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ANALYSIS OF HIGH TEMPERATURE SUPERCONDUCTORS BY MEANS OF PIXE AND RBS METHODS

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INTRODUCTION

The discovered in recent years high temperature superconducting ceramics[1] composed of Y, Ba, Cu, O are stimulating extensive studies. Recently in JINR the scientific program has been started in this area too[2]. The main attribute of precise technology of high temperature superconductors is the testing of the composition in all technological steps. The demand of compositions determination as well as preparation and characterization of superconducting thin films call for prompt analytical methods. In order to analyse bulk materials as well as a study of a diffusion of the individual elements into selected substrata, the non-destructive nuclear analytical methods based on proton or helium ions interaction with sample seem to be very suitable. For these purposes the particle induced X-ray emission (PIXE) and Rutherford back scattering (RBS) methods have been chosen, using the proton or helium beam having energy 2.6 MeV in the case of protons and 3.0 MeV in the case of $^4He^+$ ions.

EXPERIMENTAL

The protons as well as helium ions have been produced on the Van de Graaff electrostatic accelerator (EG 5) of JINR, which makes possible the production of particles with energy from 0.8 to 3.5 MeV. The experimental set up for X ray and backward scattering spectra measurement data are illustrated in Fig.1. The sample holder makes the analyses of 11 samples possible in the vacuum of 10^{-6} torr. The total number of the particles which had interacted with the sample has been measured by means of the current integrator based on total charge collection[3].

The emitted X rays were detected using the Si(Li) semiconductor detector with the 25 μm Be window. The detector was placed outside the chamber at an angle of 90° to the primary beam of ions (Fig.1). In the case of RBS method the backward scattered particles were analysed by means of the surface barrier Si detector placed inside the measurement chamber at an

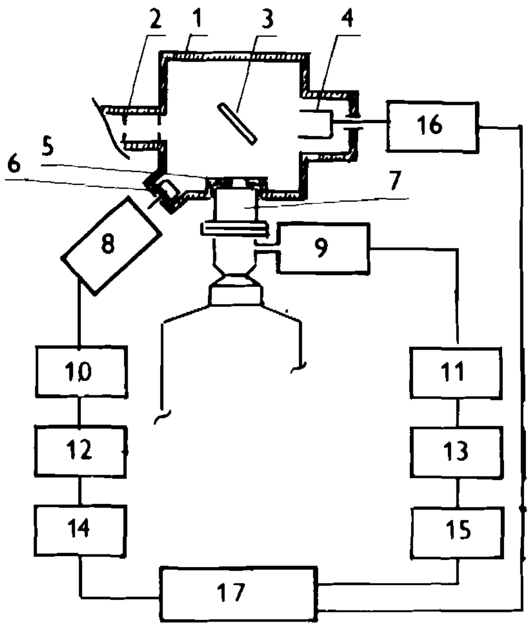

Fig.1. Experimental set-up. 1 - measurement chamber; 2 - collimator; 3 - sample holder; 4 - Faraday cup; 5 - 10 μm Al coated mylar foil; 6 - n-silicon surface barrier detector; 7 - Si(Li) semiconductor detector; 8,9 - preamplifier; 10,11 - amplifier; 12, 13 - ADC; 14, 15 - - 4k external memory; 16 - current integrator; 17 - MERA 60/55 computer.

135° angle to the beam (fig.1). The spectrometric tracts for PIXE as well as RBS methods consist of a preamplifier, an amplifier, a 100 MHz ADC and an external memory block for the coupling of the spectra. Whole experiment has been controlled simultaneously for the PIXE as well as RBS in the CAMAC system by means of a minicomputer MERA-60/55. The resolution of the spectrometric tracts has been 230 eV on the 6.4 keV (K_αFe) line in the case of PIXE method and 30 keV on the 5.499 MeV line of Pu-238 isotope in the case of RBS one. The program ACTIV[4] and the PDP-11 computer has been used to determine the areas of the X-ray peaks in the PIXE spectra, in our case K_αCu, K_αY, K_αBa as well as L_α lines of barium. The program RBSM[5] has been used for modeling of the experimental RBS spectra and to determine the thickness of the high T_c superconductor's thin films and to study the characterization of diffusion in the selected substrata with the aim to select the substratum with the good diffusion protection.

The set of the samples for external standard comparison has been prepared by weighing of Cu, Y, Ba oxides of high purity which after good mixing have been pressed into pellets.

