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Nd-DOPED $YBa_2Cu_3O_{7-x}$ FILMS DEPOSITED BY PULSED LASER ABLATION

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14. ABSTRACT
Nd doped $YBa_2Cu_3O_{7-x}$ targets ($Nd_xY_{1-x}Ba_2Cu_3O_{7-x}$;x = 0, 0.2, 0.4, 1) were prepared in-house and were used to deposit films by pulsed laser ablation in 300 mTorr of oxygen to study the Nd substitution effects on the film properties. Film composition was found to match very closely to the composition of the targets as determined from X-ray photoelectron spectroscopy. The critical transition temperature (T_c) was found to be reduced as the Nd substitutions were increased in the films. Raman spectra taken from the films indicate that c-axis misalignment and some cation disorder may be present in the films with poor T_c. Transport critical current density (J_c) of 3 x 10^6 A/cm^2 was measured in $Nd_{0.4}Y_{0.6}B_a2Cu_3O_{7-x}$ films.

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Coated conductors, Nd substitutions, pulsed laser, ablation, rare earth pinning, YBCO.

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Nd-Doped $YBa_2Cu_3O_{7-x}$ Films Deposited by Pulsed Laser Ablation

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***Abstract*—Nd doped $YBa_2Cu_3O_{7-x}$ targets ($Nd_xY_{1-x}Ba_2Cu_3O_{7-x}$; $x = 0$, 0.2, 0.4, 1) were prepared in-house and were used to deposit films by pulsed laser ablation in 300 mTorr of oxygen to study the Nd substitution effects on the film properties. Film composition was found to match very closely to the composition of the targets as determined from X-ray photoelectron spectroscopy. The critical transition temperature (T_c) was found to be reduced as the Nd substitutions were increased in the films. Raman spectra taken from the films indicate that c-axis misalignment and some cation disorder may be present in the films with poor T_c. Transport critical current density (J_c) of 3×10^6 A/cm^2 was measured in $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ films.**

***Index Terms*—Coated conductors, Nd substitutions, pulsed laser ablation, rare earth pinning, YBCO.**

I. Introduction

Although coated conductors with high critical current density ($J_c \sim 10^6$ A/cm^2) using $YBa_2Cu_3O_{7-x}$ (YBCO) films are routinely made [1], [2], further enhancement in J_c is still desired for use in high magnetic field applications. These enhancements can be achieved by creating artificial flux pinning centers in YBCO films. These pinning centers can be nm-sized nonsuperconducting particulates [3] or chemical substitutions in the YBCO crystal lattice [4]–[7], or combinations of both [8]. These chemical substitutions should help to create stress-field-induced pinning without adversely affecting the critical transition temperatures (T_c). Partial rare earth ion substitutions for Y in $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor films are of considerable interest from the point of view of the chemical substitution effects on pinning enhancements. Several studies were done earlier to process Nd substitutions in powders [9], melt processed YBCO [10] with evidence of improved pinning. In this study, several targets with different Nd substitutions for Y were made and Nd substituted YBCO films were grown using pulsed laser ablation of these targets in oxygen and the films were characterized to study the effects of Nd doping.

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II. Experimental Procedure

A. Sample Preparation

Targets used in this study were prepared in-house by mixing the calculated amounts of Nd_2O_3, Y_2O_3, $BaCO_3$, and CuO using a mortar and pestle. The powders were pressed into 1.5 inch diameter discs using a uniaxial press. These discs were sintered in a box furnace around 950 to 1000°C with several intermediate grinding, mixing and pressing steps to form homogenous composition targets. Targets with a nominal composition of $NdBa_2Cu_3O_{7-x}$, $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$, and $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ were made. All the targets were processed in air in a box furnace and were used in a PLD chamber with no further oxygenation treatment.

