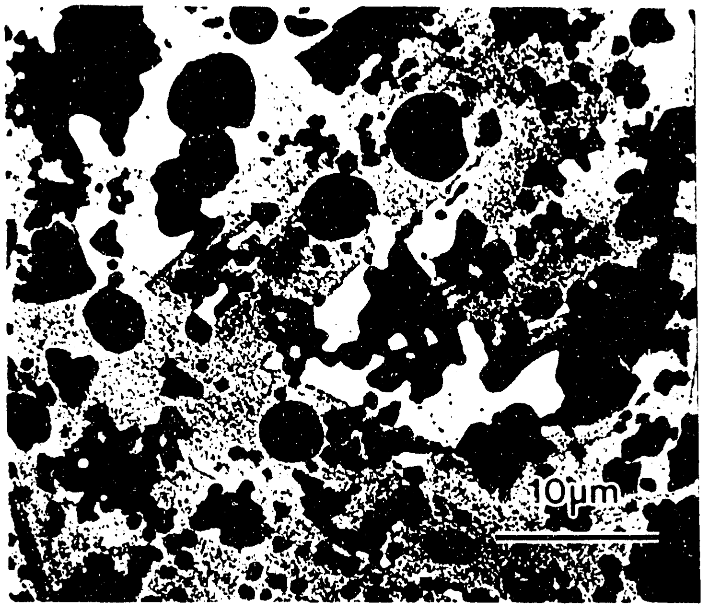

Fig. 2 SEM backscattered electron micrograph of the Tl(1223) tape subjected to partial melting at 895°C for 6 minutes prior to sintering at 845°C for 2 hours.

Silver particles were intentionally added to the precursor powders in order to improve the mechanical properties of the tapes and to lower the melting point of Tl(1223) in order to promote grain growth. However, the role these silver additions play in the development of microstructure is somewhat ambiguous. Both superconducting and impurity phases were observed to be in contact with silver in each tape. SEM showed a higher proportion of Tl(1223) grains to have nucleated along the silver particles in the case of the samples annealed without partial melting. In addition, the Tl(1223) grains along these silver particles were much larger. For example, Fig. 3 is an SEM backscattered electron image collected from the Tl tape that had been annealed without

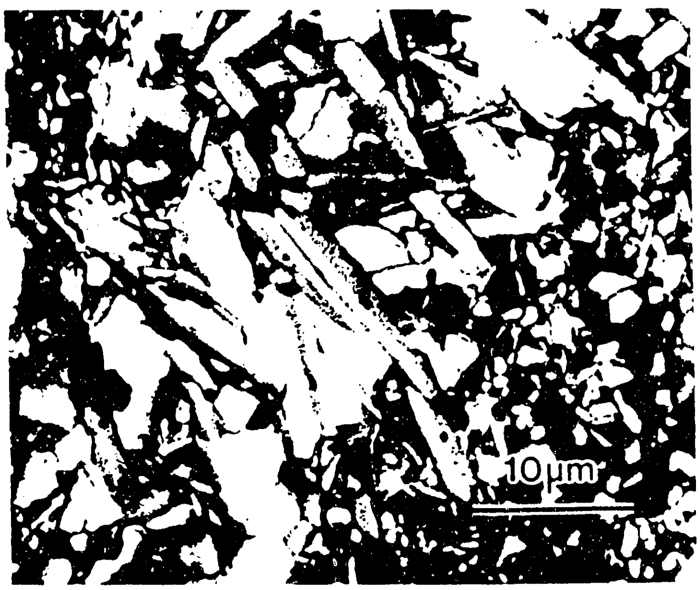

Fig. 3 The Tl tape sintered at 850°C for 36 hours. The Tl(1223) grains adjacent to the silver particles (white) are larger than in other areas.

partial melting. In this micrograph, the light area is silver, the gray area is Tl(1223) and the dark areas are voids and impurity phases. It is clear from the micrograph that the gray Tl(1223) grains in contact with the silver are much larger than those in other areas. In addition, a high fraction of the Ag interface is in contact with Tl(1223) whereas only a small fraction is occupied by impurities. Similar effects are observed along the Ag interface of the sheath, although the Tl(1223) layer is frequently very thin.