RESULTS AND DISCUSSION

The PIXE analysis of high T_c superconductors gives sufficient information about content of Cu, Y and Ba respectively

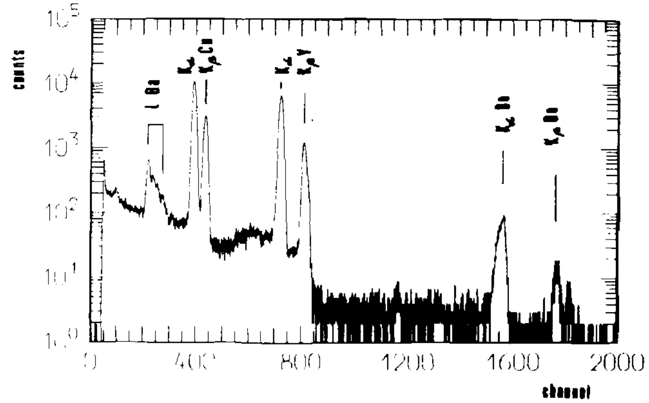

Fig.2. X-ray spectrum obtained with Si(Li) detector for high-T_c superconductor sample. The excitation with 60 μm $^4He^+$ (3 MeV) ions has been performed.

due to high X-ray production cross sections for protons as well as for $^4He^+$ ions, too. The K-shell X-ray production cross sections for Cu, Y and Ba are[6]: 67.2, 7.2 and 0.17 barn, respectively, when 2.6 MeV protons are used, and 8.03, 0.47 and 0.007 barn, respectively, in the case of 3.0 MeV He ions. For L_α-X-ray production cross section of Ba we have 110 barn for 2.6 MeV protons and 180 barn in the case of 3.0 MeV $^4He^+$ ions. Fig.2 shows a typical X-ray spectrum obtained from He ion excitation.

The X-ray yields of K_αCu (8.0 keV), K_αY (14.9 keV) and K_αBa (32.1 keV) have been used for the following development of the analytical technique. The L_α yields of barium have not been used due to the uncertainties in the peak separation from the experimental X-ray spectra. Table 1 gives the experimental yields of the K_α X-ray lines of the Cu, Y and Ba obtained using prepared external standards. All yields have been measured with total charge about 1 μC of protons as well as 60 μC in the case of $^4He^+$ ions. On the basis of these values the relationship between intensity and concentration has been solved taking into account the interelement effects in the sample. It has been found that the model proposed by Lachance Traill[7] for matrix effect correction in XRF analysis is more suitable:

$$C_i = \frac{I_i}{I_i^0} (1 + \sum_{j \neq i} \alpha_{ij} C_j), \qquad (1)$$

Table 1

Sample	Element	C (g/g)	Yield: Protons	Yield: $^4He^+$
1	O	0.1693	–	–
	Cu	0.2988	215 319	125 191
	Y	0.2090	686 262	146 816
	Ba	0.3229	14 856	1 329
2	O	0.1552	–	–
	Cu	0.2569	185 862	103 181
	Y	0.1438	464 267	97 766
	Ba	0.4441	17 014	1 880
3	O	0.1626	–	–
	Cu	0.3445	230 443	148 401
	Y	0.1205	410 591	90 806
	Ba	0.3724	–	1 722
4	O	0.1515	–	–
	Cu	0.2834	185 754	118 610
	Y	0.0930	299 918	65 951
	Ba	0.4721	–	2 088
5	O	0.1537	–	–
	Cu	0.2863	209 106	131 315
	Y	0.1067	343 085	74 667
	Ba	0.4534	–	1956
6	O	0.1558		
	Cu	0.2879	199 956	126 442
	Y	0.1208	434 395	87 343
	Ba	0.4355	19 151	1 969
7	O	0.1602		
	Cu	0.2914	208 677	127 122
	Y	0.1495	481 170	100 593
	Ba	0.3989	18 011	1 587
8	O	0.1624		
	Cu	0.2932	200 751	126 162
	Y	0.1641	517 138	105 022
	Ba	0.3803	16 812	1 418
9	O	0.1647		
	Cu	0.2951	204 093	125 490
	Y	0.1789	584 432	124 120
	Ba	0.3613	16 708	1 386
10	O	0.1716	–	–
	Cu	0.3005	215 966	123 614
	Y	0.2248	795 790	164 143
	Ba	0.3031	14 090	1 053
11	O	0.1495	–	–
	Cu	0.2827	205 823	125 556
	Y	0.0791	251 717	54 167
	Ba	0.4887	21 727	2 087
12	O	0.1670	–	–
	Cu	0.2969	224 061	119 027
	Y	0.1939	594 140	115 687
	Ba	0.3422	15 754	1 481

Table 1 (cont.)

where C_i – concentration of i-element, I_i – experimental intensity of i-element, I_i^o α_{ii} – empirical coefficient corresponding to the intensity of the pure element, α_{ij} – empirical coefficient expressing the effect of j-element on i-element. For the determination of the empirical coefficients α_{ij} the system of equations (1) has been solved using the measured experimental intensities of standard samples. For this purpose the program FUMILI [8], handling data by the method of least squares but in general by the method of maximum likelihood, has been applied. Table 2 presents the calculated empirical coefficients α_{ij} for ^4He excitation.

