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Analysis of phases in the Y–Ba–Cu–O system by lims technique laser-induced ion mass spectrometry

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Laser-induced ion mass spectrometry (LIMS) was used for the analysis of oxide phases in the Y–Ba–Cu–O system. The formation of polynuclear ions (clusters) as a result of laser sputtering of oxides was examined. The possibility of quantitative phase analysis of inhomogeneous oxide materials in the Y–Ba–Cu–O system by the LIMS technique is demonstrated.

1. Introduction

The laser-induced ion mass spectrometry (LIMS) method allows investigation of any solid materials, which are stable in a vacuum, with high spatial resolution (spot $< 2\ \mu m$, depth $> 0.1\ \mu m$) and excellent element sensitivity (up to 10^{-6} at %) [1, 2]. The peculiarity of LIMS is the possible formation of polynuclear heavy ions under certain sputtering conditions. The composition of polynuclear ions (clusters) in many cases corresponds to the character of the analysed substance.

Cluster formation in complex oxide systems has been poorly studied; however, in a number of works [3, 4] the behaviour of high-temperature superconductors (HTSC), based on the Y–Ba–Cu–O system, during laser ablation was investigated by LIMS. These investigations are important in understanding the laser-ablation processes of HTSC film preparation.

In this work we studied cluster formation in laser plasma for identification of phases in the Y–Ba–Cu–O system by the LIMS technique.

2. Experimental procedure

The objects under investigation were ceramic samples of individual phases CuO, Y_2O_3, $BaCuO_2$, $Y_2Cu_2O_5$, Y_2BaO_4, $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5, prepared from high-purity reagents by the traditional ceramic method and by mutual melting of yttrium, barium and copper nitrates.

The X-ray diffraction data (CuK_α radiation, Stade-P diffractometer) show that the samples were single phase.

The LIMS investigations were conducted using a LAMMA-1000 device (Leybold AG FRG) [1], using impulse-quadrupled radiation of a Nd: YAG laser (266 nm, $\tau = 8$ ns) with a time-of-flight mass spectrometer. Laser power density was varied in the range 10^8–10^{10} W cm^{-2}; the pressure in the analysis chamber was 10^{-6} mbar.

The mass spectra of positive and negative ions were treated by computer. Every sample was analysed at not less than 120 points with further statistical treatment to determine the general distribution parameters of the analysis results.

3. Results and discussion

At a power density of 2–5×10^{10} W cm^{-2}, monoions Y^+, Ba^+, Cu^+ were the main positive ions in the mass spectra (Fig. 1b); however, under most rigid conditions, YO^+ and BaO^+ ions were also registered.

A gradual decrease in power density leads to the origin of polynuclear ions (positive as well as negative) in the mass spectra, their relative intensity increasing with power density, and at a power density near 10^8 W cm^{-2}, the spectrum consists mainly of clusters of different composition (Fig. 1a). The most characteristic clusters in the positive-ion mass spectra were M_n^+ ($n = 2$–3), $Me_nO_x^+$ ($n = 2$–6) and mixed particles $Me_nMe'_mO_x^+$ ($n + m = 2$–5). Numerous clusters were also observed in negative-ion mass spectra for CuO, $BaCuO_2$, $Y_2Cu_2O_5$, $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5, which are discussed below.

3.1. The positive cluster formation in individual phases

The cluster spectra of investigated oxides essentially depend upon the chemical nature of the metals. So, CuO forms ions of composition Cu_n^+ and Cu_nO^+ ($n \leqslant 4$). Y_2O_3, during laser sputtering, gives a high number of $Y_nO_m^+$ clusters with masses up to 3000 a.m.u. and higher, for which stoichiometry is approached at $n/m = 2/3$ with mass increase.

