Detection of new superconductors using phase-spread alloy films

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We describe an effective method for discovery of new superconductors, which combines phase-spread alloy thin film preparation with a magnetic field modulated (MFM) microwave absorption technique. The MFM technique can detect superconductivity in $YBa_2Cu_3O_{7-\delta}$ volumes as small as 5×10^{-11} cm^3. As an illustration, $Pr_xGd_{1-x}Ba_2Cu_3O_{7-\delta}$ thin films with varying x were simultaneously grown on the same substrate using a phase-spread alloy technique. The onset temperature determined from the microwave absorption agrees with resistivity, Auger spectroscopy, and energy-dispersive x-ray microanalysis data. When phase-spread $La_x(NiB)_{1-x}N_y$ films $(0<x<1)$ were grown at several different N partial pressures and temperatures, no superconductivity was detected except that of pure La. In contrast, superconductivity was detected in $Y_x(NiB)_{1-x}C_y$ films grown on MgO. © *1995 American Institute of Physics.*

The discovery of high-temperature superconductivity by Bednorz and Müller[1] resulted in a renewed search for high-temperature superconducting materials. Since then, numerous compounds, such as $RBa_2Cu_3O_{7-\delta}$ (R=rare earths La through Lu and Y, except Pr, Ce, and Tb), BSCCO, Tl2223, and HgBCCO, have been discovered. More recently, compounds without copper, such as $Y(NiB)_2C$ and $La_3(NiB)_2N_3$,[2,3] were found to have critical temperatures greater than 10 K. However, finding the right stoichiometry for these materials is usually difficult because many different combinations need to be tested. It is also known that some superconductors, such as Bi, Be, or TaN,[4] only exist in thin film form. Another complication is that the detection of small superconducting regions in a normal host is nontrivial. Although electrical resistivity and magnetic measurements remain the most popular techniques, small fractions of the measured sample which may be superconducting could easily go undetected.

In the present work, we demonstrate an effective approach for the discovery of new superconducting systems. We utilize phase-spread alloy thin films (PSATF)[5] combined with magnetic field modulated (MFM) microwave absorption.[6] The PSATF technique was used to grow different stoichiometries in a single film. We tested this approach on $Pr_xGd_{1-x}Ba_2Cu_3O_{7-\delta}$ (PrGdBCO, $0<x<0.5$) phase-spread alloy thin films, and found that at any location the superconductivity onset temperature, determined from MFM microwave absorption, was consistent with electrical resistivity measurements, Auger spectroscopy, and energy-dispersive x-ray (EDX) chemical microanalysis. When this technique was applied to $La_x(NiB)_{1-x}N_y$, $0.13<x<1.0$ phase-spread alloy thin films, no superconductivity was detected except for that of pure La. We can only conclude that for our preparation conditions the LaNiBN compounds present in our samples are not superconducting in thin film form. On the other hand, superconductivity was detected in preliminary measurements of $Y_x(NiB)_{1-x}C_y$ films grown on MgO.

The method of PrGdBCO PSATF growth has been described elsewhere.[5] Briefly, the samples were grown by sputtering from two stoichiometric targets of pure PrBCO and GdBCO on MgO or $SrTiO_{3-x}$[100] substrates. The targets were sputtered simultaneously, and the substrate positioned for fixed amounts of time to the side of each target. A concentration gradient of Pr on a single substrate was obtained by varying the relative deposition times and the substrate position. The films were $\approx$150 nm thick as determined from contact profilometer measurements.

The MFM microwave absorption detection used a superheterodyne electron-spin-resonance (ESR) spectrometer operating at a frequency of 9.2 GHz. For optimal signal amplitude the samples were placed in the center of a TE102 cavity with the rf magnetic field lines perpendicular to the film plane. An external dc magnetic field of $\sim$ 20 Oe was applied parallel to the rf magnetic field and modulated at 260 Hz, with a peak-to-peak amplitude of 10 Oe. The superconductivity onset temperature $T_{C\mu}$ was defined as the temperature at which the MFM absorption signal was reduced to the background noise level. With the MFM microwave absorption technique YBCO superconducting volumes as small as 5×10^{-11} cm^3 can be detected.[7] The sensitivity was determined by comparing peak signal amplitudes from YBCO thin films of known thickness with the spectrometer's noise level. In comparison, for a SQUID magnetometer operating at 100 Oe, the superconducting diamagnetic signal corresponding to 5×10^{-11} cm^3 is 3.98×10^{-10} emu, a signal several orders of magnitude smaller than the usual sensitivity of commercial SQUID magnetometers. Furthermore, the SQUID is also sensitive to other substantial magnetic signals arising from the film or substrate, while the MFM technique is insensitive to them.