These results suggest that silver does promote the growth of Tl(1223) grains. However, silver may also prevent the coalescence and hence the connectivity of grains. Furthermore, the random orientations and distribution of the Ag particles and their irregular shapes may render the alignment of grains impossible. For example, Fig. 4 is a TEM micrograph which shows a high angle grain boundary in the tape processed without partial melting. The *a-b* planes of both grains are parallel to the surfaces of a silver particle. Although this feature may be suggestive of favorable nucleation on the Ag surface, it also results in a high angle grain boundary since it is likely that the angle between the two grains is defined by the angle between the two surfaces of the silver particle. Nevertheless, it is still unclear whether the Tl(1223) nucleates directly on the Ag surfaces. The tape subjected to partial melting exhibited a more random distribution of Tl(1223) grains and impurity phases along the Ag interfaces. In addition, as shown in the TEM micrograph of Fig. 5, some Tl(1223) grains were found to orient randomly with respect to the Ag interface, although it is possible that this grain may have nucleated at some other point at which it was more highly aligned. Typically, for both Bi- and Tl-based tapes, the Ag interface is not perfectly smooth, and HTS grains which appear to be aligned at one point can be misaligned with respect to the interface at another point.

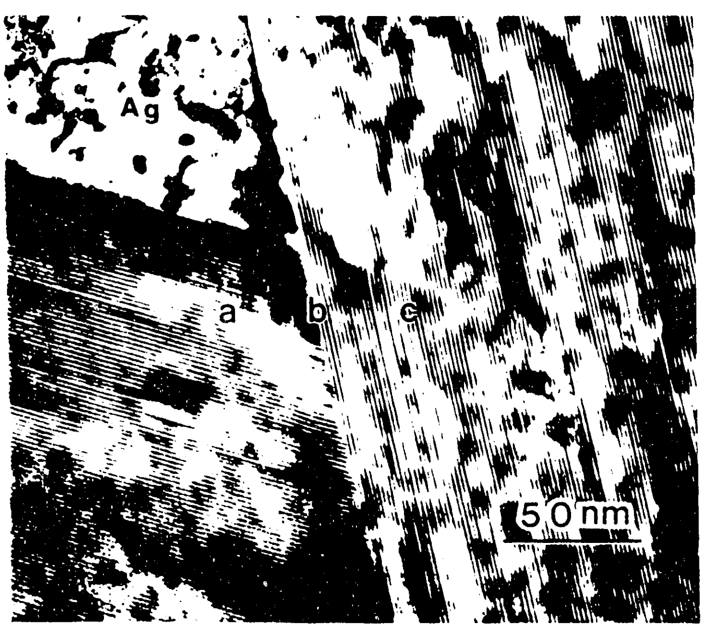

Fig. 4 TEM micrograph of a high angle grain boundary in the Tl(1223) tape annealed in the solid state at 850°C for 36 hours.

The microstructure of the Tl(1223) tapes are very different from those observed in Bi-based HTS tapes, which have been studied in some detail.[12,13] As shown in the TEM micrograph of Fig. 6, these tapes are characterized by colonies of highly aligned domains. Although each colony may be separated by a high angle grain boundary, the domains, which

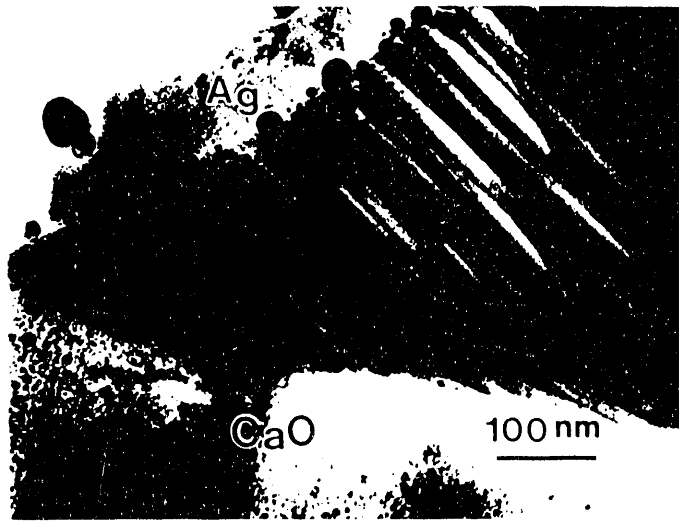

Fig. 5 TEM micrograph of a Tl(1223) grain randomly oriented with respect to Ag interface.

