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Characterization of high-Tc superconductors by mass spectral methods of surface analysis (LIMS, SNMS)

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Abstract

Sputtered neutral mass spectrometry (SNMS) and laser induced ion mass spectrometry (LIMS) have been applied to characterization of phases in the Y-Ba-Cu-O system. The results show that these techniques are useful tools for the investigation of phase and chemical composition of superconducting oxide ceramics.

1. Introduction.

Just after the discovery the high T_c superconducting (HTSC) materials become the important object under the investigation by practically all modern methods of analysis. Surface becomes an object of a special interest for the investigators of HTSC materials, because it plays the basic role in the formation of high critical current density in these materials [1].

The mass-spectral methods of the investigation of the surface enable to obtain unique information about the composition and the state of the surface and the layers adjacent to the surface. Classic SIMS is actively used for the characterization of the HTSC materials surface [2]. However, other mass-spectral methods (LIMS, SNMS, SSMS) are applied insufficiently. We can also note that these works deals with the analysis of HTSC films [3,4] and we practically do not know the investigations of the ceramic surface.

The objective of the present work is to demonstrate the abilities of non traditional surface analysis techniques (SNMS and LIMS) at the investigation of the bulk HTSC samples with the complex phase composition.

2. Experiment.

The materials of Y-Ba-Cu-O system under investigation were ceramic samples of phases CuO, Y_2O_3, $BaCuO_2$, $Y_2Cu_2O_5$, Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$. The samples were prepared by a variety of procedures, including ceramic synthesis from oxides and carbonates, mutual melting of nitrates and cryochemical method.

According to a common scheme of synthesis Ba carbonate, Y and Cu oxides mixtures (or oxide mixture after thermal decomposition of nitrates) were ground in a mortar, pressed in pellets (d = 10 mm, h = 1.5-2 mm) and sintered at 940°C during 24 hours with intermediate grinding. The composition of the sintered materials was determined by chemical analysis. X-ray data indicated all the samples to be single-phased.

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Before analysis the samples were mechanically ground and polished to eliminate the upper layer which composition could be violated.

SNMS analysis was performed using the INA-3 spectrometer (Leybold AG, Germany) in the direct bombardment mode in the high-frequency Ar plasma (P_{Ar}= 3x10^{-3} mbar, frequency 27 MHz). The sample voltage was varied from 150 to 1000 V.

To avoid charging of the insulator samples the surface under investigation was covered with metal grid (the cell length 100-150 um).

Intensities of signals in mass-spectra were determined using the program of approximating the lines by symmetric envelope. The total ion current of the elements was calculated by summing up the intensities of single-charged positive ions of the isotopes.

LIMS analysis was made by LAMMA-1000 device (Germany, Leybold AG) using Q-switched Nd-YAG laser (λ=266 nm, τ=8-10 ns) with power density on the sample surface 10^8-10^{11} W/cm^2. Analysis conditions were found, at which the spectra of the ceramics mainly consist of the clusters (both positive and negative) with various degree of fragmentation.

3. Results and discussion.

3.1. SNMS analysis.

The common approach to quantitative analysis by SIMS method implies the use of relative sensitivity factor (RSF), which are available for several common matrices. Analysis of new materials requires preliminary studies of reference samples to determine RSF. Unfortunately, the essential matrix effect which is present in classical SIMS method has not allowed so far to create a consistent set of RSF's for oxide materials.

It was stated in the literature [5] that matrix effect in SNMS method was very small for the metal alloys. This may be attributed to the independence of the degree of ionization on matrix composition due to postionisation by electron gas in plasma. For this reason, we studied the set of reference samples of ferrites Y, Ba and Cu in order to determine RSF of these elements.

We investigated $CuFe_2O_4$, $Y_3Fe_5O_{12}$ and $BaFe_{12}O_{19}$. RSF of the elements with respect to Fe were determined by statistical analysis of SNMS spectra (see Table 1). Assuming that RSF of Fe were the same for all materials (no matrix effect) we scaled the values of RSF with respect to Y.

