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Y.-A Jee, B. Ma, M. Li, B. L. Fisher, and U. Balachandran
Energy Technology Division
Argonne National Laboratory
Argonne, Illinois 60439

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# Texture Formation and Superconducting Properties of $YBa_2Cu_3O_x$ Thin Films Prepared by Solution Process on $LaAlO_3$ Single Crystals

**Y.-A Jee, B. Ma, M. Li, B. L. Fisher, and U. Balachandran**
Energy Technology Division, Argonne National Laboratory,
Argonne, IL 60439, U.S.A.

## ABSTRACT

$YBa_2Cu_3O_x$ (YBCO) thin films were fabricated by the trifluoroacetate (TFA) process on $LaAlO_3$ (LAO) single crystal in an argon atmosphere. We focused on lowering the heat treatment temperature by decreasing the oxygen partial pressure to adopt the TFA process to metallic substrates. YBCO phase formation was checked by measuring $T_c$ with the inductive method. In-plane and out-of-plane film textures were evaluated by phi-scan and omega scan, respectively. Raman spectroscopy was used to estimate grain connectivity, in-plane texture, and second-phase formation of the films. Although Raman spectroscopy revealed some evidence of cation disorder, the film prepared at 750°C shows a sharp superconducting transition at 91 K and critical current density of 1.3 MA/cm$^2$ at 77 K. Optimal heat treatment temperature was 750°C in the argon atmosphere, which is consistent with the thermodynamic estimate that heat treatment temperature decreases as oxygen partial pressure decreases.

## INTRODUCTION

For fabrication of YBCO-coated conductors on metal substrates, various processing methods were investigated to achieve high $J_c$ values. Vacuum processes [1-3] generally produce high-$J_c$ films, and the related buffer layers are also prepared by vacuum processes such as ion beam assisted deposition. However, in terms of long-length applications of coated conductors, complicated vacuum equipment and a high-cost process may not be appropriate. On the contrary, nonvacuum ex-situ processes such as metal organic decomposition (MOD) and the sol-gel process seem to be more promising. The solution techniques are now being studied by several investigators [4-11], and some of their results are comparable to those obtained by vacuum processes. MOD using trifluoroacetate (TFA) produces one of the highest $J_c$ values of all the solution techniques, but its application to metal substrates is still not consistently successful due to the lack of full understanding of processing condition. In this study, we report our work on systematically optimizing the parameters of the TFA process. Toward application to metal substrates, we have concentrated especially on lowering the heat treatment temperature.

## EXPERIMENTAL DETAILS

Metal acetates of Y, Ba and Cu in the molar ratio of 1:2:3 were dissolved in trifluoroacetic acid and refluxed for 4 h. This solution was then dried in air to evaporate the solvent and to obtain a blue solid residue. The solid residue is easily soluble in methanol, and this methanol-based solution was used throughout our experiment. The solution was coated on LAO single crystals with either a dip-coating or a spin-coating method. The precursor film was converted to an epitaxial YBCO film through two separate heat treatments. During the first step (Fig. 1a),

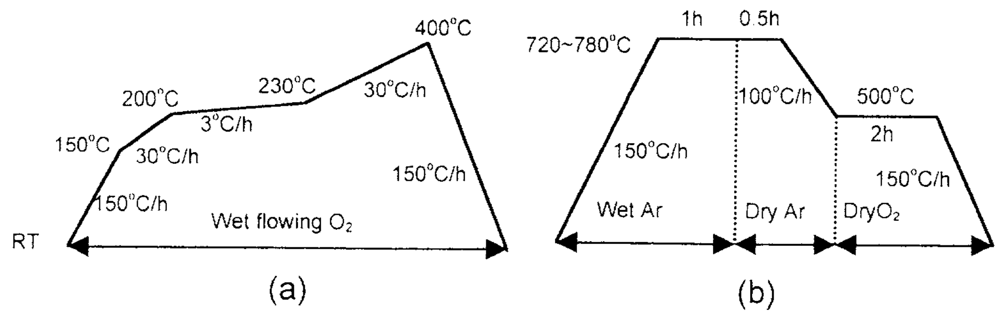


*Figure 1. Illustrations of heat schedule of (a) first step and (b) second step of heat treatment.*

