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Accuracy of energy dispersive x-ray composition analysis of YBCO films on yttrium-containing substrates as compared to Rutherford backscattering spectroscopy

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We address the accuracy of Energy Dispersive X-ray Spectroscopy (EDS) composition analysis of $YBa_2Cu_3O_{7-x}$ (YBCO) thin films. YBCO films deposited on yttrium stabilized zirconia (YSZ) and strontium titanate (STO) substrates were analyzed by EDS and Rutherford Backscattering Spectrometry (RBS) to determine their compositions. The YSZ substrates used in this work contained a common element, yttrium; therefore, EDS intensities of yttrium signals resulting from the film alone were calculated using EDS results of blank YSZ substrates. The EDS compositions of all the elements were obtained using the proportionality factor, k calculated from RBS data from a standard film deposited on silicon and the intensity ratios of the respective standard obtained from EDS. The film thickness was found to be an important factor to consider when choosing the optimum accelerating voltage for the EDS analysis. For films having comparable thickness to that of the standard (~0.8 μm), we found 25 kV was the optimum accelerating voltage for the EDS analysis that obtained compositions in good agreement with the RBS data. For films having half the thickness of the standard film, EDS composition analyses were unreliable quantitatively and were best qualitatively at 15 kV. © *2000 Kluwer Academic Publishers*

1. Introduction

Thin films of $YBa_2Cu_3O_{7-x}$ (YBCO) have played an increasingly pronounced role in electronic applications of high-T_c superconductors (HTSC). Applications of YBCO thin films include interconnects, filters, delay lines, bolometer [1] and superconducting quantum interference devices (SQUIDs). Numerous deposition techniques have been used to prepare YBCO thin films. In order to optimize these thin-film deposition techniques, information on crystalline structure, chemical composition, and the degree of homogeneity of the film is required.

There are many methods of determining the composition of YBCO superconducting films. Table I summarizes the different methods of film characterization, their advantages and disadvantages. Commonly used methods such as Auger Electron Spectroscopy (AES) or Secondary Ion Mass Spectroscopy (SIMS) are, however, destructive. In addition, samples under investigation can be unintentionally modified by preferential ion sputtering yielding inaccurate results.

One accepted technique for composition analysis of YBCO thin films is Rutherford backscattering spectrometry (RBS). It is preferred because it is non-destructive, has high depth resolution and high elemental or isotopic sensitivity [2]. In addition to this, in thin-films analysis, the backscattering signals of both the front and the substrate-film interfaces are identifiable [3]. The most ideal sample for backscattering spectrometry is one with the elements in the film of higher atomic numbers than those present in the substrate. This is because the signal of the heavier elements from the film will appear at the higher energy end of the spectrum and will be unaffected by the low energy signal coming from the substrate. Thus, these discernible signals facilitate the analysis of the backscattering spectrum. Therefore, RBS is a preferred method for analyzing samples of YBCO thin films, particularly those deposited on carbon or silicon substrates.

While RBS can provide simple, straightforward composition analyses, EDS is more readily available and when coupled with scanning electron microscopy

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TABLE I The advantages and disadvantages of different film characterization methods

Methods	Advantages	Disadvantages
Auger Electron Spectroscopy (AES) Secondary Ion Mass Spectroscopy (SIMS)	• Readily available in most facilities	• Induce modification of samples, thus, deemed as destructive methods.
Inductive Couple Plasma Spectroscopy (ICPS)	• Readily available in most facilities	• Difficult to find a dissolving agent. • Deemed as a destructive methods.
Rutherford Backscattering (RBS)	• Non-destructive method	• Expensive, occupies space. • Not available in most facilities.
Energy Dispersive X-ray Spectrometry (EDS)	• Non-destructive method • Readily available in most facilities • Composition mapping available	• Not easily calibrated. • Common element between films and substrates cause overlapping signals.

(SEM), it can give important composition mapping to provide information on film homogeneity at micron scale. The reasons for the infrequent use of EDS for HTSC thin films composition analyses have never been clearly addressed in the literature.

In this work, EDS was used in conjunction with RBS for thin film composition analyses and results are compared for a variety of films. Beside the standards (YBCO films on silicon substrates), films deposited on yttrium stabilized zirconia (YSZ) were also analyzed. This is because YSZ substrates are being used extensively in the growth of YBCO thin films as they form an interfacial $BaZrO_3$ buffer layer that can provide a barrier layer against further reaction between the substrate and the film [4–6]. For electronic applications, where substrates such as Al_2O_3 and Si are favored, epitaxial buffer layers such as YSZ are required for these reactive substrates [7–9].