The same procedure was applied to the analysis of ceramics $YBa_2Cu_3O_{7-x}$ obtained by cryo-chemical method. The calculated values of RSF of Ba, Cu and O with respect to Y are presented in Table 1.

Comparison of RSF calculated for various materials leads to an interesting and promising conclusion: if we even attribute the discrepancies in RSF to matrix effect only, then this effect does not exceed 25% for materials completely different in structure and chemical composition.

Therefore, it may be suggested that usage of the RSF of Y, Ba, Cu and O enables to carry SNMS analysis of any unknown oxide material in the Y-Ba-Cu-Fe-O system with an accuracy $\leq$ 25 at.%. For SIMS this approach is unreliable.

The special feature of SNMS

Table 1. SNMS relative sensitivity factors (RSF) of Y, Ba, Cu and O.

Element	RSF/Fe (relative to Fe)			RSF/Y (relative to Y)		Δ(%)
	$Y_3Fe_5O_{12}$	$CuFe_2O_4$	$BaFe_{12}O_{19}$	ferrites	$YBa_2Cu_3O_x$	
Fe	1.0±0.0	1.0±0.0	1.0±0.0	2.95±0.06	–	–
Y	0.33±0.01	–	–	1.00±0.0	1.00±0.0	0.0
Cu	–	1.46±0.02	–	4.31±0.1	5.84±0.05	26.2
Ba	–	–	0.23±0.01	0.68±0.04	0.58±0.01	17.2
O	14.0±1.8	13.2±0.5	16.6±3.0	43.6±7.6	49.9±1.4	12.6

method is the layer-by-layer analysis of material during an etching from surface to bulk. It gives the opportunity of analysis of bulk samples as a layered materials, to investigate their chemical homogeneity. The criterion of chemical homogeneity of samples in this case is the standard deviation of layer-by-layer analysis results. The results of this analysis of $YBa_2Cu_3O_{7-x}$ samples prepared by the different methods are presented in Fig. 1.

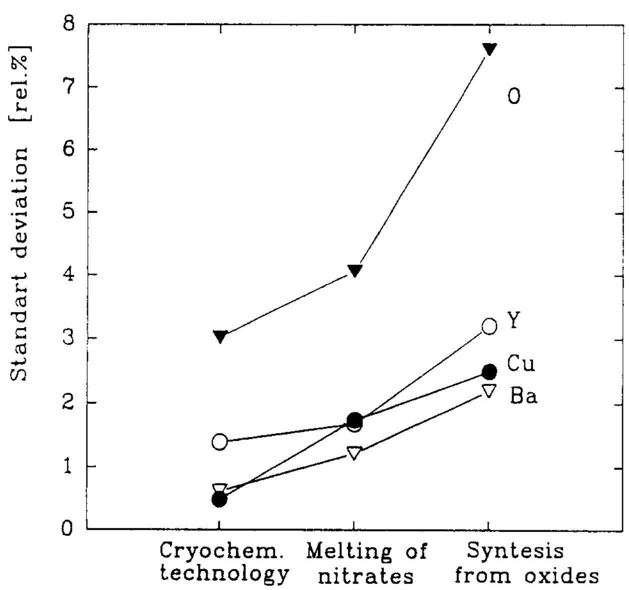

Figure 1. Reproducibility of SNMS data for $YBa_2Cu_3O_{7-x}$ ceramics.

It follows from the analysis of these data that cryochemical samples are more homogeneous (at least, with respect to Cu and Ba) than samples obtained by melting of nitrates, the deviation for the former samples being of the same order of magnitude as the error of SNMS method - 0.5% for metals and 5% for oxygen. It is remarkable, that homogeneity of samples prepared by traditional ceramic method is significantly lower.