may be microns thick, are separated by low angle grain boundaries (a few degrees). At silver interfaces the plates are parallel to the interface within a few degrees, and grains which are highly misaligned with the silver are rarely observed. In the Tl(1223) samples, on the other hand, both aligned and misaligned grains are observed, as shown above. Luo et. al. [13] suggested that BSCCO phase growth is two dimensional. The non-plate like morphology of Tl tapes may indicate a three dimensional growth mechanism. In light of the high degree of anisotropy exhibited by both the Tl- and Bi-based superconductors, however, it is difficult to resolve the basis for these different growth mechanisms. In fact, most of our recent work on polycrystalline thin films of Tl(1223) on ZrO_2 shows that grains are plate-like with small angles between plates. Thus, although the data above suggests that Ag promotes the growth of the Tl(1223) phase, the alignment of grains is viewed as a nucleation and growth phenomenon and is the subject of further study. For example, it is possible that the growth mechanism is altered in the presence of silver. Future efforts will be aimed at resolving this issue in order to develop a plate-like microstructure in Tl tapes.

Finally, the incorporation of Ag into the Tl(1223) phase was examined by EDS. Spectra were collected from the points labeled (a), (b) and (c) in Fig. 4, and these spectra are plotted in Fig. 7. The silver peak is small and of the same intensity in each spectrum, indicating no segregation of Ag to the grain boundary. Furthermore, the low intensity of the Ag peak is approximately the same as that recorded during an in-hole count, suggesting that all the Ag detected arises from spurious x-rays and not from Ag contained within the Tl(1223) phase. Thus, it is concluded that the incorporation of Ag into the Tl(1223) phase is negligible.

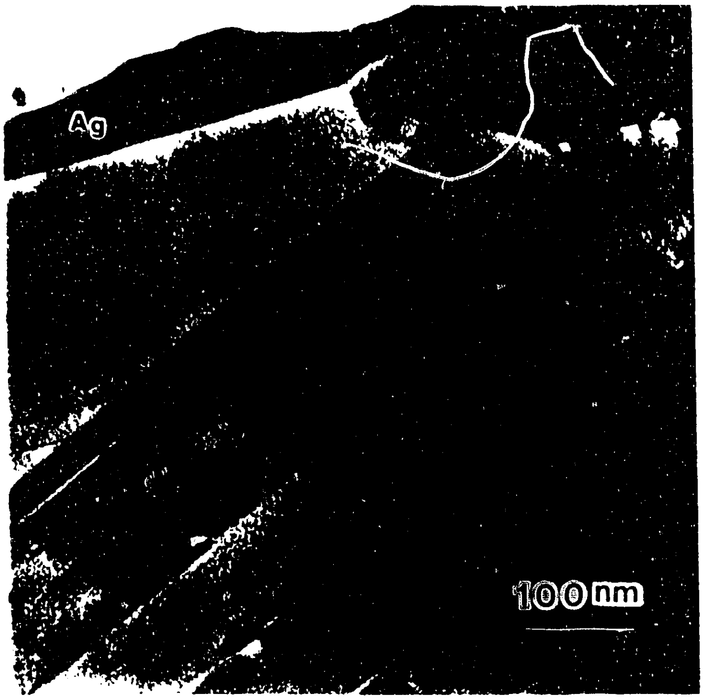

Fig. 6 TEM micrograph showing the morphology of the Bi(2223) tape.