Our paper focuses on the accuracy issue of the EDS composition analyses and how film thickness and accelerating voltages affect the results.

2. Experimental

2.1. Thin film preparation

To overcome the hydroscopic problem of YBCO films, we used YBCO precursor films consisting of co-evaporated yttrium, BaF_2, and CuO_x which are more robust for handling. Thin films were prepared by the co-evaporation of yttrium, BaF_2 and copper with electron-beam/thermal sources at room temperature [10]. Yttrium and BaF_2 were evaporated using electron-beam guns while copper was evaporated using a resistively heated source. These three sources were in a triangular configuration with respect to the substrate holder. The system background pressure was 2×10^{-6} Torr and the oxygen pressure at the substrate was 5×10^{-5} Torr. The combined deposition rates from the three sources (BaF_2, Y_2O_3, and Cu), ranging from 0.5–1.0 nm/s, were monitored using three separate quartz oscillators. The substrates used were YSZ (10% Y_2O_3), silicon, and strontium titanate (STO). The films on Si and STO have the same composition of the corresponding films on YSZ since they were placed (two different substrates of each pair) side by side in the same co-evaporation run. The films on Si and STO substrates were used as the standards to compare RBS to EDS data. The thickness of the films was either 0.5 or 0.9 μm approximately (Table II) and they were homogeneous.

TABLE II The YBCO standard films thicknesses and composition as measured by RBS

Sample[a]	Standard substrate	Thickness (μm)	Normalized composition (RBS data) of the standards (Y, Ba, Cu)
E104/Si	Si	0.862	0.113, 0.321, 0.566
E105/Si	Si	0.879	0.151, 0.283, 0.566
E150/STO	$SrTiO_3$	0.470	0.110, 0.370, 0.520
E119/Si	Si	0.870	0.079, 0.379, 0.542

[a] Samples E104, E105, E150 on YSZ substrates are expected to have same thickness and compositions as they were co-evaporated simultaneously with those deposited on Si and STO.

2.2. RBS measurements of standard films

The RBS measurements were performed on the YBCO films on Si substrates. The compositions of Y, Ba and Cu for the standards were normalized and are tabulated in Table II.

2.3. EDS measurements

The EDS measurements on all the samples and standards were performed in an AMRAY 1400 scanning electron microscope at 250× magnification.* The tilt angle was set at 45°, the working distance was 16 mm and the collecting time was 100 seconds. Five random spots in each sample were chosen to collect data and the average values of these five measurements were used in the calculations.

A crucial factor which will influence the accuracy of EDS measurements is the accelerating voltage of the system. In this work, we study the effect of different accelerating voltages. If the accelerating voltage is too low, the elements in the sample will be poorly excited, producing insufficient counts for a thorough analysis. On the other hand, if the accelerating voltage is too high, the penetration depth will be greater and deeper into the substrate, giving extra signals from the substrate. Moreover, secondary fluorescence may occur and will contribute to an erroneous analysis of the samples [11]. The accelerating voltages of the EDS were 10, 15, 20

* In order to perform an accurate analysis of the thin films from the EDS data, all the operating conditions of the SEM/EDS system should be kept the same for all the samples. The parameters that should be taken into account are the tilt angle of the sample towards the detector, the working distance, the signal collection time, and the beam current. These variables must be kept constant for all EDS spectra obtained.

and 25 kV. In addition to this, EDS measurements at 30 kV were performed on three YBCO film/substrate samples (E104/YSZ, E105/YSZ) and standard E119/Si. The signals used for composition analyses of yttrium, barium and copper were that of the K_α lines.

The advantage of using thin film standards is that the measurements can be made for the same operating conditions used for the specimen. Thin film standards were analyzed according to the Cliff-Lorimer method. Cliff and Lorimer [12] have proposed an analysis method where the x-ray intensity ratio of the elements present in the thin film is related directly to their mass concentration ratio:

$$\frac{C_A}{C_B} = k_{AB}\frac{I_A}{I_B} \tag{1}$$

where k_{AB} is the proportionality factor; C_A and C_B are the concentrations of elements A and B respectively; and I_A and I_B are the intensities of the characteristic x-ray lines of A and B. The term k_{AB} is independent of the sample thickness and composition so long as the thin film criterion is satisfied; however, it varies with the operating voltage of the instrument.