The unknown concentration of elements (Cu, Y and Ba) in analysed sample can be calculated using the empirical coefficients (tab.2) and experimental X ray intensities by solving the system of equations (1) under the condition that:

$$\sum_i C_i + C_o = 1. \qquad (2)$$

To have the possibility of solving the above equation system (1) we need to know concentration of oxygen C_o in the sample. For solving this problem the method of backward scattering spectrometry with 2.6 MeV proton beam has been applied. The form of the spectrum is shown in Fig.3. Due to the fact that proton backward scattering cross sections are non Rutherford the following technique has been applied. The calibration curve describing dependence of the height of edge of oxygen spectrum H_{oxygen} on oxygen concentration C_{oxygen} in standard

Table 2.

α_{ij}	$\alpha_{\bullet 1}$	$\alpha_{\bullet 2}$	$\alpha_{\bullet 3}$
$\alpha_{1\bullet}$	$0.5662\cdot 10^{6}$	$0.1150\cdot 10^{1}$	0.3957
$\alpha_{2\bullet}$	-0.9489	$0.4009\cdot 10^{6}$	-0.3862
$\alpha_{3\bullet}$	-0.8343	$0.1124\cdot 10^{1}$	$0.3809\cdot 10^{4}$

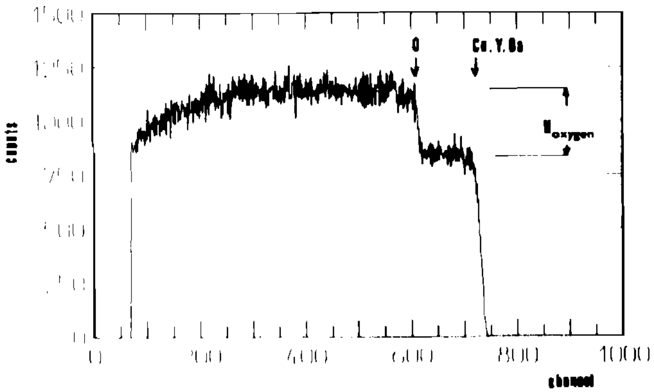

Fig.3. Backward scattered ion spectrum obtained with Si-surface barrier detector for high-T_c superconductor sample. The 2.6 MeV protons with total charge 4.5 μC have been used. H_{oxygen} represents number of counts corresponding to oxygen at the edge of oxygen spectrum.

samples has been used. From this dependence the unknown concentration C_O can be evaluated with the accuracy not less than 3%. Then the following determination of Cu, Y and Ba concentrations can be performed using an iteration technique in the solved equation system (1).

The accuracy of the above approach has been tested on the samples with known composition. The determined results are illustrated in Fig.4, where dependence of calculated concentrations on true values is presented. The described above technique gives results of concentration with accuracy not less than 4.5, 4.0 and 4.5% for Cu, Y and Ba, respectively. The RBS method has been applied to investigation of the high T_c superconductive thin films focussing our attention to study the diffusion of the components in SITAL, $SrTiO_3$, corundum and saphire

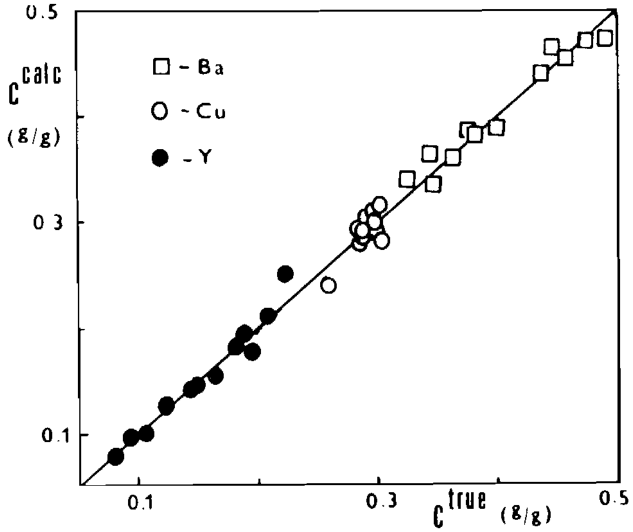

Fig.4. The dependence of calculated values C_{Cu}, C_Y and C_{Ba} on true concentrations in standard samples. C^{calc} has been evaluated by external standards technique. The solid line expresses ideal case when C^{calc} = = C^{true}.