Films were deposited on single crystal lanthanum aluminate (100) substrates in a Neocera Inc., pulsed laser deposition system using a Lambda Physik USA Inc., model LPX 305i KrF excimer laser (laser wavelength is 248 nm). The laser fluence was approximately 4.0 J/cm^2 and a pulse rate of 4 Hz was used during the film growth. The oxygen pressure during the deposition was maintained at 300 mTorr. Samples were deposited at 730 to 760°C for 20 minutes and then annealed in oxygen at 500°C for 30 minutes before cooling down to room temperature.

B. Characterization

The superconducting transition temperature (T_c) was measured using an ac susceptibility technique with an external magnetic field that varied from 0.025 Oe to 2.2 Oe. Magnetization measurements were taken using a Quantum Design Physical Property Measurement System (PPMS) in magnetic fields up to 9 T at several temperatures. Magnetic field was applied perpendicular to the sample surface (parallel to c-axis). A ramp rate of 100 Oe/sec was used during the generation of hysteresis loops at several temperatures. The J_c of the samples was estimated using a simplified Bean model with $J_c = 30\ \Delta M/ab^3$, where ΔM is magnetization loop width at a given magnetic field, a is the film thickness and b *is* the length of one side of a square sample. Micro-Raman measurements were carried out with a Renishaw Raman spectrometer attached to a charge coupled device array detector. The Raman spectra were obtained in multi-spectra detection mode in order to reduce the noise. The excitation of the sample was accomplished with an Ar^+ laser. The laser power was kept low enough to avoid film degradation due to overheating of the probed volume. X-ray photoelectron spectroscopy was done using a Kratos AXIS Ultra system. After ion milling the surface to remove the surface adsorbed carbon, the Y/Nd ratio at several points on the films was noted.

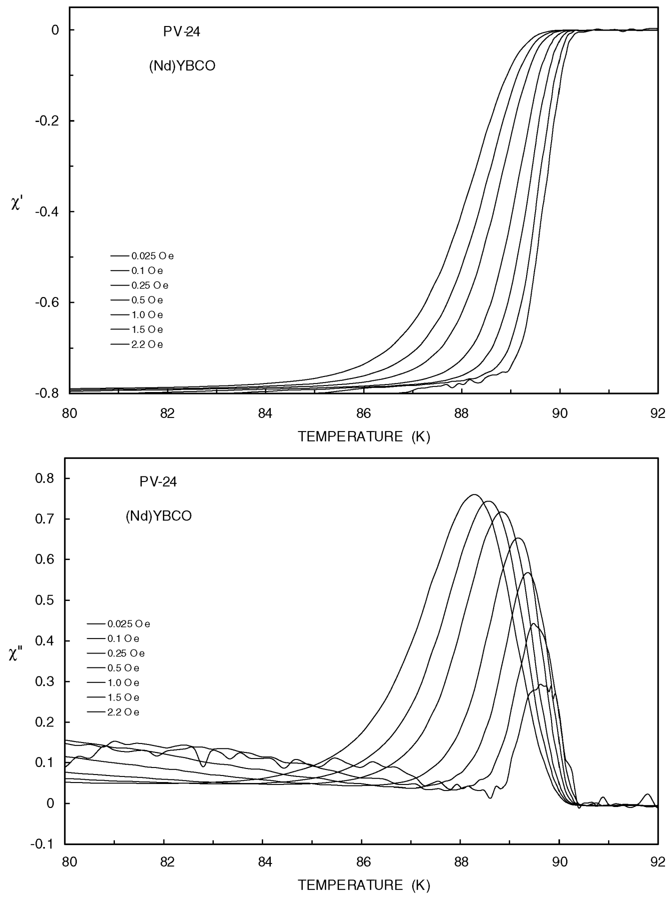

Fig. 1. Ac susceptibility curves from a $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film on (100) lanthanum aluminate single crystal.

