# Low-temperature growth of YBCO thin films by pulsed laser ablation in reducing environment

**Akiharu Morimoto [a,1], Katsuhito Takezawa [a], Toshiharu Minamikawa [b], Yasuto Yonezawa [a,2], Tatsuo Shimizu [a]**

[a] *Department of Electrical and Computer Engineering, Kanazawa University, Kodatsuno, Kanazawa 920-8667, Japan*

[b] *Industrial Research Institute of Ishikawa, Tomizu, Kanazawa 920-0223, Japan*

**Abstract**

The effect of ambient gas on the preparation of $YBa_2Cu_3O_x$ (YBCO) high-$T_c$ superconducting thin films by pulsed laser ablation was explored in gas mixtures of argon + oxygen, argon + nitrous oxide, and nitrous oxide + oxygen. These experiments revealed that a reducing environment for the preparation of YBCO films enhances the film growth with the high temperature phase (trilayered perovskite YBCO) rather than the low temperature phase (cubic YBCO). This phenomenon is explained in terms of thermodynamic phase diagram. The effect of nitrous oxide on the thermodynamic phase diagram is far smaller than that of oxygen by a factor of two to three orders of magnitude.

PACS: 61.10.-i, 74.70.Vy, 74.75.+t, 81.30.-t

---

[1] Corresponding author: Tel +81-76-234-4876, Fax +81-76-234-4900, amorimot@ec.t.kanazawa-u.ac.jp

[2] On leave from the Industrial Research Institute of Ishikawa.

Keywords:

$YBa_2Cu_3O_x$ films, PLD, reducing environment, nitrous oxide, argon, oxygen

## 1. Introduction

It is very important for growth of high-quality films to clarify the effect of ambient gas and the mechanism of film growth in pulsed laser ablation (PLA). So far, the effect of ambient gas in PLA has been studied for high-$T_c$ materials using $O_2$, $N_2O$, $NO_2$ , and $O_3$ gases [1-3]. They mainly discussed the effect of atomic oxygen from the viewpoint of the gas phase oxidation and insisted that $N_2O$, $NO_2$ , and $O_3$ gases are more effective for oxidation of depositing particles than $O_2$ gas. Kuhle et al. reported the effect of Ar dilution in PLA deposition using $O_2$ gas on the surface morphology and the superconducting properties [4]. The effect of oxidation gas pressure for in situ preparation [5,6] and post-deposition annealing [7] of the $YBa_2Cu_3O_x$ (YBCO) films in various oxidation environments were also investigated. In most of these experiments, the excitation effect and the thermodynamical effect of ambient oxidation gas on the structure and properties of YBCO films are not necessarily discriminated. Thus, the effect of ambient gas is still controversial.

In the present study, the effect of ambient gas on the preparation of YBCO high-$T_c$ superconducting thin films by PLA was explored for high-quality film synthesis with a low substrate temperature. Gas mixtures employed are $Ar + O_2$, $Ar + N_2O$ , and $O_2 + N_2O$. The point of this study is the simplified preparation condition for discussing the effect of ambient gas from the viewpoint of the thermodynamic phase diagram. First, the second harmonic of YAG laser with a wavelength of 532 nm was used instead of UV excimer lasers, because no direct excitation of the ambient gas by the incident laser light with this wavelength is expected. Second, the total pressure of gas mixture was kept at 40 Pa using inert Ar gas for maintaining the similar expansion of the

ablation shock-front. Otherwise, a change of the total gas pressure in a wide dynamic range is expected to bring about a large change in the dynamics of ablated particles.

## 2. Experimental

The pulse duration, the laser fluence, and the repetition rate of YAG laser were 7 ns, 2.6 J/cm$^2$, and 2 Hz, respectively. Substrates employed were (100) MgO annealed at 1200 °C for 5 hours in oxygen flow of atmospheric pressure for excellent reproducibility of YBCO crystal orientation [8]. The substrate temperature was varied from 560 to 760 °C. The thickness of various films was nearly constant under the constant ambient gas pressure, irrespective of the gas composition. After the deposition, YBCO films were cooled down to the room temperature at a rate of 5 °C/min in an oxygen environment of 100 hPa.