Ions of $Ba_nO_m^+$ composition, as well as mixed ions $Ba_nCu_mO_x^+$, were observed for $BaCuO_2$. Investigation of $Y_2Cu_2O_5$ did not reveal clusters containing both yttrium and copper. Y_2BaO_4 forms a large number of clusters of the following composition: $Ba_nO_m^+$, $Y_nO_m^+$ and $Y_nBa_mO_x^+$. Table I shows the positive mass

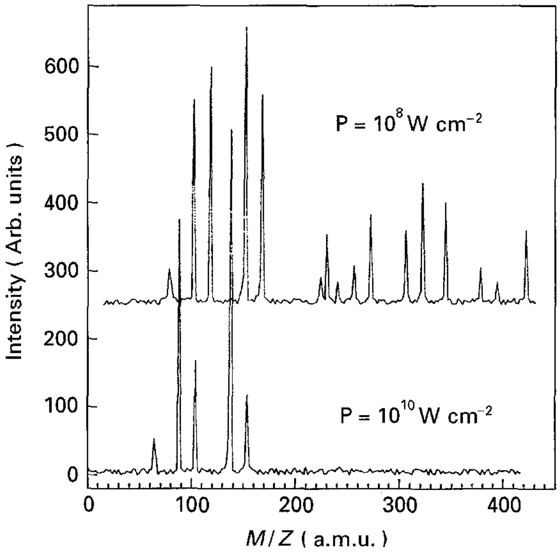

Figure 1 Positive LIMS mass spectra of $YBa_2Cu_3O_{7-x}$ at different laser power densities.

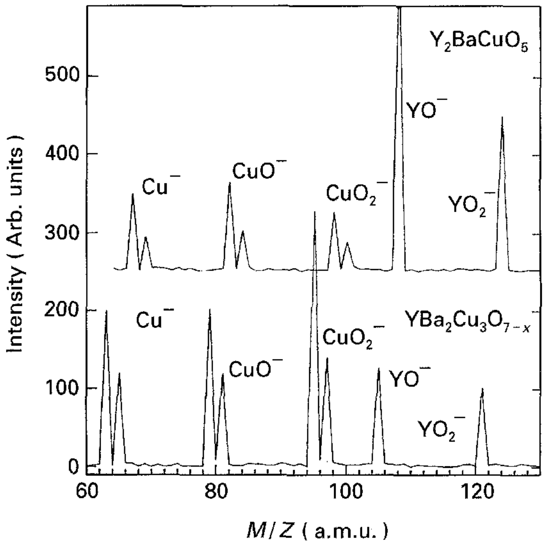

Figure 2 Typical negative LIMS mass spectra of Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$ phases.

TABLE I The positive ions in LIMS spectra of simple, binary and complex oxides

Substance	Laser-induced positive ions
CuO	O, Cu, Cu_2, Cu_2O, Cu_3, Cu_3O
Y_2O_3	Y, YO, Y_2O_2, Y_2O_3, Y_3O_4, Y_5O_7, Y_6O_8, Y_7O_9, Y_9O_{12}, Y_9O_{12}, $Y_{10}O_{13}$, $Y_{11}O_{14}$, $Y_{13}O_{18}$, $Y_{13}O_{19}$, $Y_{15}O_{21}$, etc.
$BaCuO_2$	Cu, Ba, BaO, BaOH, BaCuO, Ba_2O, Ba_2O_2, Ba_2CuO, Ba_2CuO_2, Ba_3O_3, Ba_3CuO_3, Ba_4O_4, Ba_4CuO_4
$Y_2Cu_2O_5$	Cu, Y, YO, same as Y_2O_3
Y_2BaO_4	Y, YO, Ba, BaO, $YBaO_2$, Ba_2O, Ba_2O_2, Y_3O_4, YBa_2O_3, Ba_3O_3, Y_4O_8, $Y_2Ba_2O_3$, YBa_3O_4, etc.
Y_2BaCuO_5	Cu, Y, YO, Ba, BaO, Y_2O_2, BaCuO, YBaO, $YBaO_2$, Ba_2O, Ba_2O_2, Y_3O_4, Y_3O_6, YBa_2O, YBa_2O_3, Y_4O_8, same as Y_2O_3
$YBa_2Cu_3O_{7-x}$	Same as Y_2BaCuO_5