a uniform fluorine-containing solid film formed. The epitaxial texture of the YBCO film was developed and fluorine was eliminated in the high temperature heating step shown in Fig. 1b. Samples were prepared at five different temperatures ranging from 720 to 780 °C in an argon atmosphere. Superconductivity of the films was characterized by measuring inductive $T_c$ and $J_c$ as described in Refs. 12 and 13. Because a magnetic field penetrates into the samples through the weakest link, the inductively measured $T_c$ or $J_c$ is known to be slightly lower than that obtained by transport measurement. Texture development of the films was evaluated with X-ray diffraction (XRD) equipment using Cu-kα line. In-plane texture was quantified by measuring the full width at half maximum (FWHM) of (113) phi scans of the samples. For analysis of out-of-plane texture, FWHMs of (005) and (007) peaks were measured from an omega scan of each sample. Insight on second-phase formation and grain connectivity that was virtually unavailable from other measurements was obtained via Raman spectroscopy.

## RESULTS AND DISCUSSION

### $T_c$ measurement

Figure 2 shows inductive $T_c$ values of samples prepared at different temperatures. A sharp transition was observed in samples prepared between 740 and 760°C. On the contrary, the samples prepared at 720 and 780°C have transitions broader than 10 K. In the Ar atmosphere, the optimal temperature to form a YBCO phase is thus considered to be between 740 and 760°C, based on these data.

### Texture analysis via phi scan and omega scan

In-plane and out-of-plane sample texture was evaluated via phi scan and omega scan using Cu-kα line, and FWHMs of their peaks were measured to obtain a quantitative reference. Figure 3 shows the FWHMs of (113) phi scan of the samples prepared at various temperatures. The FWHMs were distributed from 0.55 to 0.8° at all temperatures. Although the samples prepared at 720 and 780°C have the broadest $T_c$ transitions, the difference in in-plane

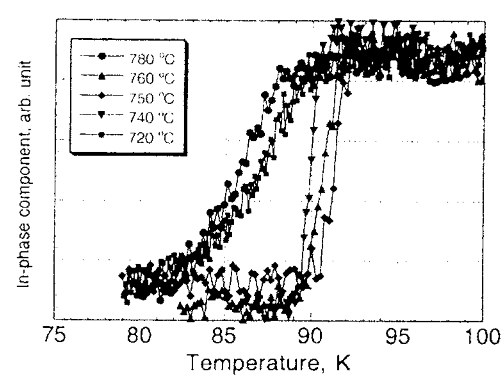


*Figure 2. Inductively measured $T_c$s of samples prepared by TFA process at various temperatures in an argon atmosphere.*

texture does not seem to be the significant factor causing the broad transition. Figure 4 shows FWHMs of omega scans of (005) and (007) peaks using the Cu-kα line as a function of heat treatment temperature. The FWHMs were 0.38° at minimum and 0.68° at maximum, and did not seem to be strongly correlated with heat treatment temperatures. The quantitative FWHMs from phi scans and omega scans obtained by other groups are ≈1.5° and 0.5°, respectively. Thus, our TFA samples have excellent in-plane and out-of-plane textures.