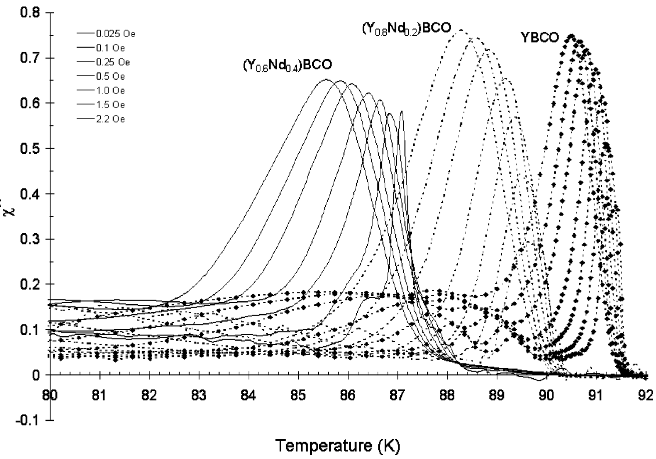

Fig. 2. The T_c onset decreases with increasing composition of the Nd doping in the Nd-doped YBCO films processed in 300 mTorr of oxygen.

TABLE I
RELATIVE COMPOSITION OF THE $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ FILMS AS COMPARED TO A STANDARD YBCO FILM

Element	Sample1	Sample2
Y	58.26%	60.43%
Nd	41.74%	39.57%
Ba	99.15%	100.05%
Cu	95.21%	93.42%
O	97.46%	95.94%

Monochromatic Al K_α X-ray line was used for enhanced spectral resolution. The analysis spot size was approximately 110 μm. A Leica FE scanning electron microscope was used to determine the microstructure of Nd-doped YBCO films.

III. RESULTS AND DISCUSSION

A. AC Susceptibility

AC susceptibility data taken from a $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film is shown in Fig. 1. It can be seen that T_c onset is around 90 K. However the T_c is less than YBCO films processed in similar conditions as shown in Fig. 2 where T_c values of different composition films are compared. It can be seen that as the Nd content is increased, the films showed gradual decrease in T_c. It is thought that Nd may be substituted in Ba sites due to similar atomic sizes, and this may cause a reduction in the T_c of the films. By varying the processing conditions, it may be possible to further improve the T_c of these films.

B. X-Ray Photoelectron Spectroscopy (XPS)

XPS data was collected on at least five different points on the doped films and the data was compared to that taken from a standard YBCO film. Table I shows the relative composition of two films as compared to a standard YBCO sample. These films were grown using a $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ target. Data collected at different spots on the films were similar indicating good compositional uniformity. The numbers in Table I represent the relative atomic percentages of Y, Nd, Ba, Cu, O as compared to a standard YBCO sample. It can be seen that the composition of the films matches very closely with the composition of the target.

C. Raman Spectroscopy

Raman micro-spectroscopy is a simple, nondestructive characterization tool for analyzing the quality of YBCO films. The presence of secondary phases such as CuO, $BaCuO_2$ as well as the information about the cation disorder, c-axis alignment problems in the films can be easily obtained in brief data collection and analysis time as compared to other techniques such as x-ray diffraction [11]. Fig. 3 shows a Raman spectrum taken from a $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film with a T_c of 90.3 K deposited by pulsed laser ablation on a lanthanum aluminate single crystal substrate. A peak at around 335 cm^{-1} indicates the presence of orthorhombic phase of YBCO with good c-axis texture. The weak peaks that can be seen around 500 cm^{-1} and 585 cm^{-1} indicate some c-axis alignment problem and cation disorder, respectively. There were no other peaks observed corresponding to CuO or $BaCuO_2$, indicating that these films are free from these impurity phases.

Fig. 4 shows the Raman spectra taken from a $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film with a T_c of 88 K. These films also show the absence of CuO and $BaCuO_2$ phases

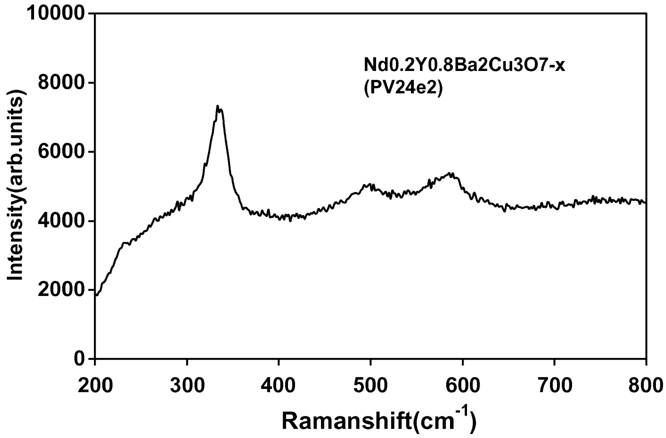

Fig. 3. Raman spectrum from a $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film.