## 3. Results and discussion

Figure 1 shows X-ray diffraction (XRD) spectra of films prepared in various oxidation environments at a substrate temperature of 620 °C. In 100 % $O_2$ environment the film shows (100) and (200) diffraction peaks without any diffraction peaks from the c-axis-oriented YBCO. These two diffraction peaks are conventionally ascribed to a-axis-oriented YBCO. The reduction of the fraction of $O_2$ gas reduces the intensity of diffraction peaks from the a-axis-oriented YBCO. The highly reducing environment with 0.03 % $O_2$ enhances the diffraction peaks from the typical c-axis-oriented YBCO. The perfect reducing environment with 0 % $O_2$ shows no diffraction peaks from the film, suggesting that the YBCO is unstable in the completely reducing environment. The broad and weak diffraction peak around $2\theta$=22 ° is the formally forbidden one arising from the MgO substrate due to some imperfection.

On the contrary, films prepared in the gas mixture of Ar + $N_2O$ also show the ambient dependence of the XRD spectra largely different from Fig. 1. The films prepared in the gas mixture of Ar + $N_2O$ were found to have the c-axis-oriented YBCO structure throughout the whole gas fraction range without any diffraction peaks from a-axis-oriented YBCO. Films prepared in the gas mixture of $N_2O$ + $O_2$ show the ambient dependence of the XRD spectra similar to Fig. 1. The film prepared even in the environment of 0 % $O_2$, however, was found to have the c-axis-oriented YBCO structure because of the presence of $N_2O$.

Figure 2 shows the XRD intensity of (200) and (006) diffraction peaks of YBCO films as a function of the fraction of oxidation gas in two gas-mixtures. For Ar + $O_2$ gas mixture, with a decrease in the fraction of $O_2$ gas the (006) intensity increases and the (200) intensity decreases. For Ar + $N_2O$ gas mixture, the (006) intensity increases with a decrease in the fraction, and then decreases after passing a maximum at approximately 10 % $O_2$. No (200) diffraction peak can be seen. An excessively reducing environment prevents crystallization for both series of films. As the $O_2$ fraction is decreased, there is a large difference in the gas fraction by a factor of three orders of magnitude for obtaining the same (006) intensity between Ar + $O_2$ and Ar + $N_2O$ gas mixtures. The results for the films prepared in the gas mixture of $N_2O$ + $O_2$ were similar to the Ar + $O_2$ case. For comparison, the XRD spectra for YBCO films prepared in pure $O_2$ gas with various $O_2$ pressures were also investigated. The result revealed that the (200) intensity increases without the appearance of the (006) diffraction peak with a decrease in the $O_2$ pressure, suggesting an opposite trend probably caused by the crystallization enhancement due to suppression of scattering and cooling of depositing particles by ambient gas. This reveals the importance of how to select the preparation condition for discussing the pure effect of oxidation gas.

The resistivity of these films prepared in the Ar + $O_2$ gas mixture as a function of the

temperature (ρ-T) was measured. The result revealed that the film with the (200) orientation prepared in 50 % $O_2$ shows a semiconducting behavior while the film with the (006) orientation prepared in 0.03 % $O_2$ shows a superconducting transition at approximately 40 K, suggesting that the former film has a non-superconducting phase while the latter film has a superconducting phase. Figure 3 is the X-ray pole figure of the film prepared at a substrate temperature of 640 °C in pure $O_2$ gas. The MgO substrate with the YBCO film was loaded on the sample holder in order to align the [001]- and [100] directions of the MgO substrate along Ψ=0 and Φ=0, respectively. The diffraction plane used for this measurement is (110) , (103) or (013) plane in the trilayered perovskite YBCO (t-YBCO) phase. This figure revealed that the normal direction of this plane is directed to Ψ = 45 degree, and this plane has approximately four-fold rotational symmetry without any other orientations. These results suggest that the YBCO film is epitaxially grown on the MgO substrate. The result of the ρ-T and the X-ray pole figure measurements suggest that this films has a cubic YBCO phase (c-YBCO) with a-axis-orientation. The identification of the c-YBCO phase was reported using XRD and transmission electron microscopy (TEM) measurements by Agostinelli et al. [9]. They assigned the metastable phase formed by PLA with KrF excimer laser in 13 to 26 Pa of $O_2$ on the MgO substrate held at a low temperature to a c-YBCO phase where Y and Ba ions occupy the A cation site of $ABO_3$ perovskite structure with random distribution and Cu ions occupy the B sites. The c-YBCO was reported to be a non-superconductor down to 4 K. The present preparation condition for these films is very similar to that of Agostinelli et al., except for the kind of the laser used. Hereafter, we assign the phase formed in highly oxidizing environment to the c-YBCO.

