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Analysis of stoichiometry of high- T_c superconducting films by RBS and PIXE methods

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Abstract

Lateral inhomogeneity has been studied in thin films of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ deposited from aerosol on MgO substrates. RBS and PIXE analyses distinguished areas that were found to differ in the critical temperature T_c values. The PIXE results confirmed the differences in composition between those areas. Variations in layer thicknesses were found by means of RBS analysis. Measurements made with a microbeam showed that the film within each of those areas was homogeneous. However, significant variations in the Y–Ba–Cu–O stoichiometry and local changes in the film thickness were found in the intermediate zone between areas with $T_c = 85$ K and $T_c \leq 80$ K.

1. Introduction

Since the discovery of high- T_c superconducting materials (HTS) by Bednorz and Muller [1], various systems have been developed and are well known, such as for instance the yttrium-base $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) material with critical temperature $T_c = 90$ K, the bismuth-base (BSCCO) with $T_c = 110$ K, and the thallium-base (TBCCO) with $T_c = 125$ K. Of these systems, YBCO material is still intensively studied in both bulk and thin film forms [2,3]. From the point of view of practical applications, thin films are of higher interest.

Nowadays, a number of physical vapour deposition (PVD) and chemical vapour deposition (CVD) methods are well developed and used for growing high- T_c films [4,5]. One such method is the chemical deposition from aerosol generated either by pneumatic nebulizer, or by ultrasonic excitations [6]. This was the method used for preparation of YBCO films which are the subject of the following study.

The superconducting properties of HTS materials depend strongly upon their chemical composition. Knowledge of the exact stoichiometry of the studied material is therefore of primary importance for improving the technol-

ogy and for the study and understanding of the basic physical properties and phenomena. HTS technology requires the analytical techniques flexible, fast, and non-destructive, with sufficient precision and accuracy. For the characterization of the structure of HTS materials, ion beam analytical techniques are widely used [7–9]. The RBS method has been used for determination of the composition and layer thickness, as well as for the study of layer mixing. The PIXE technique has been applied mainly for the determination of composition and for trace element analysis. Both methods are currently used for testing the lateral composition and homogeneity using the microbeam experimental setup.

This work follows up RBS and PIXE techniques previously developed for analyses of HTS materials [10–13]. In the case of analysis of YBCO material an accuracy of better than 3.3% for yttrium and better than 2.5% for barium and copper was achieved, with a precision of about 2–3%.

The aim of this present work is to demonstrate the application of the developed analytical techniques to non-standard HTS samples. The demonstration will be performed on a YBCO/MgO sample on which two different regions were formed after the thermal annealing of the precursor film. In the centre of the sample, an area with $T_c = 85$ K was formed, surrounded by an area with $T_c \leq 80$ K. In the following we will refer to these two areas as AREA-85 and AREA-80, respectively. Two analytical aspects were considered. In the first we tried to determine

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the average chemical composition and the film thickness in both, i.e. AREA-85 and AREA-80. For this purpose, standard (non-microbeam) RBS and PIXE methods were used. Next, we attempted to determine whether local concentration inhomogeneities could be observed, and if so, which areas were affected. Here, the microbeam experimental setup was applied.

2. Experimental details

2.1. Sample preparation

Our preparation process has already been described in detail elsewhere [14], therefore here we give only a very brief outline. In principle, our YBCO films were deposited from aerosol generated pneumatically from an aqueous solution of metallic Y, Ba and Cu nitrates. After the deposition, an annealing of the precursor Y–Ba–Cu–O films followed in an initial vacuum of 10^{-6} Torr, degraded by the partial pressure of oxygen to 10^{-4} Torr. As substrates we used single crystal MgO. The temperatures during both the deposition and annealing did not exceed

600°C. The prepared samples were characterized by measuring the resistance vs. temperature $R(T)$ dependence, from which the critical temperature T_c values were determined. In a similar way, using the classical four-point DC method, we measured values of critical current density J_c . Information about the films was also obtained from X-ray data and by measuring the surface roughness.

2.2. Analytical methods

In the case of standard RBS and PIXE, $^4\text{He}^+$ ions with an energy of 2.0 MeV from the NEC Tandatron of Tsukuba Laboratories have been used. The 2 mm diameter beam was incident on the sample at an angle of 45° with respect to the sample normal. The beam current was 55 nA. All the analyses were performed with a total collected charge of 25 μC . For the X-ray detection a Si(Li) detector with an energetic resolution of 165 eV was used. In the RBS experiment a silicon surface barrier detector was used, positioned at an angle of 165° to the direction of the beam. The energy resolution of the spectrometer was 15 keV. Because of the limited dimensions of the sample, Sn spots along the sample (from the T_c measurements) and the



Fig. 1. Surface image of the investigated YBCO/MgO thin film S-162. In the centre the gray area with $T_c = 85$ K can be seen, surrounded by the dark area with $T_c \leq 80$ K. The points labeled A, B, C, etc. correspond to analyses with a 2 mm diameter $^4\text{He}^+$ beam with an energy of 2.0 MeV. Numbered points identify those spots where the microbeam analyses were performed, scanning over $2000 \mu\text{m} \times 2000 \mu\text{m}$ areas with a proton beam focused to $1 \mu\text{m}$ with an energy of 2 MeV.

diameter of the beam, the number of measuring points available was limited.

