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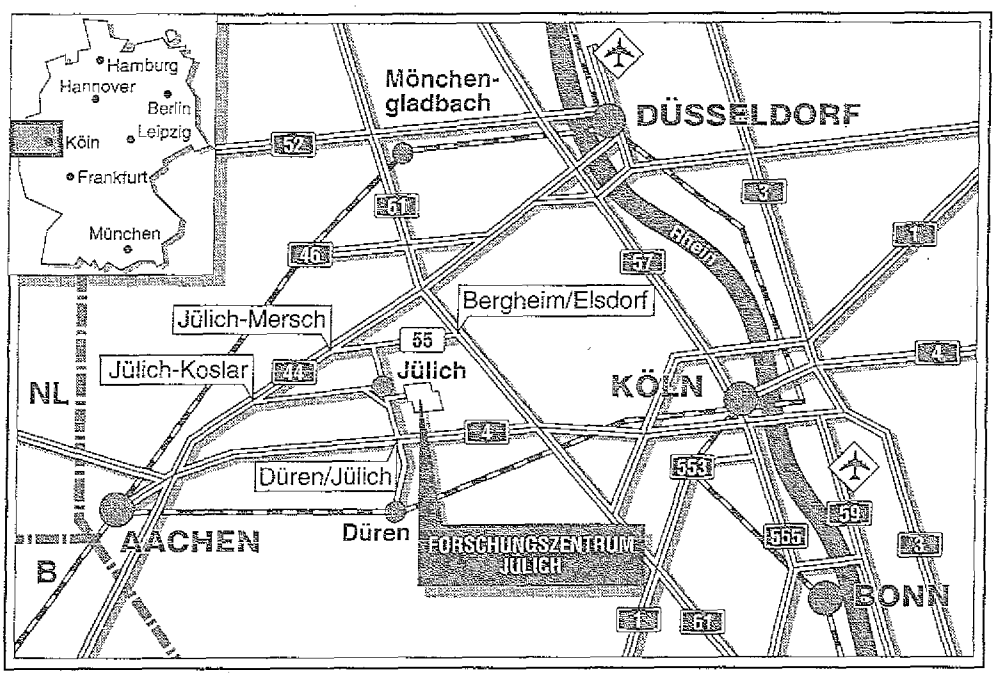
J.S. Becker H.-J. Dietze



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Summary

Among the different spectrometric techniques for trace analysis Laser Ionization Mass Spectrometry (LIMS) is well suitable as an analytical method for the determination of trace impurities in ceramics. With the LIMS technique the ceramic sample material is evaporated and ionized by means of a focused pulsed laser beam in a laser microplasma, which is formed in the spot area of the irradiated sample. All chemical elements in the sample materials are evaporated and ionized in the laser plasma. The ions formed are separated according to mass and energy by a double- focusing mass spectrometer. In this paper the characteristics, analytical features and application of laser ionization mass spectrometry in trace analysis of ceramics are described.

Zusammenfassung

Die Bestimmung von Spurenelementen in keramischen Probenmaterialien stellt wegen deren physikalischen und chemischen Eigenschaften an die Analysenverfahren hohe Anforderungen. Bei der Elementkonzentrationsbestimmung an keramischem Probenmaterial nimmt die Laserionisations-Massenspektrometrie unter den verschiedenen spektrometrischen Methoden einen bevorzugten Platz ein, weil sie eine Analyse ohne chemische Probenvorbereitung erlaubt.

Das keramische Probenmaterial wird in der LIMS-Technik mittels eines fokussierten Laserstrahls verdampft und ionisiert. Die bei der Wechselwirkung von Photonen mit der Festkörperoberfläche in einem Mikroplasma entstehenden Ionen werden entsprechend ihrer Masse und Energie in einem doppelfokussierenden Massenspektrometer getrennt. In dieser Arbeit werden die analytischen Besonderheiten und die Anwendung der Laserionisations-Massenspektrometrie in der Spurenanalyse von Keramiken beschrieben.

1. Introduction

Laser ionization mass spectrometry for trace analysis is widely used in all fields of modern science and technology: in materials research (e.g. high-purity materials or ceramics), in metallurgy, in semiconductor production and microelectronics, in geology or mineralogy, in environmental and biological research, and in medical science.

The development of laser ionization mass spectrometry was started by HONIG and WOOLSTON /1/ with studies of ionization in the interaction of focusing laser radiation (using a ruby laser) with the surface of a solid, where positive ions are produced from metals, semiconductors, and insulators. The authors describe the formation of ions, electrons and neutrals in a laser cloud. Almost at the same time and in subsequent years HONIG /2/, DUMAS /3/, BAN and KNOX /4/ and other authors /5,6/ published their papers on laser ion sources and on mass analysis by means of time of flight mass spectrometers or double-focusing static mass spectrometers. The application of laser ionization mass spectrometry to solids has been reviewed by MAKSIMOV and LARIN /7/, KOVALEV et al. /8/, and CONCEMIUS and CAPELLEN /9/.