Cliff and Lorimer have shown that if the composition of a thin film is known, the thin film specimen can be used as a standard. If the characteristic x-ray intensities of the two elements in the standard, I_A and I_B, are measured simultaneously from the same point, and the composition C_A and C_B in the standard is known, then the proportionality factor k_{AB} can be determined empirically. The k_{AB} value for each operating voltage was calculated for the standards using the concentration and intensities data obtained from RBS and EDS, respectively.

Using these k_{AB} values, we calculated the composition of the YBCO thin film, and compared the values to that obtained from the standards using RBS. We concluded that the optimum voltage for the EDS system was the one that gave us the least deviation from the RBS composition values.

3. Results and discussions

The yttrium characteristic x-ray intensities of the YBCO thin films on substrates obtained from the EDS techniques are actually the sum of the Y-signals coming from the film and the substrate. Therefore, we needed a method to calculate the intensity of the Y signal originating from the film out of the Y signal from the film-on-substrate sample. This can be accomplished in several steps:

1) Making use of EDS measurements of blank YSZ substrates, the yttrium signal coming from the substrate alone is given by

$$I_{Y,s,f+s} = \left(\frac{I_{Y,s,s}}{I_{Zr,s,s}}\right) \bullet I_{Zr,s,f+s} \tag{2}$$

2) Obtaining the yttrium signal coming from the film alone from

$$I_{Y,f,f+s} = I_{Y,f+s,f+s} - I_{Y,s,f+s} \tag{3}$$

The notation in the above equations is as follows:

$I_{i,j,k}$ = general format
I = the intensity of the characteristic line
i = the element in question (Zr, Y, Ba or Cu)
j = the location where the signal is coming from (blank substrate: s, film: f, film and substrate: f+s)
k = the sample under analysis (blank substrate: s, film-on-substrate: f+s)

Thus, we first obtained the EDS measurement of a blank YSZ substrate in order to get the Y and Zr intensities. Using Equation 2, we then calculated the intensity of the Y signal originating from the substrate alone of the film-on-substrate sample by using the Y/Zr singal ratio of a blank YSZ substrate. This calculated value was then substituted into Equation 3 to give the intensity of Y signal originating from the film of the film alone. Table III is an example of how the final value was calculated for sample E104/YSZ at an accelerating voltage of 10 kV.

Next, we calculated the k_{AB} value of E119/Si standard using the Cliff-Lorimer equation (Equation 1). We then used this k_{AB} value to calculate the relative composition of yttrium, barium and copper for each film using the corresponding EDS intensities. Table IV illustrates how this next step was carried out.

Similar calculations were performed for the standard film E119/Si at different accelerating voltages. Table V gives the corresponding k-values. Table VI summarizes the final normalized EDS composition (fraction of the elements) of all the samples evaluated using E119/Si as the standard at all accelerating voltages used. The deviation in compositions of the thin films is defined as the difference of the calculated EDS compositions

TABLE III Step-by-step calculation of the intensity of Y signal from the film alone derived from EDS intensities of film-on-substrate sample

Sample	E104/YSZ
Accelerating voltage	10 kV
$I_{Ba,f,f+s}$ measured (Intensity of barium signal from the film of the film-on-substrate sample)	0.521
$I_{Cu,f,f+s}$ measured (Intensity of copper signal from the film of the film-on-substrate sample)	0.349
$I_{Y,s,s}$ measured (Intensity of yttrium signal from the blank substrate)	0.137
$I_{Zr,s,s}$ measured (Intensity of zirconia signal from the blank substrate)	0.862
$I_{Zr,s,f+s}$ measured (Intensity of zirconia signal from the film-on-substrate sample)	0.022
Using Equation 2, $I_{Y,s,f+s}$ is calculated (Intensity of yttrium signal from the substrate of the film-on-substrate sample)	$(0.137/0.862) * 0.022 = 0.004$
$I_{Y,f+s,f+s}$ measured (Intensity of yttrium signal from the film and substrate of the film-on-substrate sample)	0.117
Using Equation 3, $I_{Y,f,f+s}$ is calculated (Intensity of yttrium signal from the film of the film-on-substrate sample)	$0.117 - 0.004 = 0.114$