For confirmation of the above idea, the phase transition of YBCO depending on the preparation temperature was examined. Below the substrate temperature of 670 °C the (200)

diffraction is dominant while above this temperature the (006) diffraction is dominant. The a-axis -oriented c-YBCO films prepared in a high oxidation environment at a low substrate temperature were found to be turned to the c-axis-oriented t-YBCO with an increase in the substrate temperature. This result is similar to that for the films prepared by PLA using ArF excimer laser in $O_2$ gas on the same MgO substrates [8].

These results suggest that a reducing environment enhances the film growth of YBCO with a high temperature phase while a highly oxidizing environment, that is, an oxidation gas of pure $O_2$ gas of 40 Pa, produces the film with a low temperature phase. These results can be interpreted in terms of the phase diagram of YBCO, $O_2$ partial pressure vs. the reciprocal temperature, reported by Hammond and Bormann [5], Matijasevic et al. [6], and Feenstra et al. [7]. That is, the change in the preparation condition into the higher temperature and/or the lower $O_2$ partial pressure melts or destabilizes the YBCO film. In other words, the reducing environment decreases the melting and/or decomposition temperature followed by a reduction of the growth temperature, leading to the enhancement of the growth of high temperature phase at the low temperature.

The c-lattice parameters of these c-axis-oriented t-YBCO films prepared in Ar + $O_2$ and Ar + $N_2O$ gas mixtures are plotted against the gas fraction in Fig. 4. The horizontal dotted line indicates the equilibrium value for $YBa_2Cu_3O_7$. The c-lattice parameters for both series of the films are much larger than that for the equilibrium value while it seems that the c-lattice parameter decreases with a decrease in the fraction of oxidation gas. The large c-lattice parameter suggests the oxygen deficiency in the t-YBCO structure. It should be noted that there is a large difference in the fraction for obtaining the same c-lattice parameter between the two oxidation gases. The difference is as large as two to three orders of magnitude. The different results obtained in Ar + $O_2$

and Ar + $N_2O$ gas mixtures indicate that the effect of $N_2O$ on thermodynamic phase diagram is less than 1/100 of the effect of $O_2$. This finding is consistent with the result that there is no essential difference in the XRD spectra as a function of the gas fraction between Ar + $O_2$ and $N_2O$ + $O_2$ except for the limit of 0 % $O_2$.

Consistent with the vaule of the c-lattice parameter, the critical temperature $T_c$ of the YBCO films prepared by the reducing environment is quite low in spite of the presence of sufficient oxygen during the cooling, compared with the films prepared in highly oxidizing environment. For clarification of the origin of the $T_c$ degradation and the oxygen deficiency, the intensity ratio of (006) to (005) peaks was investigated for c-axis-oriented t-YBCO films prepared in three series of oxidation gas mixtures. The result shows that the values for all the films are in the range between 1.6 and 2.7 even after the low temperature annealing below the deposition temperature at 100 hPa. The reported value for the high quality YBCO film is 1.4 [10]. Thus it was found that the larger value than the ideal one is not simply coming from the oxygen deficiency but coming from the cation disorder. Ye and Nakamura reported that films prepared at a low substrate temperature show the cation disorder between Y and Ba atoms based on an analysis of the intensity ratio of (006) to (005) XRD peaks and the disorder is not removed by the low temperature annealing in oxidation environment [10]. Therefore, the present films exhibit cation disorder although the high temperature phase is obtained in the reducing environment even at the low temperature.

**4. Conclusions**

The effect of ambient gas on the preparation of $YBa_2Cu_3O_x$ (YBCO) high-$T_c$ superconducting thin films by PLA using (100)MgO substrates was explored from the viewpoint of

thermodynamic phase diagram. These experiments revealed that a reducing environment for the preparation of YBCO films enhances the film growth with a high temperature phase. This phenomenon is explained in terms of the thermodynamic phase diagram; the reducing environment decreases the melting and/or decomposition temperature followed by a decrease in the growth temperature, leading to an enhancement of the growth of the high temperature phase at low temperature. The effect of nitrous oxide on the thermodynamic phase diagram is far smaller than that of oxygen by a factor of two to three orders of magnitude. The YBCO films with the high temperature phase prepared in the reducing environment at low temperature include some cation disorder, resulting in a poor superconducting property. Based on the present results, an excitation of oxidation gas should be required for obtaining a high quality film at the low substrate temperature.