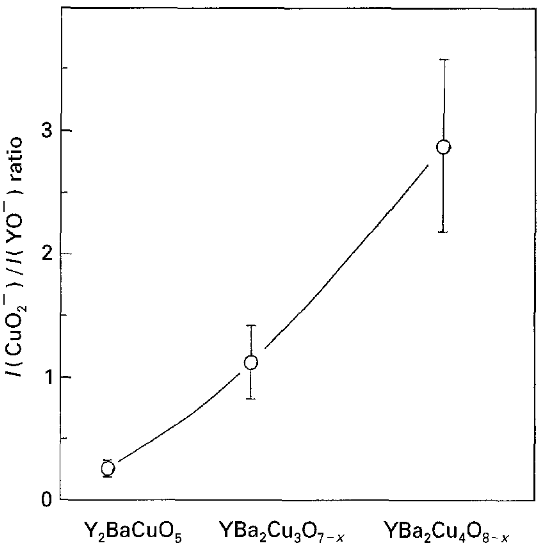

Figure 3 Ratio of intensities of CuO_2^- and YO^- ions in mass spectra of different ceramics.

spectra composition for the simple, double and complex oxides.

On comparing the cluster spectra of $YBa_2Cu_3O_7$, $YBa_2Cu_4O_{8-x}$ and Y_2BaCuO_5 phases, no principal differences could be found. Clusters formed by copper, yttrium and barium were not detected simultaneously.

It is interesting that stoichiometric mixtures of $BaCO_3$, CuO and Y_2O_3 (particles size 0.5–2 μm), corresponding to the $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 compositions, produce mass spectra which are close to the spectra of triple oxides with regard to the set of clusters, but the intensity of the complex clusters in oxide mixture spectra is considerably lower. This fact confirms the data [4], and provides evidence that the positively charged clusters are formed not only by laser-induced fragmentation of the substance, but also, apparently, by association of ions in the laser plasma.

From the microanalysis point of view, it should be noted that cluster mass spectra enable single and double oxides to be identified in polyphase ceramics and in films of Y–Ba–Cu–O composition rapidly and easily. However, it seems difficult to distinguish triple oxides $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 from the mass spectra of positive ions.

3.2. The negative cluster formation

Another situation is observed in the investigation of negative-ion mass spectra of $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5. In this case the main cation-contained particles are Cu^-, CuO^-, CuO_2^-, YO^- and YO_2^- ions. The characteristic feature of these spectra is the considerable differences in the intensities of CuO_2^- and YO^- ions for $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5, (Fig. 2). The relative intensity of the CuO_2^- signal is sharply increased and the YO^- signal is decreased, on going from Y_2BaCuO_5 to the $YBa_2Cu_3O_{7-x}$ phase. The value of the $I(CuO_2)/I(YO)$ ratio is also considerably decreased, see Fig. 3.

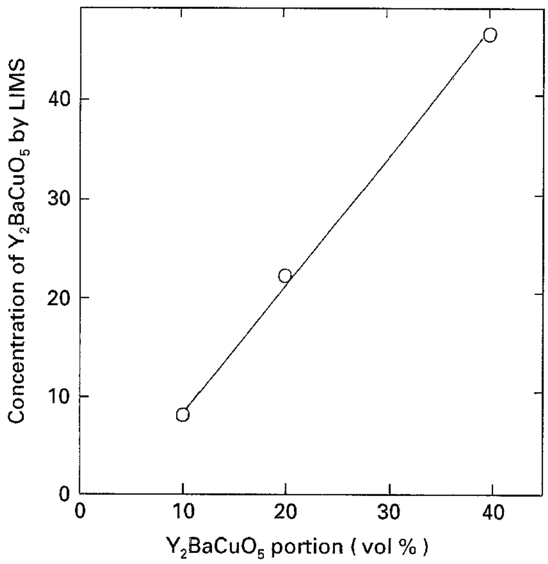

Figure 4 The results of LIMS analysis at a threshold criterion $g = 0.65$ from the composition of $YBa_2Cu_3O_{7-x}$–Y_2BaCuO_5 reference mixture.