## Raman microspectroscopy

Raman spectroscopy was used to examine the texture and second-phase formation intensively, and the spectra at various temperatures are shown in Fig. 5. Perfect epitaxial YBCO films should have only one peak (marked with an inverted triangle in the spectrum) within the range of 200-800 $cm^{-1}$ [14]. Presence of other peaks is an indication of defects in texture or formation of second phases. For example, the peaks shown in region BB represent broken M-O chain structures at either the microscopic or macroscopic scale. These peaks are rarely observed at temperatures of 740 and 750°C, as shown in the figure. Sometimes a set of small peaks was observed in this region at 720°C, indicating imperfect connectivity between grains. When the heat treatment temperature was increased to 780°C, intensity of the BB peaks also increased. The BB peaks (not presented in this figure) began to appear at 760°C and became stronger and more frequent at 780°C. In the samples prepared at 760°C, these peaks are not as frequent as in the 780°C sample. These BB peaks were usually accompanied by strong $BaCuO_2$ peaks (marked with BC in the figure). This indicates that either the $BaCuO_2$ phase causes the imperfect grain connectivity or the BB peaks are part of a $BaCuO_2$ phonon. At 780°C, two different types of spectra usually were observed, representing local variation of composition. One shows a strong CuO peak, marked in the figure with CU instead of BB and BC ($BaCuO_2$). The other spectrum shows strong BB peaks accompanied by the appearance of the BC peak. It is likely that the YBCO phase decomposes easily at the high temperature of 780°C and then solidifies during cooling to form second phases such as CuO and $BaCuO_2$. In terms of YBCO phase formation, therefore, a temperature lower than 780°C is suggested. On the other hand, signs of reduction of texture (RT) are also detected at almost every temperature except 740 and 750°C. Appearance of RT peak indicates that the samples prepared at temperatures other than the optimal have

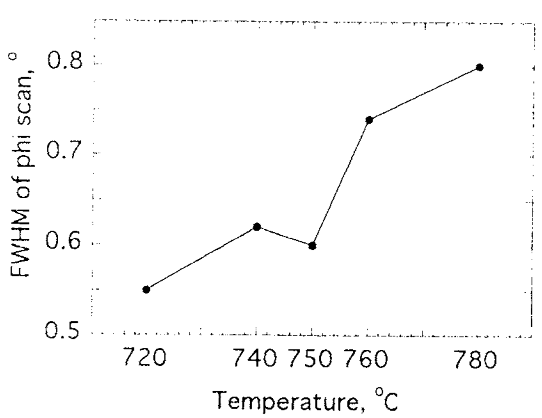


*Figure 3. Relationship of FWHM vs. heat treatment temperature.*

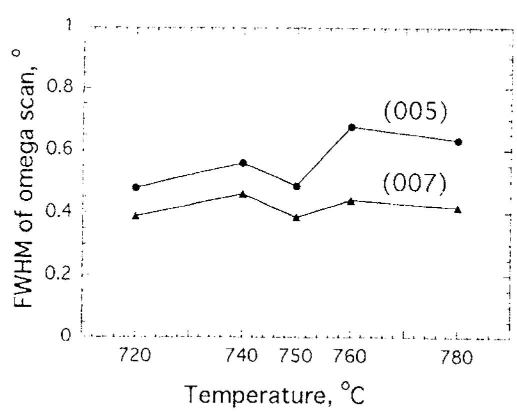


*Figure 4. FWHMs of omega scans for (005) and (007) peaks of TFA samples prepared at various temperatures.*

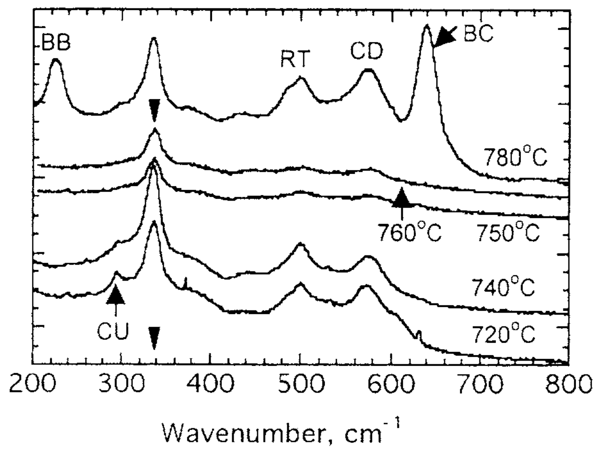


*Figure 5. Raman spectra of TFA samples prepared at various temperatures in an argon atmosphere.*