3.2. LIMS analysis.

The positive mass-spectra of Y_2O_3, $YBa_2Cu_3O_{7-x}$, Y_2BaCuO_5 and $Y_2Cu_2O_5$ have a big number of heavy clusters, contain yttrium, for example $Y_{13}O_{19}^+$, $Y_{13}O_{21}^+$, $Y_{15}O_{21}^+$ and so on. Cu- and Ba-contained clusters such as Ba_2O^+, Ba_2CuO^+, $Ba_nCuO_n^+$ (n=1-4), $YBaO^+$, $YBaO_2^+$ are also formed. Formation of the clusters of complex composition (with Y, Ba and Cu) is not observed practically.

Individual phases CuO, Y_2O_3, $BaCuO_2$, $Y_2Cu_2O_5$ can be easily identified using LIMS-data due to the differences in spectra of mononuclear ions. However, positive ion spectra of $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 have practically identical sets and relative intensities of peaks. It was found that mass spectra of negative ions of these compounds are highly different

Cu^-, YO^- and YO_2^- ions were detected as main metal-contained components of Y_2BaCuO_5 mass-spectra; Cu^-, CuO^- and CuO_2^- were found to be such components of $YBa_2Cu_3O_{7-x}$ spectrum. Results were reproduced during the analysis of $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 phase samples, films and single crystals obtained by different methods. Mentioned above peculiarities of mass-spectra allowed us to develop the method of phase microanalysis in Y-Ba-Cu-O system by LIMS technique.

Ratio of intensities $g=I(CuO_2)/I(YO)$ was chosen as the main parameter. Statistic treatment of spectra shows that these ratio is considerably different for analyzed phases and sharply increases from Y_2BaCuO_5 (g=0,26) to $YBa_2Cu_3O_{7-x}$ (g=1.13).

Model samples were prepared by molding of mixtures of single phase $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 powders. The field on the sample's surface was randomly chosen with dimensions 70x70 μm. After that 64 points situated in the knots of net with step 10 μm were analyzed. For each point $I(CuO_2)/I(YO)$ ratio was calculated. Preliminary, using the statistical treatment of LIMS analysis data for pure phases, value of threshold criteria g=0,65 was chosen.

When the logical expression $g=I(CuO_2)/I(YO)\geq 0,65$ was true, then the phase was identified as $YBa_2Cu_3O_{7-x}$, if not - as Y_2BaCuO_5. Concentration of Y_2BaCuO_5 phase was equal to the part of analyzed points, having value of g<0,65.

Application of the threshold criteria to the results of the analysis of the model mixtures allows us, using least-square fit method, to obtain calibration curve for the quantitative phase microanalysis (Fig 2).

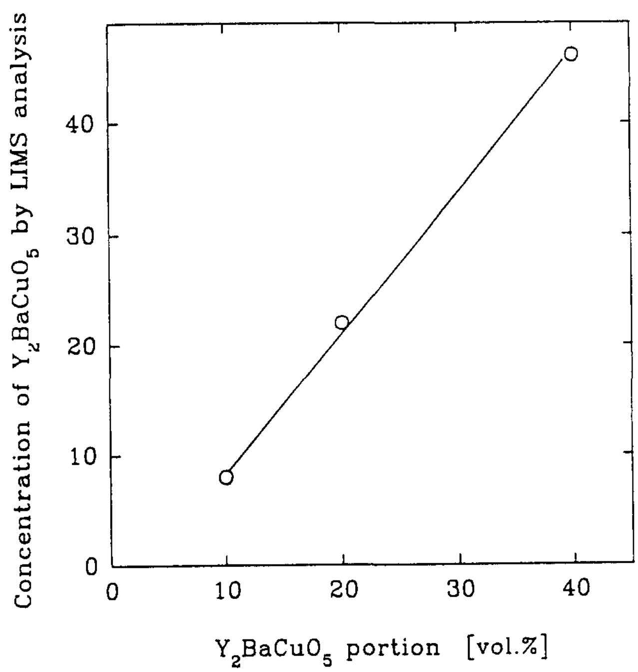

Figure 2. LIMS phase analysis of $YBa_2Cu_3O_{7-x}$-Y_2BaCuO_5 mixtures.

The results, shown in Fig.2 show the possibility of LIMS technique for the quantitative phase analysis of small areas on the surface of Y-Ba-Cu-O system materials.

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