The PrGdBCO samples were chemically analyzed by EDX and Auger microanalysis. The EDX measurements were carried out with an electron microscope set to 20 keV and 500× magnification. The Auger spectroscopy was carried out as described elsewhere.[5] The Pr concentration was determined by comparing the results to pure PrBCO and

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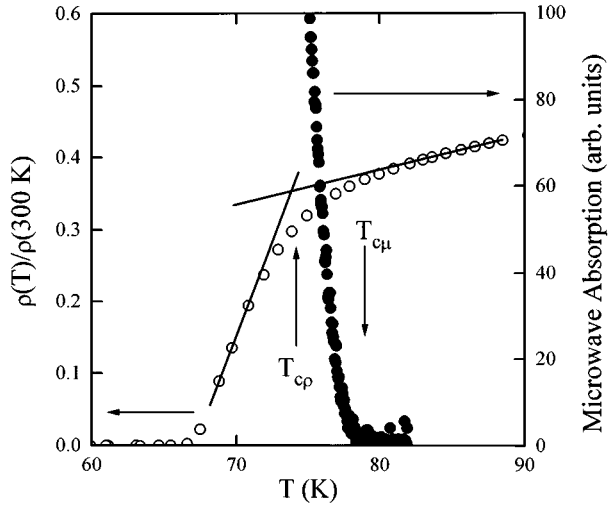

FIG. 1. Normalized resistivity $\rho(T)/\rho(300\ \mathrm{K})$ and MFM microwave absorption signal as functions of temperature for a PrGdBCO film (~5% Pr). The superconductivity onset temperatures $T_{C\rho}$ and $T_{C\mu}$ corresponding to the two techniques are indicated.

GdBCO standard thin films. Then the samples were photolithographically patterned into five strips, each with four electrical contact points, such that the Pr gradient was perpendicular to the length of the strips. Their electrical resistivities as functions of temperature were measured in a closed-cycle helium refrigerator in the temperature range $10\ \mathrm{K}<T<300\ \mathrm{K}$. The superconductivity onset temperatures $T_{C\rho}$ were defined by the intersection of straight lines drawn from the resistivity just above T_c and the resistivity near the center of the transition (Fig. 1). The Pr concentrations were inferred from these measurements by assuming a linear dependence of T_c on Pr concentration[5] (50% corresponds to $T_c=0$ K and 0% corresponds to $T_c=90$ K).

Finally, after spinning photoresist on the sample (to protect it from the external environment), the individual strips were cut with a diamond-wheel. Their superconducting onset temperatures were individually determined using MFM microwave absorption. The Pr concentrations were calculated from the T_c onset as discussed for the resistivity measurements.

Figure 1 compares the MFM and resistivity data of a PrGdBCO sample near the superconducting transition temperature. While $T_{C\mu}$ is well defined to within a few tenths of a degree, $T_{C\rho}$ is not well defined. Using the definition of $T_{C\rho}$ mentioned above, we find $T_{C\rho}<T_{C\mu}$. For most of our samples this was the case, which is expected from the definition of $T_{C\rho}$, although this could also be due to the greater sensitivity of the MFM technique to superconducting transitions in small volumes. However, if the experimental error of $T_{C\rho}$ is defined as the transition width, the two measurements agree with each other.

In Fig. 2 we compare the onset temperatures determined from the electrical resistivity along the film plane and the MFM microwave absorption techniques for three samples. The two results agree within the experimental uncertainties. In order to compare these results with the EDX and Auger data, in Fig. 3 we plot the Pr concentration deduced from the