**Acknowledgements**

The authors thank Prof. M. Kumeda for helpful discussions and H. Yoshida of the Industrial Research Institute of Ishikawa for supporting our experiments. We acknowledge K. Nagai and E. Kitajima for performing the experiments and Shibuya Kogyo Co., Ltd. for supplying the ArF excimer laser. We also acknowledge Dr. K. Shiratsuyu of Murata Mfg. Co., Ltd. for measurements of the X-ray pole figure. The present work was partly supported by the Grant-in-Aid for Developmental Scientific Research (C) No. 0865008 from the Ministry of Education, Science, Sports, and Culture of Japan.

**References**

[1] G. Koren, A. Gupta, and R. J. Baseman, Appl. Phys. Lett. **54** (1989) 1920.

[2] C. E. Otis, A. Gupta, and B. Braren, Appl. Phys. Lett. **62** (1993) 102.

[3] A. Gupta, J. Appl. Phys. **73** (1993) 7877.

[4] A. Kuhle, J. L. Skov, S. Hjorth, I. Rasmussen, and B. Hansen, Appl. Phys. Lett. **64** (1994) 3178.

[5] R. H. Hammond and R. Bormann, Physica C **162-164** (1989) 703.

[6] V. Matijasevic, P. Rosenthal, K. Shinohara, A. F. Marshall, R. H. Hammond, and M. R. Beasley, J. Mater. Res. **6** (1991) 682.

[7] R. Feenstra, T. B. Lindermer, J. D. Budai, and M. D. Galloway, J. Appl. Lett **69** (1991) 6569.

[8] T. Minamikawa, T. Suzuki, Y. Yonezawa, K. Segawa, A. Morimoto, and T. Shimizu, Jpn. J. Appl. Phys. **34** (1995) 4038.

[9] J. A. Agostinelli, S. Chen, and G. Braunstein, Phys. Rev. B **43** (1991) 11396.

[10] J. Ye and K. Nakamura, Phys. Rev. B **50** (1994) 7099.