TABLE IV Sample calculation of the k values and EDS compositions of a YBCO film

Standard	E119/Si
Accelerating voltage	10 kV
$I_{Ba,f,f+s}$ measured (Intensity of barium signal from the film of the film-on-substrate standard)	0.626
$I_{Cu,f,f+s}$ measured (Intensity of copper signal from the film of the film-on-substrate standard)	0.260
$I_{Y,f+s,f+s}$ measured (Intensity of yttrium signal from the film and substrate of the film-on-substrate standard)	0.099
C_Y (RBS data)	0.079
C_{Ba} (RBS data)	0.379
C_{Cu} (RBS data)	0.542
$k_{Ba,Y} = C_{Ba}/C_Y * I_{Y,f+s,f+s}/I_{Ba,f,f+s}$ (Calculation of k_{AB} constants using RBS determined compositions and EDS intensities for the same film)	$= 0.379/0.079 * 0.099/0.626 = 0.752$
$k_{Cu,Y} = C_{Cu}/C_Y * I_{Y,f+s,f+s}/I_{Cu,f,f+s}$	$= 0.542/0.079 * 0.099/0.260 = 2.592$
Analysis of E104/YSZ using E119/Si as standard: Taking $C'_Y = 1$	
$C'_{Ba} = k_{Ba,Y} * I_{Ba,f,f+s}/I_{Y,f+s,f+s}$	$C'_{Ba} = 0.752 * 0.521/0.114$ $C'_{Ba} = 3.453$
$C'_{Cu} = k_{Cu,Y} * I_{Cu,f,f+s}/I_{Y,f+s,f+s}$	$C'_{Cu} = 2.592 * 0.349/0.114$ $C'_{Cu} = 7.940$
(Concentrations in film determined using k_{AB} from the previous step and EDS)	
Normalized EDS composition of YBCO film of sample E104/YSZ	$C_Y = 0.081$ $C_{Ba} = 0.278$ $C_{Cu} = 0.642$

from the measured RBS data of the standards. We plotted these deviations against the accelerating voltages for each element detected: Y, Ba and Cu in Figs 1–3 respectively.

TABLE V Calculated k values for E119/Si standard at different accelerating voltages

Accelerating voltage (kV)	$k_{Ba,Y}$	$k_{Cu,Y}$
10	0.752	2.592
15	0.709	0.713
20	0.587	0.616
25	0.764	0.793
30	3.365	3.294

For samples E104/YSZ and E105/YSZ, whose thicknesses were approximately 0.8 and 0.9 μm (comparable to thickness of the standard film E119/C) the fractional deviations from RBS results were small (−0.001 to 0.02) when the accelerating voltages were between 15 and 25 kV. At 30 kV, the deviations became large again, and the proportionality factors, k_{AB} were significantly larger than that at lower voltages. However, for samples E150/YSZ and E150/STO, which have much thinner YBCO films (around 0.5 μm), the optimum accelerating voltage for the EDS system that gave the lowest variation was 15 kV.

More specifically, Fig. 1 shows the deviation of the normalized composition from RBS data for yttrium. At low accelerating voltages, 10 kV for example, the normalized compositions for all the samples were lower than the RBS data. This indicates that there were insufficient counts from the EDS data because the samples were poorly excited. The same trend was also observed for the barium compositions in Fig. 2. As the accelerating voltage increased, the deviation gradually approached zero. The optimum accelerating voltage for samples E104/YSZ and E105/YSZ was around 25 kV for yttrium and between 15 and 20 kV for barium.

The analysis on the composition of copper, on the other hand, exhibited different results. Fig. 3 shows that at 10 kV, the normalized compositions were higher than those obtained from the RBS data; thus, the deviations were positive. Copper has a lower atomic mass