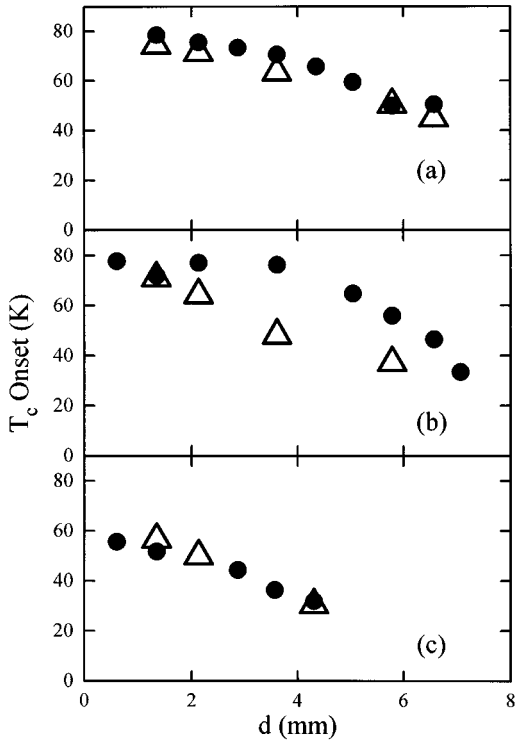

FIG. 2. T_c onset as a function of sample position using electrical resistivity (△) and MFM microwave absorption (●). Sample (a) was grown on MgO(100) and samples (b) and (c) on $SrTiO_{3-x}$. All samples were nominally ≈150 nm thick.

different techniques as a function of sample position for samples grown on MgO and $SrTiO_{3-x}$. For the sample grown on MgO [Fig. 3(a)], the resistivity and microwave measurements imply slightly larger Pr concentrations (lower T_c's) than the EDX and Auger measurements. This might be due to a degradation of the sample (oxygen loss, etc.) which may have occurred during sample preparation. For the samples grown on $SrTiO_{3-x}$ the agreement is better. In any case, the different techniques agree with each other to within the experimental uncertainties.

Motivated by the PrGdBCO results, we next attempted to measure $La_x(NiB)_{1-x}N_y$ thin films. The compound $La_3Ni_2B_2N_3$ has been reported to be superconducting in bulk form[3] with $T_C=12-13$ K. The films were sputtered from separate La (dc) and NiB(rf) targets on MgO(100) substrates. The amount of N was controlled by introducing 99.999% pure N_2 gas into the chamber during deposition and varying its partial pressure as described below. After growth, samples with the highest La concentrations reacted strongly with air, as was deduced from their color change and increased electrical resistance as a function of exposure time. In order to avoid this problem as much as possible, samples were stored in an evacuated desiccator. Whenever possible, samples were measured immediately after growth. Measurements were carried out in the temperature range between 2.0 and 300 K. The following combinations of Ar and N_2 were used: (i) 25 mTorr Ar/5 mTorr N_2, (ii) 29 mTorr Ar/1 mTorr N_2, and (iii) 30 mTorr Ar/0.1 mTorr N_2.

For case (i), the power of the NiB gun was fixed at 67 W,

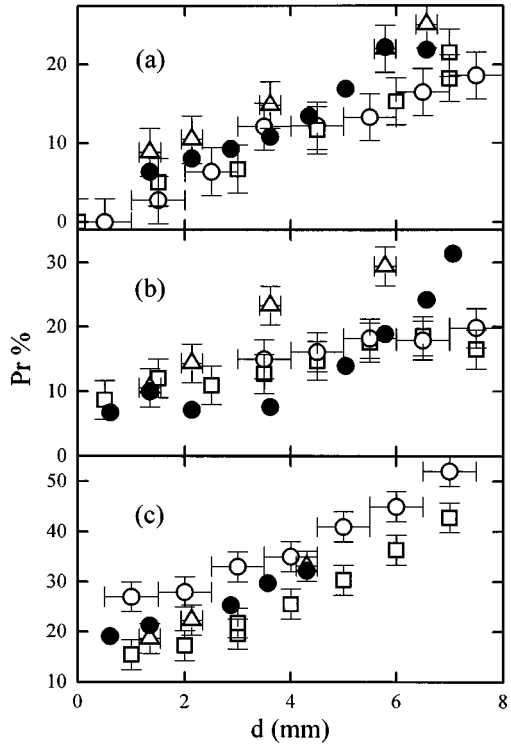

FIG. 3. Pr concentration as a function of sample position determined from Auger spectroscopy (○), EDX microanalysis (□), electrical resistivity (△), and MFM microwave absorption (●). Sample (a) was grown on MgO(100) and samples (b) and (c) on $SrTiO_{3-x}$. All samples were nominally ≈150 nm thick. Error bars result from uncertainties in sample position and numerical analysis of raw data.

while the La gun was varied from 5 to 40 W in order to achieve a wide range of concentrations. According to EDX, this resulted in a relative atomic concentration ranging from La/Ni=0.15 to 2.65 (for the superconducting phase $La_3Ni_2B_2N_3$, La/Ni=1.5). With a fixed ratio La/Ni=1.5, the deposition temperature was varied from room temperature to 950 °C. Some of the samples grown with different ratios were also post-annealed in flowing Ar and vacuum at temperatures ranging from 800 to 1000 °C. In all cases, *no superconductivity was detected* using the MFM microwave absorption technique.