FIGURE CAPTIONS

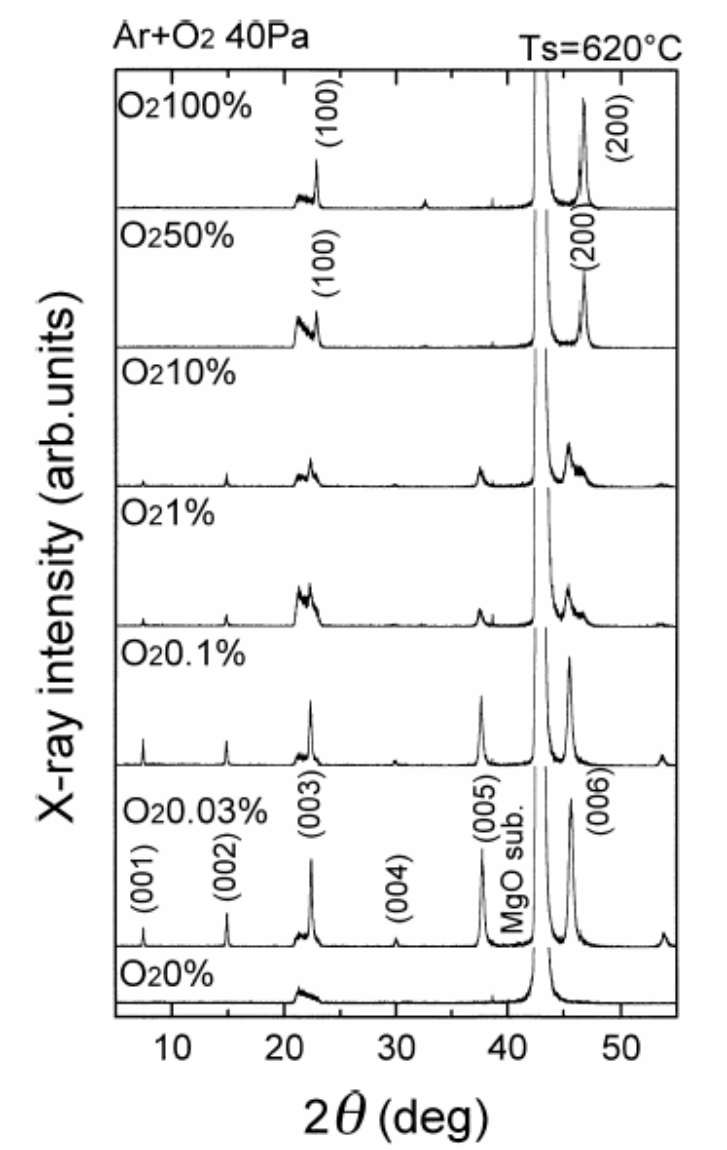


Fig.1. XRD spectra of films prepared in various oxidation-environments at a substrate temperature of 620 °C.

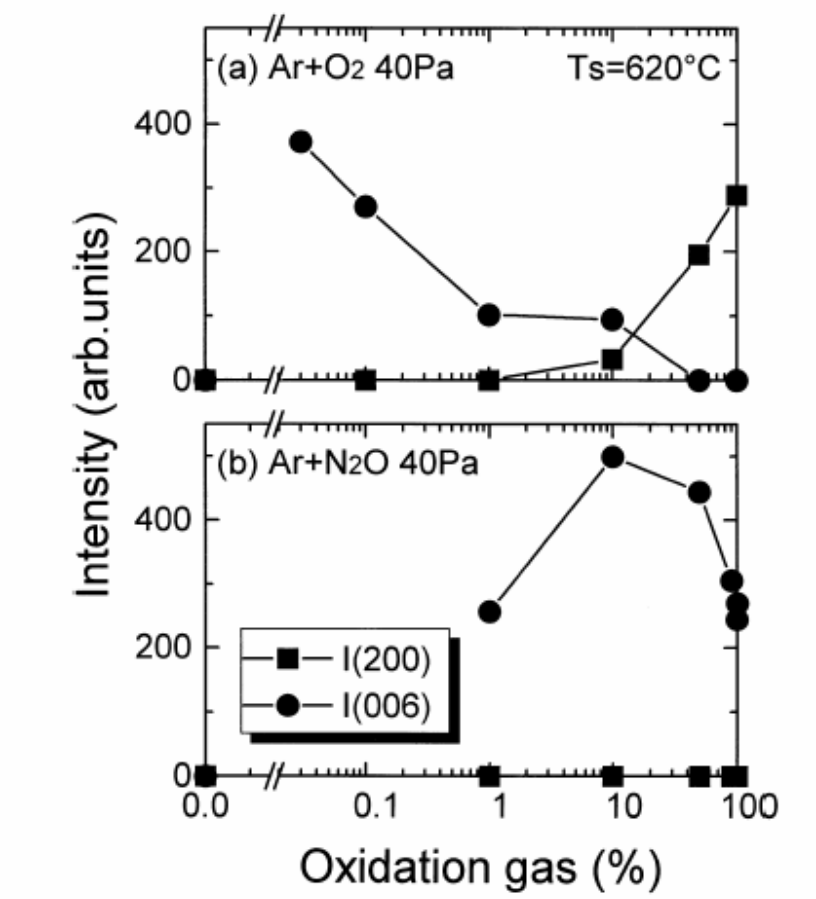


Fig. 2. XRD intensity of (200) and (006) diffraction peaks of YBCO as a function of the fraction of oxidation gas in the two gas mixtures: (a) Ar + $O_2$ and (b) Ar + $N_2O$.