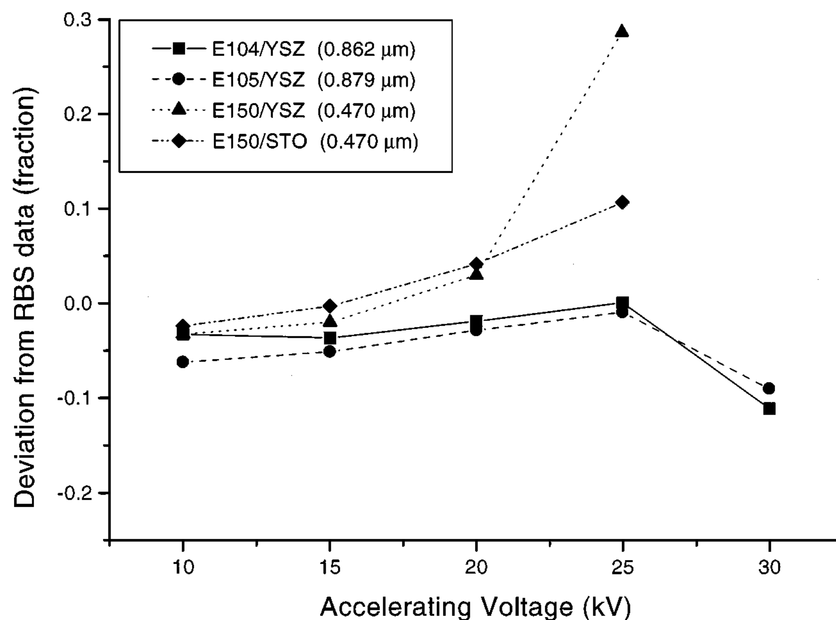

Figure 1 Deviation of EDS determined composition from RBS data for yttrium.

TABLE VI The final normalized EDS compositions of the samples analyzed with their corresponding deviations

Sample	C_Y (RBS data)	C_{Ba} (RBS data)	C_{Cu} (RBS data)	C_Y (Normalized)	C_{Ba} (Normalized)	C_{Cu} (Normalized)	Variance in C_Y	Variance in C_{Ba}	Variance in C_{Cu}
10 kV									
E104 (YSZ)	0.113	0.321	0.566	0.081	0.278	0.642	−0.033	−0.043	0.076
E105 (YSZ)	0.151	0.283	0.566	0.089	0.173	0.739	−0.062	−0.113	0.173
E150 (YSZ)	0.110	0.370	0.520	0.077	0.308	0.615	−0.033	−0.062	0.095
E150 ($SrTiO_3$)	0.110	0.370	0.520	0.086	0.354	0.560	−0.024	−0.016	0.040
15 kV									
E104 (YSZ)	0.113	0.321	0.566	0.077	0.329	0.594	−0.036	0.008	0.028
E105 (YSZ)	0.151	0.283	0.566	0.100	0.283	0.617	−0.051	−0.0001	0.051
E150 (YSZ)	0.110	0.370	0.520	0.090	0.327	0.583	−0.020	−0.043	0.063
E150 ($SrTiO_3$)	0.110	0.370	0.520	0.107	0.418	0.474	−0.003	0.048	−0.046
20 kV									
E104 (YSZ)	0.113	0.321	0.566	0.095	0.323	0.583	−0.018	0.002	0.017
E105 (YSZ)	0.151	0.283	0.566	0.123	0.291	0.586	−0.028	0.008	0.020
E150 (YSZ)	0.110	0.370	0.520	0.140	0.284	0.576	0.030	−0.086	0.056
E150 ($SrTiO_3$)	0.110	0.370	0.520	0.152	0.457	0.392	0.042	0.087	−0.129
25 kV									
E104 (YSZ)	0.113	0.321	0.566	0.114	0.310	0.576	0.001	−0.011	0.0102\
E105 (YSZ)	0.151	0.283	0.566	0.142	0.283	0.576	−0.009	−0.0002	0.010
E150 (YSZ)	0.110	0.370	0.520	0.397	0.197	0.406	0.287	−0.173	−0.114
E150 ($SrTiO_3$)	0.110	0.370	0.520	0.217	0.492	0.291	0.107	0.122	−0.229
30 kV									
E104 (YSZ)	0.113	0.321	0.566	0.003	0.345	0.653	−0.11	0.024	0.087
E105 (YSZ)	0.151	0.283	0.566	0.061	0.314	0.626	−0.090	0.031	0.059