For the microbeam study, 2 MeV protons from an HVEC AN2500 Van de Graaff accelerator of the National University of Singapore were used. The beam focusing system is based around an Oxford Microbeams end-station OM2000. The target is mounted on a target ladder which is inserted on an XYZ-translator. The vacuum in the measuring chamber during the measurements was better than 10^{-6} Torr.

For the X-ray detection, a horizontal PGT 30 mm² Si(Li) detector was used. The energy resolution was 160 eV. In the RBS experiment a silicon surface barrier detector was used with a solid angle of 185 msr. An energy resolution of 14 keV was obtained for RBS measurements.

The data acquisition system was based around a 486 PC operating under Windows, and an Oxford Microbeams DAQ system. X and Y signals of the scanning circuitry and DAQ interface were derived from a sensitive charge digitizer (OM35e). The beam was focused to 1 μm diameter. The beam current was 100 pA.

In addition to RBS and PIXE energy spectra, two-dimensional 256 × 256 pixel maps were accumulated in areas from 50 μm × 50 μm to 2000 μm × 2000 μm. To obtain detailed information on composition, point analyses were performed in selected areas of interest.

2.3. Data evaluation

The evaluation of the experimental PIXE spectra was performed using the program ACTIV [15]. The X-ray yields of Kα lines for Cu (8.0 keV) and Y (14.9 keV,) and Lα for Ba (4.4 keV) have been used for quantitative determination of Cu, Y and Ba concentrations, respectively. The achieved precision of the PIXE analysis was 3.0% for yttrium and 2.5% for barium and copper.

The RBS spectra were analysed using the computer program DVBS [16]. The program is based on a compari-

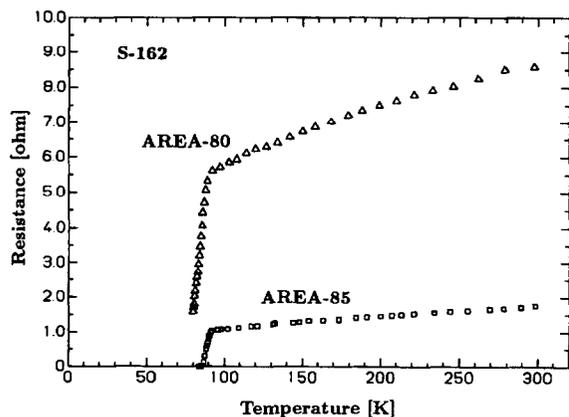


Fig. 2. The resistance vs. temperature $R(T)$ dependence, corresponding to AREA-80 and AREA-85 of the investigated YBCO film S-162.

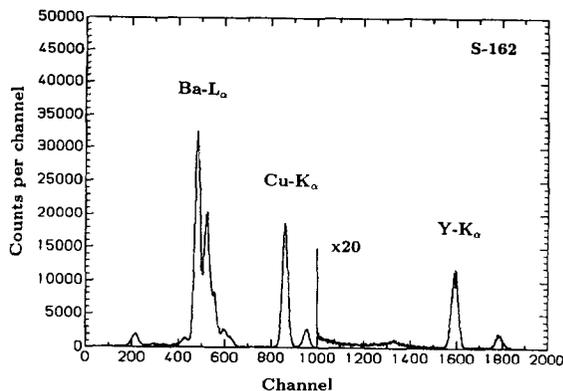


Fig. 3. PIXE spectrum obtained for the YBCO (S-162) film with 2.0 MeV $^4\text{He}^+$ ions. The spectra were accumulated for 25 μC.

son between experimental and simulated spectra. A model of the sample and the experimental conditions are inputs for the calculation of simulated spectra.

The ideal $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ high- T_c superconducting sample possesses the following composition: 13.44 wt.% Y (7.87 at.%), 41.53 wt.% Ba (15.75 at.%), 28.82 wt.% Cu (23.62 at.%) and 16.21 wt.% O (52.75 at.%). In the present work the results of the analyses are expressed in terms of atomic concentrations normalized to the yttrium concentration. It is necessary to notice that the oxygen concentrations were not determined in the present work. From the point of view of the quantitative analysis we may consider the $\text{Y}_x\text{Ba}_y\text{Cu}_z\text{O}_{7-\delta}$ sample as a compact system. The concentrations of all elements except oxygen can be determined by the PIXE method.