For case (ii), samples were grown at 350 °C, corresponding to the growth temperature that yielded the lowest sample resistance (~10 mΩ cm). The ratio was varied between La/Ni=0.5 and 2.12. Some of these samples were also postannealed as in case (i). Again, *no superconductivity was detected*.

Finally, for case (iii) a sample was grown at 350 °C. X-ray $\Theta-2\Theta$ scans showed that a significant sample fraction was composed of pure La. This sample exhibited superconductivity at $T_c=5.4$ K. To confirm that the superconductivity was indeed due to pure La, a pure La film was grown and measured. This sample exhibited superconductivity at 5.5 K.

We note that although we were unable to quantify B or N concentrations, we detected their presence using Auger spectroscopy. The possibility remains that we did not have the correct concentrations for these elements. However, in the case of B we expect the Ni:B relative concentration to be 1:1, because that is the sputtering target concentration. As for the N concentration, the N_2 partial pressure was varied over two orders of magnitudes. In addition, we did not find conclusive evidence in our films of the $La_3(NiB)_2N_3$ structure[3] from x-ray $\Theta-2\Theta$ scans compared to Rietveld x-ray simulations. The observed T_C signals corresponded either to pure La or another as yet unidentified compound.

In contrast, superconductivity was detected in $Y_x(NiB)_{1-x}C_y$ films grown on MgO, with a maximum critical temperature of 12.6 K. The details of this experiment will be published elsewhere.[8]

In conclusion, superconducting regions in PrGdBCO phase-spread alloy films were easily detected using MFM microwave absorption. The MFM and electrical transport measurements agree well with the EDX and Auger chemical probes. Given the extreme sensitivity of the MFM technique and the correlation of the T_c onset with the other techniques discussed, we suggest that, in combination with phase-spread alloy sample preparation, one has a general approach to aid the discovery of new high-temperature superconducting materials. Using this approach, no traces of superconductivity were observed in $La_x(NiB)_{1-x}N_y$ films grown on MgO, despite using a wide range of growth temperatures, stoichiometries, and annealing treatments. However, superconductivity was detected in $Y_x(NiB)_{1-x}C_y$ films grown on MgO.

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[1] J. G. Bednorz and K. A. Müller, Z. Phys. B Condens. Matter **64**, 189 (1986).
[2] R. Nagarajan, C. Mazumdar, Z. Hossain, S. K. Dhar, K. V. Gopalakrishnan, L. C. Gupta, C. Godart, B. D. Padalia, and R. Vijayaraghavan, Phys. Rev. Lett. **72**, 274 (1994); R. J. Cava, H. Takaji, H. W. Zandbergen, J. J. Krajewski, W. F. Peck Jr., T. Siegrist, B. Batlogg, R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki, and S. Uchida, Nature **367**, 252 (1994).
[3] R. J. Cava, H. W. Zandbergen, B. Batlogg, H. Eisaki, H. Takagi, J. J. Krajewski, W. F. Peck, Jr., E. M. Gyorgy, and S. Uchida, Nature **372**, 245 (1994).
[4] B. W. Roberts, *Superconductive Materials and Some of Their Properties*, NBS Technical Note 408 (U. S. Government Printing Office, Washington, D. C., 1966).
[5] D. Lederman, T. J. Moran, J. Hasen, and Ivan K. Schuller, Appl. Phys. Lett. **63**, 1276 (1993).
[6] K. Khachaturyan, E. R. Weber, P. Tejedor, A. M. Stacy, and A. M. Portis, Phys. Rev. B **36**, 8309 (1987); A. M. Portis, K. W. Blazey, K. A. Müller, and J. G. Bednorz, Europhys. Lett **5**, 467 (1988).
[7] I. N. Chan, D. C. Vier, O. Nakamura, J. Hasen, J. Guimpel, S. Schultz, and Ivan K. Schuller, Phys. Lett. A **175**, 241 (1993).
[8] A. Hoffmann, B. Knigge, D. Lederman, D. Vier, D. Mendoza, S. Schultz, and Ivan K. Schuller (unpublished).