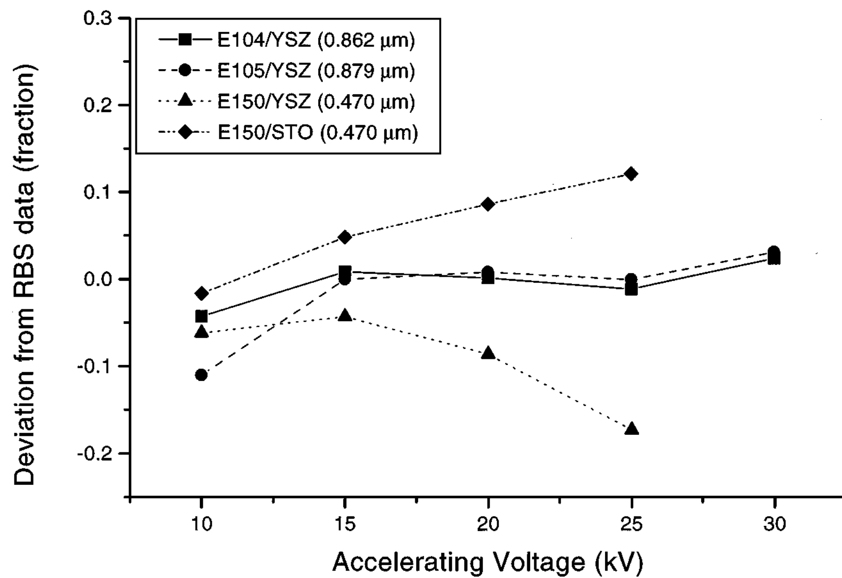

Figure 2 Deviation of EDS determined composition from RBS data for barium.

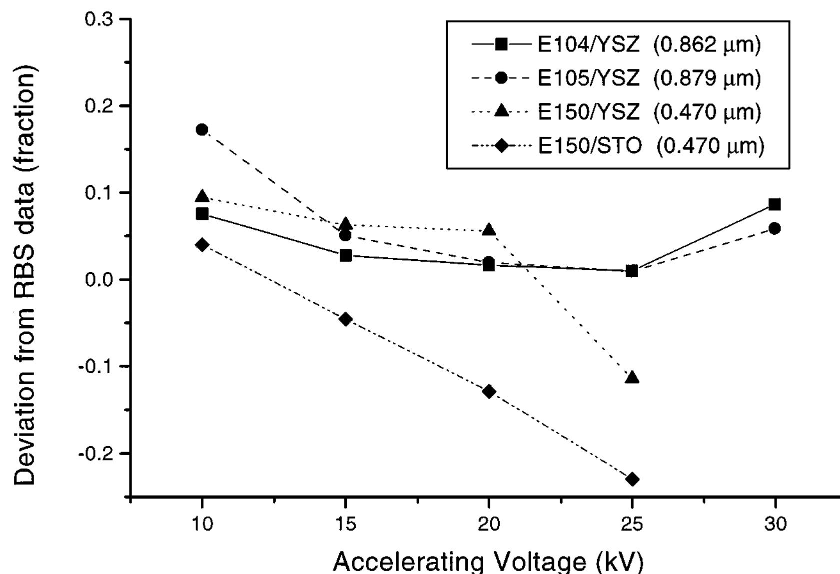

Figure 3 Deviation of EDS determined composition from RBS data for copper.

than yttrium and barium; therefore, the scattering factor would be different. As the accelerating voltage increased, the deviations approached zero and the least deviation for copper of samples E104 and E105 was between 20 and 25 kV. Therefore, we concluded that for films of comparable thickness as the standard, the optimal accelerating voltage is 25 kV.

However, for samples E150/YSZ and E150/STO, as the accelerating voltage was increased above 20 kV, the deviations in yttrium, barium and copper compositions changed enormously either increasing or decreasing rapidly (refer to Figs. 1–3). This discrepancy could be ascribed to the thicknesses of both samples which was around 0.5 μm (half the thickness of the standards). These samples seemed to produce significantly more reliable results at accelerating voltages around 15 kV. However, the results were not as quantitatively accurate as for the films whose thicknesses were similar to those of the standards used.

4. Conclusions

Though Rutherford backscattering spectrometry (RBS) is used widely for the characterization of the composition of YBCO thin films, Energy Dispersive X-ray Spectroscopy (EDS) may also be used as it is widely available in many laboratories. Since the accuracy of EDS analysis on YBCO thin films had never been addressed before, we used EDS in conjunction with RBS to document the extent of accuracy of composition analysis of YBCO thin films by EDS. We employed the Cliff-Lorimer method to analyze the thin film compositions with standard films. The optimum accelerating voltage for the EDS system which produced compositions that were in good agreement with the RBS data for Y, Ba and Cu was found to be at 25 kV for films having comparable thickness to that of the standard (0.8 and 0.9 μm). Accelerating voltages of 10 to 25 kV in general produced acceptable results. We also found that the thickness of the thin films is an important factor to consider when choosing the optimum accelerating voltage for the EDS analysis. For films having half the thickness of the standard film, EDS composition analyses are very unreliable quantitatively and are best qualitatively at 15 kV. Therefore, EDS analyses are best done with standards of comparable thickness.

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