3. Results and discussion

When evaluating the properties of prepared YBCO samples, on the surface of one of them (S-162) we distinguished two different (gray and black) areas. Their location and differences may be seen in the photograph of the sample surface, shown in Fig. 1. Four measuring contacts from the four-point $R(T)$ resistance measurements may be seen in the centre of each region. According to the $R(T)$ measurements, the gray area in the centre of the sample (AREA-85) possessed $T_c = 85$ K. The surrounding black area (AREA-80) was found to have $T_c \leq 80$ K. The data obtained from measurement of the $R(T)$ dependence of sample S-162 are plotted in Fig. 2.

From the PIXE results with a 2 mm diameter beam, significant differences in the YBCO stoichiometry between these two areas were found. The chosen points for the analyses are illustrated and marked with capital letters A, B, C, etc. in Fig. 1. A typical PIXE spectrum obtained with 2.0 MeV $^4\text{He}^+$ is shown in Fig. 3. In AREA-85 the determined values of stoichiometric coefficients for Ba and Cu were within the range 1.95–2.05 and 2.93–3.04, re-

Table 1

The normalized Ba and Cu stoichiometric coefficients determined for YBCO/MgO (S-162) film using a 2 mm beam and microbeam analysis (scanning over $2500 \mu\text{m} \times 2500 \mu\text{m}$ areas). The positions correspond to the marks in Fig. 1

Sample area	2 mm beam			Microbeam		
	Position	Ba/Y	Cu/Y	Position	Ba/Y	Cu/Y
AREA-85	B	1.95	2.93	3	2.06	3.05
	C	2.03	3.04	4	1.99	2.91
	D	1.97	3.01	5	1.96	3.04
	F	2.05	2.96	6	1.99	2.99
	mean	2.00	2.99	mean	2.00	3.00
	stand. dev.	0.05	0.05	stand. dev.	0.04	0.06
Intermediate area				2	2.05	2.84
				7	1.89	2.97
				8	1.99	2.88
				mean	1.98	2.90
				stand. dev.	0.08	0.07
AREA-80	A	1.67	2.65	1	1.75	2.68
	D	1.53	2.53	9	1.83	2.79
				10	1.8	2.75
	mean	1.6	2.59	mean	1.79	2.74
	stand. dev.	0.1	0.08	stand. dev.	0.04	0.05

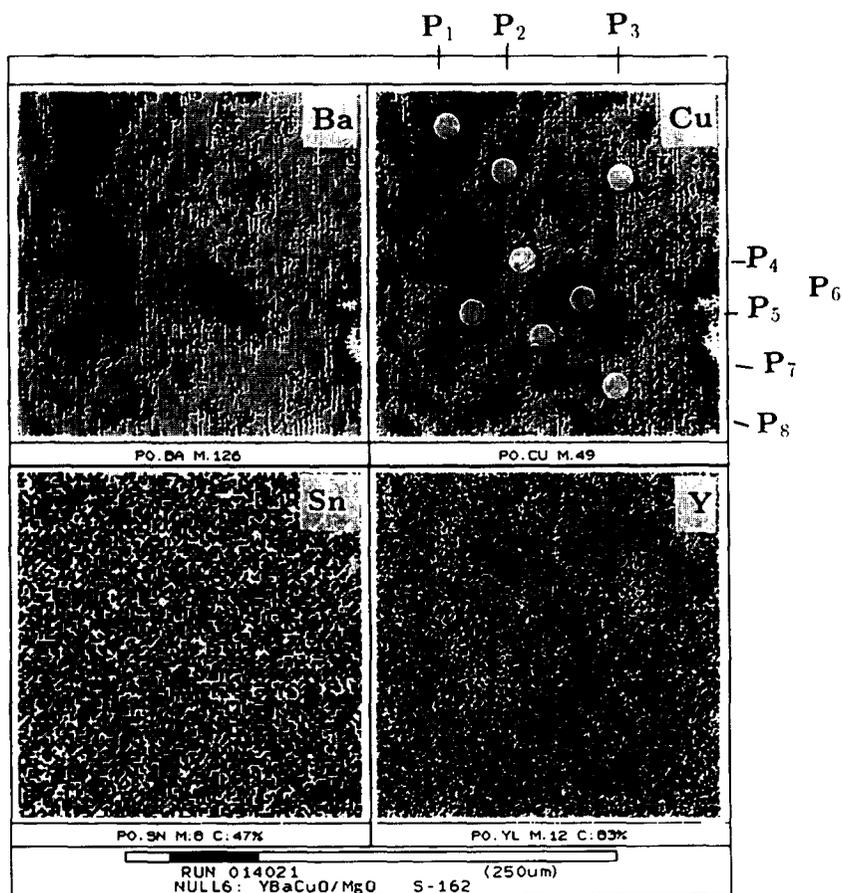


Fig. 4. PIXE maps of Y, Ba, Cu and Sn obtained for the YBCO/MgO film S-162 from measuring spot No. 8 (Fig. 1) with the proton beam focused to $1 \mu\text{m}$ with an energy of 2 MeV. The scanning was performed over $250 \mu\text{m} \times 250 \mu\text{m}$ areas. The labels P_1, P_2 , etc., mark the spots of point analyses.