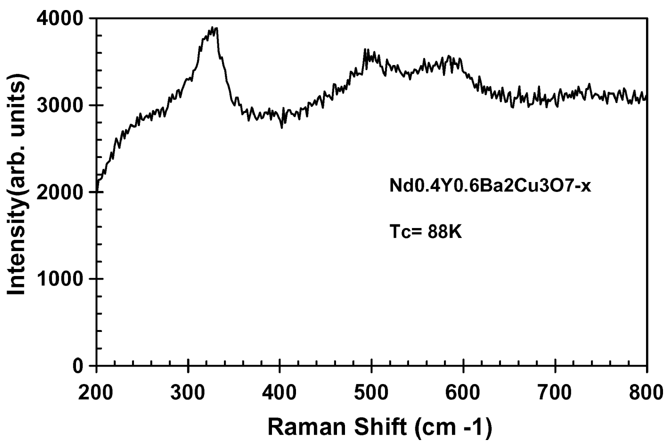

Fig. 4. Raman spectrum taken from a $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film. This sample had a T_c of 88 K.

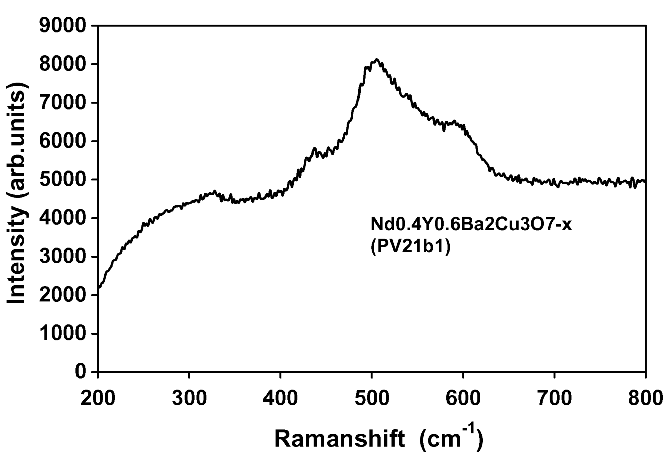

Fig. 5. Raman spectrum taken from a $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film. This film had a T_c of 85 K.

and good c-axis texture similar to $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$. However, in the $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film, it can be seen that the peaks corresponding to cation disorder and c-axis alignment problem are strong.

In Fig. 5, Raman spectra taken from a different $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film with lower T_c than the film of Fig. 4 is shown. It can be seen that the peak at 335 cm^{-1} is reduced considerably and peaks corresponding to 437 cm^{-1}

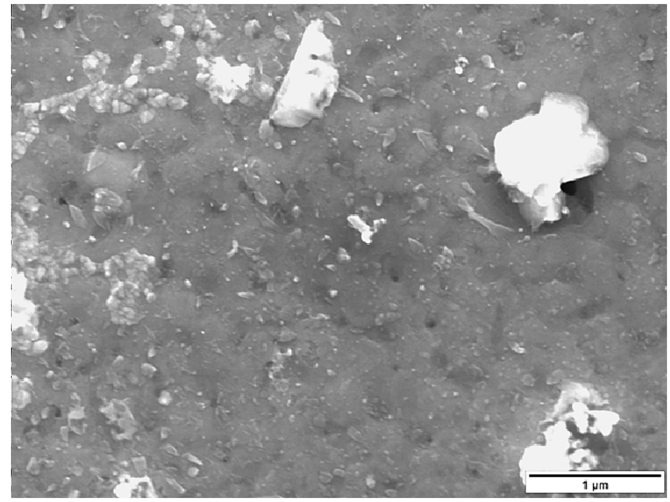

Fig. 6. SEM micrograph of $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ film.