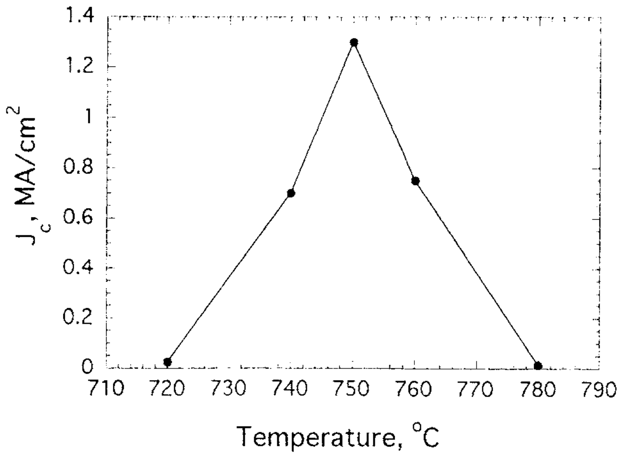


*Figure 6. Temperature dependence of $J_c$ values for samples prepared by TFA process in Ar atmosphere.*

slightly disturbed texture, although this difference was too slight to be observed through pole figures. Besides, evidence of cation disorder (CD) was also detected in every sample; cation disorder may reduce the $J_c$ value compared to those obtained from vacuum processes, including PLD.

Considering the Raman spectra, the broad $T_c$ transition in the 720 and 780°C samples (shown in Fig. 2) could be due to the phase decomposition, second-phase formation, or disturbance of texture. The information from the Raman spectra therefore supports the $T_c$ and $J_c$ data well.

## $J_c$ measurement

Figure 6 shows inductive $J_c$ data from samples prepared at various temperatures. As can be predicted from the characterization results, the highest $J_c$ value of 1.3 MA/cm$^2$ was obtained at 750°C. Slightly lower values were obtained for samples 740 and 760°C. However, for samples prepared at 720 and 780°C, the $J_c$ was very low.

## Oxygen partial pressure vs. processing temperature

In this study, high-$J_c$ films were successfully made at 750°C in an argon atmosphere, the oxygen partial pressure of which was much lower than that reported in previous works. The processing temperature achieved in this study is attributed to this low oxygen partial pressure. Bormann et al. [15] reported that the stability limit of YBCO phase depends strongly on oxygen partial pressure and processing temperature, and that the temperature decreases as oxygen partial pressure decreases. The experimental correlation between YBCO fabrication temperature and oxygen partial pressure is shown in Fig. 7, together with the estimate of Bormann et al. [15]. The experimental data were

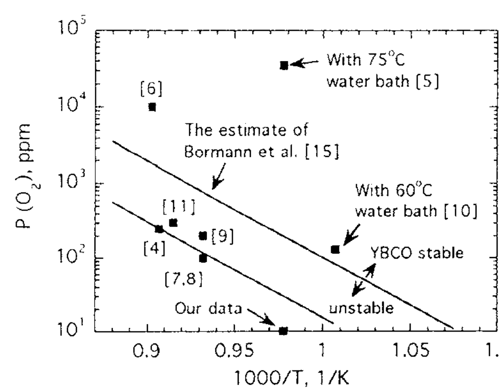


*Figure 7. Variation of oxygen partial pressure as a function of heat treatment temperature.*

shifted to the high-temperature region at the left side, relative to the thermodynamic data; this is thought to be related to reaction kinetics. On the other hand, the data of McIntyre et al. [5] and Solovyov et al. [10], also shown in the figure, indicate that the temperature could be further reduced with a hot water bath in the case of the TFA or $BaF_2$ process. The water vapor is considered to enhance elimination of fluorine elements, so that YBCO phase could form and develop a texture at lower temperatures. Our data point is at the lowest heat treatment temperature in the lowest oxygen partial pressure without a hot water bath, so it is well consistent with the trend of thermodynamic estimates and previous reports. Thus, our study suggests a practical approach to coated-conductor development by focusing on lowering the heat treatment temperature to adopt metallic substrates to the MOD process.