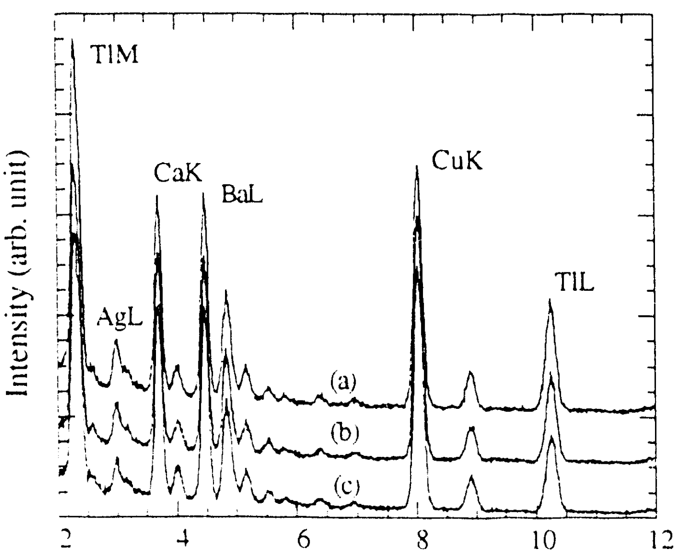

Fig. 7 EDS spectra collected from the points labeled (a), (b) and (c) in Fig. 4.

IV SUMMARY

The microstructures of Ag sheathed Tl(1223) tapes and Pb-doped Bi(2223) tapes have been investigated by SEM, TEM and EDS. The Tl tapes sintered at 845°C for 36 hours contains pores and impurity phases within a matrix of fine-grained Tl(1223) grains. Tapes subjected to partial melting at 895°C for 6 minutes followed by solid state sintering at 845°C showed significantly reduced porosity and a larger grain size. Silver additions tended to promote the growth of the Tl(1223) phase, presumably by lowering the melting point and providing favorable nucleation sites, but also made alignment of grains more difficult due to the random distribution and orientation of silver particles. Both superconducting and impurity phases form at silver which makes it difficult to minimize the amount of impurity phases. In contrast to the Bi(2223) tape, in which the superconducting grains are well aligned, the grains in Tl tapes have irregular shapes and are randomly oriented.

REFERENCES

[1] L. Schultz, B. Raos, P. Schmitt, P. Kummeth and G. Saemann-Ischenko, IEEE Trans. Magn., MAG, vol. 27, pp.990-996, Feb., 1991.

[2] J. H. Kang, K. E. Gray, R. T. Kampwirth and D. W. Day, Appl. Phys. Lett. vol. 53, pp. 2560-2562, Dec., 1988.

[3] S Jin, R. B. van Dover, T. H. Tiefel, J. E. Graebnar, N. D. Spencer, Appl. Phys. Let., 58 (8), pp. 868-870, Feb., 1991.

[4] J. E. Tkaczyk, R. H. Arendt, M. F. Garbauskas, H. R. Hart, K. W. Lay, F. E. Luborsky, Phys. Rev. B, 45 (21), pp. 12506-12511, June, 1992.

[5] M. Huth, M. Schmitt, H. Adrian, Physica C. 178, pp. 203-212, 1991.

[6] A. C. Wright, K. Zhang, A. Erbil, Phys. Rev. B. 44 (2), pp. 863-866, July, 1991.

[7] D. H. Kim, K. E. Gray, R. T. Kampwirth, J. C. Smith, D. S. Richeson, T. J. Marks, J. H. Kang, J. Talvacchio and M. Eddy, Physica C 177, pp. 431-437, July, 1991.

[8] G.J. Yurek, J.B. Vander Sande, W.-X Wang, D.A. Rudman, Y. Zhang and M.M. Matthiesen, Metall. Trans. vol. 18A, pp. 1813-1817, Oct., 1987.

[9] K. Matsuzaki, A. Inoue and T. Masumoto, Jpn. J. Appl. Phys. vol. 27 pp. L195-L198, Feb., 1988.

[10] C.-T. Wu, K. C. Goretta and R. B. Poeppel , Applied Superconductivity vol. 1 (in press).

[11] K. C. Goretta, C.-T. Wu, M. T. Lanagan, M. A. Boling, Donglu Shi, D. J. Miller, Nan Chen, W. G. Hanewald, S. Sengupta, Z. Wang, R. P. Poeppel, F. Foong and S. H. Liou, Proc. 1992 Spring Meeting of MRS, San Francisco, CA.

[12] Y.Feng, K. E. Hautanen, Y. E. High, D. C. Larbalestier, R. Ray II, E. E. Hellstrom and S. E. Babcock, Physica C (submitted).

[13] J. S. Luo, N. Merchant, V. A. Maroni, D. M. Gruen, B. S. Tani, W. L. Carter, G. N. Riley, Jr. and K. H. Sandhage, Applied Physics Letters (submitted).

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