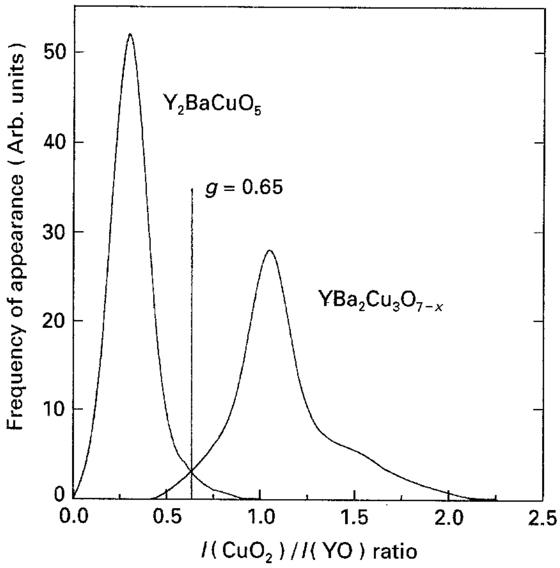

Figure 5 Frequency distribution of the $I(CuO_2^-)/I(YO^-)$ ratio for Y_2BaCuO_5 and $YBa_2Cu_3O_{7-x}$ and the position of the threshold criterion, g.

The possible connection of this result with crystal structure features of the investigated complex oxides, requires additional study.

3.3. Phase analysis

The obtained results are interesting from the point of view of local phase microanalysis in the Y–Ba–Cu–O system. Reference samples of $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 mixtures with concentrations of Y_2BaCuO_5 of 10, 20 and 40 vol%, were prepared to estimate the accuracy of such analysis. After milling and moulding, the samples were analysed by a laser spot size of about 3–4 μm.

The field on the samples surface was randomly chosen with dimensions 70 μm × 70 μm. Then 64 points were analysed in this field at the knots of an imaginary square net with a cell 10 μm × 10 μm. For each point, the $I(CuO_2)/I(YO)$ ratio was calculated.

Further mathematical treatment consists in the selection of threshold criteria, g, to identify phase ($YBa_2Cu_3O_{7-x}$ or Y_2BaCuO_5) at the analysed point by the value of the $I(CO_2)/I(YO)$ ratio. For example, if the inequality $I(CuO_2)/I(YO) \geqslant g$ is true, then the phase is $YBa_2Cu_3O_{7-x}$; if it is false, the phase is Y_2BaCuO_5.

In that case, the concentration of Y_2BaCuO_5 phase in the mixture was calculated as the number of points which have a value of threshold criteria larger than the $I(CuO_2)/I(YO)$ value (threshold test passed). An optimum g value equal to 0.65 was obtained by minimization of the functional using the least square fit

$$R = \left[\sum_{i=1}^{3} (C_{\text{calc}} - C_{\text{fact}})^2 \right]^{1/2} \qquad (1)$$

where C_{calc} and C_{fact} are calculated from LIMS data and the real concentration of Y_2BaCuO_5 phase, accordingly. An example of such treatment of the analysis data at $g = 0.65$ is demonstrated in Fig. 4.

It seems very important that the threshold criteria g can also be obtained from the frequency distribution of the $I(CuO_2)/I(YO)$ experimental value, for $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 phases (see Fig. 5). It can be seen that the formally obtained value of threshold criteria, 0.65, is the crossing point of two frequency distributions.

On the base of the analysis data we constructed a map of the phase distribution for any Y–Ba–Cu–O sample, containing a phase with a grain size >5 μm.

References

1. H. HEINEN, F. HILLENKAMP, R. KAUFMANN, W. SCHROEDER and R. WECHSUNG, in "Proceedings of the 6th International Symposium on Mass Spectrometry of Biochemistry in Medicine (Venice, 1979).
2. P. FEIGL, B. SCHUELER and F. HILLENKAMP, *Int. J. Mass Spectrom Ion Phys.* **47** (1983) 15.
3. A. MELE, D. CONSALVO, D. STRANGES, A. GIARDINI-GUIDONI and R. TEGHIL, *Appl. Surf. Sci.* **43** (1989) 398.
4. S. BEKER and H. J. DIETZE, *Phys. C* **167** (1990) 509.

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