substrata, respectively. In the case of small thickness of the film (less than 1 μm) the He ions have been chosen. In the case of He measurement the decreasing of copper content in the film about two-three times after annealing for all substrata has been observed. Practically no change of concentration of other two elements (Y and Ba) after annealing has been observed. An example of the spectrum obtained is shown in Fig.5. Analysing the more thick films using protons the least effect of diffusion has been observed for the sample having saphire substratum. The diffusion in other substrata after annealing was greater. The comparison of the spectra obtained before and after annealing of the selected sample ($SrTiO_3$ substratum) is shown in Fig.6. The peaks of Cu, Y and Ba in the spectrum shown in Fig.6 are not separated because the kinematic factors of proton scattering for these elements are near each other.

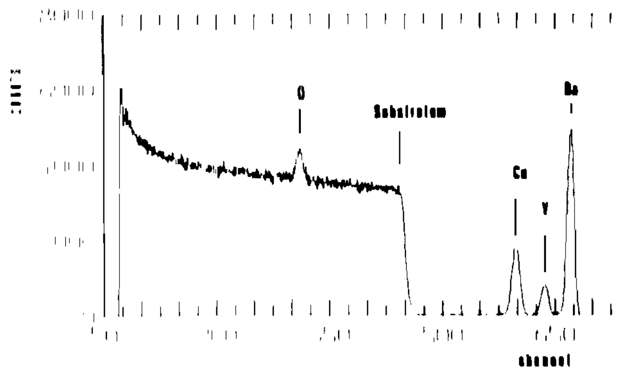

Fig.5. The backward scattering spectrum of 500 Å thick Y-Ba-Cu-O film deposited on the saphire substratum. 3 MeV He ions with total charge of 60 μC have been used.

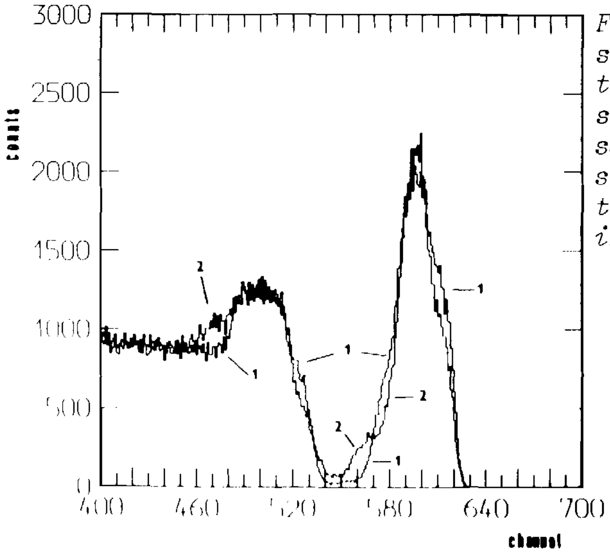

Fig.6. The backward scattering spectra for the 1 μm thick Y-Ba-Cu-O samples; 1 - the primary sample; 2 - the annealed sample. The 2.6 MeV protons have been used for irradiation.

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Ильхамов Р.А. и др. E14-88-568
Элементный анализ высокотемпературных сверхпроводников методами ионного возбуждения ХРИ и POP

Представлены неразрушающие методы элементного анализа высокотемпературных сверхпроводников на пучках ускоренных ионов. Предложены анализ элементного состава массивных образцов, состоящих из Ba, Y, Cu и O, методом ионного возбуждения характеристического рентгеновского излучения /ХРИ/ и исследование тонких пленок того же состава методом резерфордовского обратного рассеяния /POP/. Концентрации элементов определялись с помощью метода внешнего стандарта в случае метода ХРИ и методом моделирования экспериментального спектра в случае метода POP. Элементный состав может быть измерен с точностью не хуже, чем 4,5; 4,0 и 4,5% для Cu, Y и Ba соответственно.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

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Analysis of High Temperature Superconductors by Means of PIXE and RBS Methods

The non-destructive ion beam analyses of the high temperature superconductors are presented. The bulk analysis of materials of Y-Ba-Cu-O composition by the PIXE method and study of thin films of these materials by RBS method are proposed. The concentrations of the elements have been calculated by means of external standards technique in the case of PIXE method and by means of experimental spectrum modeling in the case of RBS. The elemental composition can be measured with accuracy not less than 4.5, 4.0 and 4.5% for Cu, Y and Ba respectively.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

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