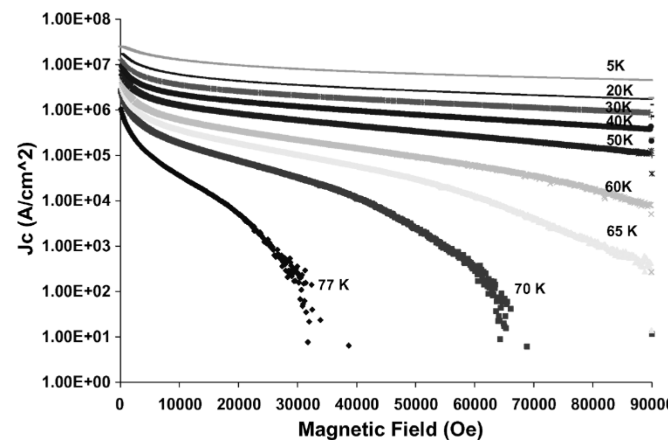

Fig. 7. Magnetization J_c of a $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film.

(this peak refers to the oxygen content [12]), 500 cm^{-1} and 585 cm^{-1} are increased further. These results reveal that room temperature Raman spectroscopy can be used to assess the superconducting quality of the Nd doped YBCO films.

D. Scanning Electron Microscopy

Scanning electron microscopy (SEM) of Nd doped YBCO films showed that the films are very dense and generally have small grain size compared to similarly-processed undoped YBCO films. A typical microstructure of an Nd doped YBCO film with occasionally seen particulates (bright areas) is shown in Fig. 6.

E. Magnetization J_c

Both $Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}$ and $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ films showed self-field magnetization J_c values ($> 10^6\ A/cm^2$) comparable to typical PLD processed YBCO samples [13] at 77 K. However, the magnetization J_c in these samples was found to decrease rapidly at higher magnetic fields at 77 K.

It was also noticed that the J_cs of Nd doped films and undoped YBCO films tend to be similar at all magnetic fields up to 9 T at lower temperatures. In Fig. 7, magnetization J_c for an $Nd_{0.2}Y_{0.8}Ba_2Cu_3O_{7-x}$ film measured at several temperatures is shown. It is thought that the doping levels studied in this study (20 and 40%) may be too high to realize the benefits of stress related pinning effects at 77 K.

F. Transport Current Measurement

Transport current measurements were taken on $\mathrm{Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}}$ films at 77 K in self field. The measurements were taken on a bridge patterned with a width of 0.5 mm and the film thickness of the sample was 0.25 μm. This sample carried 3.7 A and the calculated $\mathrm{J_c}$ was found to be $3.1 \times 10^6\ \mathrm{A/cm^2}$.

IV. Conclusions

Nd doped YBCO films at different doping levels were processed by PLD. Composition of the films matched the composition of the target very well as determined by XPS. When similar processing conditions were used, Nd-doped YBCO films (at the doping levels of greater than 20%) showed a tendency to reduce $\mathrm{T_c}$ with increasing amounts of doping. Raman studies indicated cation disorder and c-axis alignment problems in the films that showed reduced $\mathrm{T_c}$. VSM measurements indicated that the Nd doped films have similar $\mathrm{J_c}$ as YBCO films at 77 K at low magnetic fields but show rapid decrease in $\mathrm{J_c}$ at high magnetic fields. However, the $\mathrm{J_c}$s of Nd doped films and YBCO films were found to be similar at high magnetic fields in lower temperatures. Self field critical transport current density of $3 \times 10^6\ \mathrm{A/cm^2}$ was measured in $\mathrm{Nd_{0.4}Y_{0.6}Ba_2Cu_3O_{7-x}}$ films at 77 K.

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