spectively. In AREA-80, the determined mean stoichiometric coefficients were 1.60 and 2.59 for Ba and Cu, respectively. Results of the analyses are summarized in Table 1. According to the RBS data the average layer thicknesses were determined to be 2.10 μm in AREA-85 and 1.65 μm in AREA-80. Within each area, no significant variations in layer thickness were found.

The microbeam measurements confirmed the differences in the heavy element stoichiometry of the YBCO (S-162) sample, when comparing AREA-85 with AREA-80 (the areas chosen for analysis are numbered in Fig. 1). The values of stoichiometric coefficients obtained with the microbeam are in agreement with the results obtained using the 2 mm beam. According to PIXE maps using the 1 μm beam scanning over 2000 $\mu\text{m} \times 2000 \mu\text{m}$ areas, no inhomogeneities were observed within these two regions.

However, in the intermediate zone on the boundary between AREA-85 and AREA-80, which can be seen in Fig. 1, the PIXE maps indicated local variations in the YBCO stoichiometry. The average values of the stoichiometric coefficients determined in this zone do not significantly differ from values of AREA-85, but the standard deviations are higher. The detailed 250 $\mu\text{m} \times 250 \mu\text{m}$ PIXE maps for Y, Ba, Cu and Sn obtained in the intermediate zone are given in Fig. 4. Here, it is necessary to note that the black/white maps shown are less informative compared with their colour originals. More detailed information concerning the stoichiometry variations in this zone was obtained by point analyses. These point analyses were performed in places of low and high yields of Y, Ba and Cu from measured PIXE maps. We chose 2×4 spots with different combinations of high and low Cu and Y yields. The spots where the point analyses were performed are marked in Fig. 4 as P₁, P₂, etc. The results of the point analyses are summarized in Table 2. The stoichiometric coefficients varied from 1.53 to 2.55 for Ba, and from 2.47

Table 2

The normalized Ba and Cu stoichiometric coefficients determined for YBCO/MgO (S-162) film as a result of point analyses of a 1 μm beam. The position of analysis corresponds to the marks in Fig. 4

Measuring position on the sample	Ba/Y	Cu/Y
P ₁	2.16	3.02
P ₂	1.53	2.57
P ₃	2.34	3.76
P ₄	2.81	3.67
P ₅	1.83	3.02
P ₆	2.06	2.95
P ₇	1.63	2.47
P ₈	2.55	4.11
mean	2.11	3.20
stand. dev.	0.45	0.59

to 4.11 for Cu. Small local changes of the film thickness were observed by RBS in this zone.

To explain the differences in stoichiometry between AREA-85 and AREA-80 it is necessary to stress that the aerosol deposition from metallic nitrates is a rather complicated chemical and physical process, in which the chemical decomposition of nitrates as a function of substrate temperature plays a crucial role. In other words, the stoichiometry of the deposited layer and the stoichiometry of the initial solution serving as a source of aerosol may differ substantially from each other, depending upon the substrate temperature used, i.e. the Ba/Y and Cu/Y ratio may be changed. In our particular case, the thickness of the film is not homogeneous, i.e. the temperature on the surface of the film heated from the bottom is also not homogeneous during the deposition and annealing steps, and, as a result of this temperature gradient, the chemical composition of the film may also be changed. More details about this particular problem can be found in Refs. [14,17], where the authors studied in detail the dependence of Ba/Y and Cu/Y ratios as a function of the substrate temperature. For further studies we may therefore say that, to avoid the problems mentioned above, we have to prepare superconducting films which are homogeneous in thickness.

4. Conclusion

The PIXE results have confirmed the differences in the film stoichiometry between the surface areas with $T_c = 85$ K and $T_c \leq 80$ K, formed in the investigated YBCO thin film S-162. Using the RBS method the difference in the thickness between the surface areas with $T_c = 85$ K and $T_c \leq 80$ K was determined and some variations in the layer thickness were found in the intermediate zone between these two regions. The microbeam experiments confirmed the film homogeneity within each area. However, significant variations in the Y–Ba–Cu stoichiometry were observed by means of the microbeam experimental setup in the intermediate zone separating the $T_c = 85$ K and $T_c \leq 80$ K areas.

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