## CONCLUSIONS

Highly textured YBCO thin films were fabricated by the TFA process in an argon atmosphere, with the idea of lowering the processing temperature by using extremely low oxygen partial pressure. The superconducting properties of the resulting samples were evaluated by measuring inductive $T_c$ and $J_c$. Quantitative in-plane and out-of-plane texture was obtained from FWHMs of phi scans and omega scans, respectively. Insight about second-phase formation, texture disturbance, and cation ordering was obtained by Raman spectroscopy. Although all of the films had excellent in-plane and out-of-plane textures, the sharpest $T_c$ transition and the highest $J_c$ value were achieved in the sample prepared at 750°C. The Raman spectra supported these $T_c$ and $J_c$ data well. In this study, the lowest optimal temperature was between 740 and 750°C in an argon atmosphere. It was proved that the high-quality films were successfully made by the nonvacuum process, without a complicated experimental setup at low temperature, by using extremely low oxygen partial pressure. The relationship between oxygen partial pressure and optimal processing temperature was discussed on the basis of previous reports and thermodynamic estimates by other investigators. As a result, the optimal processing temperature was found to decrease as the oxygen partial pressure decreases. The TFA process at low temperature in an argon atmosphere is thus suggested as a promising approach for fabricating long-length coated-conductors.

## ACKNOWLEDGMENT

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## REFERENCES

1. T. G. Holesinger, S. R. Foltyn, P. N. Arendt, H. Kung, Q. X. Jia, R. M. Dickerson, P. C. Dowden, R. F. DePaula, J. R. Groves, and J. Y. Coulter, *J. Mater. Res.* **15**[5], 1110-1119 (2000).
2. Y. Iijima, *Supercond. Sci. Technol.* **13,** 68-81 (2000).
3. B. Schey, W. Biegel, M. Kuhn, and B. Stritzker, *IEEE Trans. Appl. Supercond.* 9[2], 2359-2362 (1999).

4. P. C. McIntyre, M. J. Cima, J. A. Smith, R. B. Hallock, M. P. Siegal, and J. M. Phillips, *J. Appl. Phys.* **71**[4], 1868-1877 (1992).
5. P. C. McIntyre, M. J. Cima, and M. F. Ng, *J. Appl. Phys.* **68**[8], 4183-4187 (1990).
6. J. A. Smith, M. J. Cima, and N. Sonnenberg, *IEEE Trans. Appl. Supercond.* **9**[2], 1531-1534 (1999).
7. S. Sathyamurthy and K. Salama, *Physica C*, **329**, 58-68 (2000).
8. S. Sathyamurthy and K. Salama, *J. of Supercond.* **11**[5], 543-553 (1998).
9. K. Yamigawa, H. Hiei, Y. Takahashi, S. B. Kim, K. Matsumoto, H. Ikuta, U. Mizutani, and I. Hirabayashi, *Physica C*, **334**, 301-305 (2000).
10. V. F. Solovyov, H. J. Wiesmann, L. Wu, M. Suenaga, and R. Feenstra, *IEEE Trans. Appl. Supercond.* **9**[2], 1467-1470 (1999).
11. I. Matsubara, M. Paranthaman, A. Singhal, C. Vallet, D. F. Lee, P. M. Martin, R. D. Hunt, R. Feenstra, C.-Y. Yang, and S. E. Babcock, *Physica C*, **319**, 128-132 (1999).
12. M. Bauer, J. Schwachulla, J. Egly, P. Berberich and H. Kinder, *Advances in Superconductivity X* (Proc. 10$^{th}$ Int. Symp. on Superconductivity (ISS'97), Oct. 27-30, 1997, Gifu, Japan), pp. 979-982.
13. M. Bauer, R. Semerad, and H. Kinder, *IEEE Trans. Appl. Supercond.* **9**[2], 1502-1505 (1999).
14. M. N. Iliev, *Spectroscopy of Superconducting Materials* (ACS symposium series; 730), ed. Eric Faulques (American Chemical Society, Washington, DC, 1999), pp. 107-117.
15. R. Bormann and J. Nölting, *Appl. Phys. Lett.* **54**[21], 2148-2150 (1989).