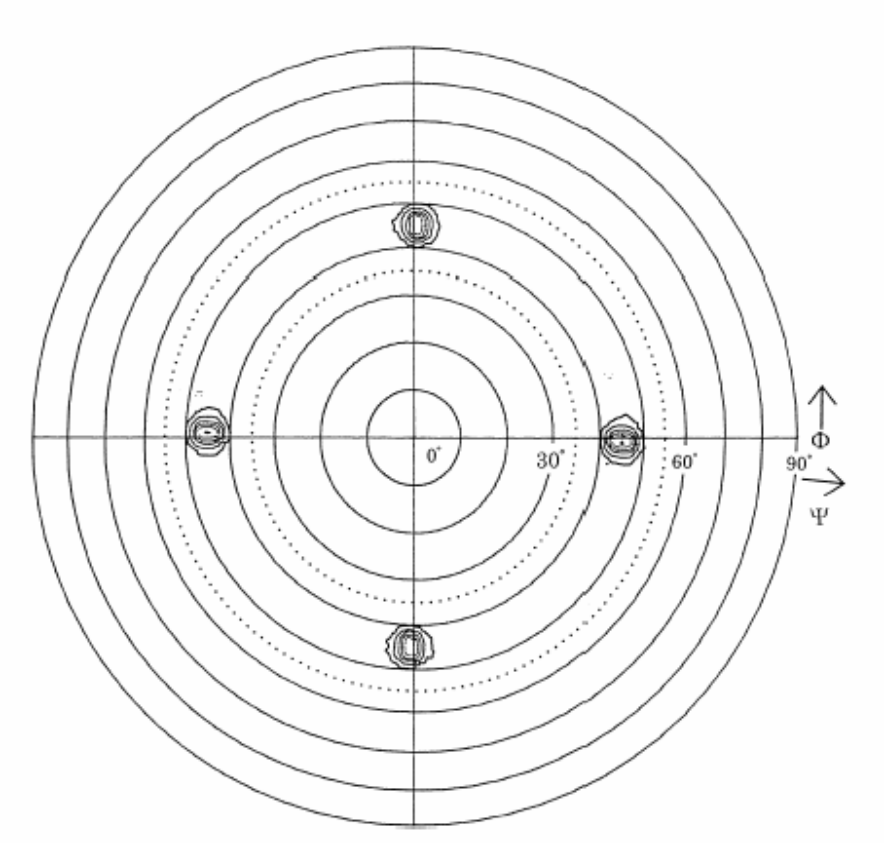


Fig. 3. X-ray pole figure of the film prepared at 640 °C in the pure $O_2$ of 40 Pa. The diffraction plane used for this measurement is (110) , (103) or (013) plane in formulation of the trilayered YBCO perovskite phase.

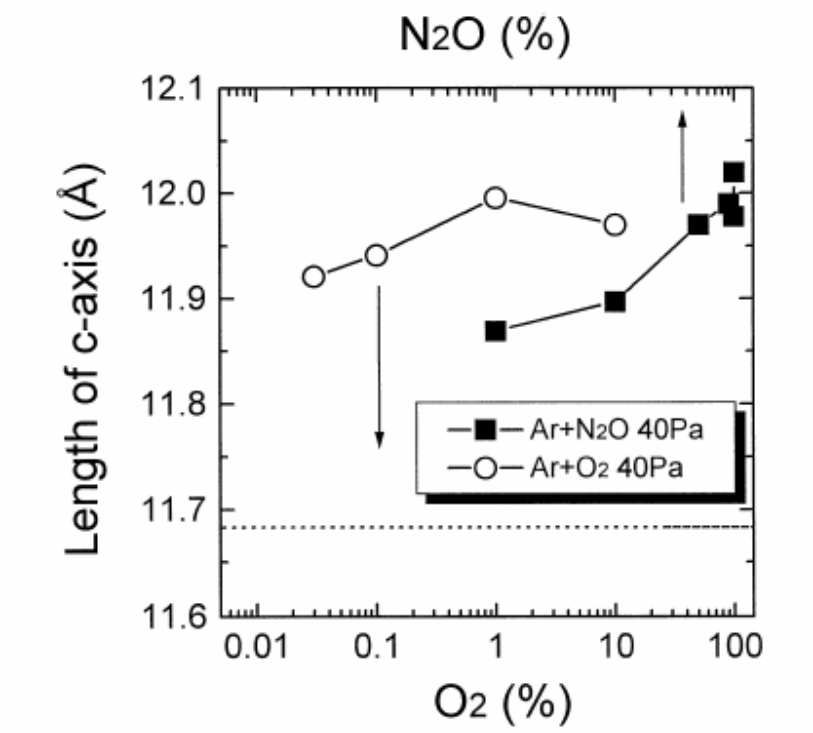


Fig. 4. c-lattice parameter of c-axis-oriented t-YBCO films prepared in Ar + $O_2$ and Ar + $N_2O$ gas mixtures. The horizontal dotted line indicates the equilibrium value of 11.68 A for $YBa_2Cu_3O_7$.

Total: 2,655 words + 200 words x 4 figures = 3,455 words ; limits: 3,500 words / 6 printed pages