Laser ionization mass spectrometry is a universal analytical method in determination of trace amounts in solids with a wide coverage. Its special features qualify laser ionization mass spectrometry for the quantitative determination of trace elements in inorganic compounds. The advantages of LIMS for the analysis of ceramic materials are:

- high efficiency of evaporation and ionization,
- high absolute and relative sensitivity,
- capability of a direct analysis of ceramics,
- coverage of the entire periodic table in the concentration range from $3*10^{-7}$ % to 100 %,
- simplicity of the mass spectra obtained,
- capability of depth profile (layer-by-layer) analysis in the µm range,
- determination of the distribution of traces in ceramics.

Besides these most attractive features for trace analysis by laser ionization mass spectrometry, the technique can also be used for accurate and precise multielement analysis of minor and even major components in inorganic samples. As universal multielement method, laser ionization mass spectrometry permits the simultaneous determination of all chemical elements and their isotopes in ceramics. Furthermore, the power density is effective in the spot area can be varied by adjustment of the laser parameters (e.g. laser energy, wavelength) and can be better controlled in comparison to the ionization parameters of other analytical mass spectrometric methods for the analysis of solids. It can be easily applied as an absolute method without the use of standards under certain experimental conditions. These features and the general advantages of mass spectrometric methods favour laser ionization mass spectrometry for the analysis of the composition and distribution of traces in solids.

Ceramics are widely used as materials more resistant to high temperatures, oxidation and corrosion processes in engineering industry and also electronic industry, where insulating multilayers are desirable because their small size, high capacitance, electric stability and low cost. Among the ceramics are inorganic sintered compounds that include nitrides, carbides, borides, silicates and oxides. Especially, impurities are of interest in ceramic materials used as well as substrate material or for the thin film preparation (also of HTSC ceramics /10/) or as crucible material for the growing of single crystals (e.g. GaAs growing in p-BN crucible).

For the trace analysis of ceramics the application of LIMS is barely known, only some applications of LIMS in the analysis of glasses are described. Tab. 1 summarizes some applications of laser induced mass spectrometry in insulator research.

Table 1: Application of Laser Ionization Mass Spectrometry to Trace Analysis of Insulators
LAMMA = Laser Micro Mass Analyzer; MH-MS = Mattauch-Herzog type mass spectrometer

Ref.	Laser					target	analyzed chemical elements
	system / MS /	wave length [nm]	power density [W cm^{-2}]	energy per pulse [J]	pulse length [ns]		
Eloy et al. /11/	Nd-YAG single foc.MS	353	10^8-10^{10}	10^{-7}-10^{-5}	30	glass	O,Si,Na,Al,Ca,Cr,Mn,Zn,Sr,Zr,Mo
Bingham and Salter /12/	Nd-YAG MH-MS	1064	10^9-10^{11}	10^{-2}	15	glass	Pb,B,U,Sr,Th,Ag,Zn,Co,Fe,Cu,Mn, Rb,Ti,K
Surkyn and Adams /13/	Nd-YAG LAMMA	265	10^8-10^{10}	$5*10^{-8}$-$2.5*10^{-5}$	15	glass	Na,Mg,Al,P,Si,K,Ca,Ti,Mn,Fe,Ba
Spurny et al./14/	Nd-YAG LAMMA	265	10^8-10^{10}	-	15	glass fibers	Mg,K,Ca,Fe
Leybold Hereaus /15/	Nd-YAG LAMMA	265	10^8-10^{10}	-	15	glass NBS standard	K,Ca,Sc,Ti,Mn,Fe,Ni,Co,Cu,Zn,Ga, Ge,As,Sb,Rb,Si,Cr,Y,Zr,Nb,Mo,Ag, Cd,In,Sn,Se,Te,Cs,Ba
Sander-son /16 /	Nd-YAG MH-MS	1064	$2*10^{11}$	-	-	glass NBS standard	K,Ti,Fe,Co,Ni,Cu,Rb,Ag,Ba,La,Ce, Nd,Eu,Pb,Th,U
Michiels et al. /17/	Nd-YAG LAMMA	265	10^8-10^{11}	-	15	glass NBS standard	Li,Be,B,Mg,Si,K,Ti,Y,Nb,In,Cs, Ba,La,Ce,Pr,Ho,Tm,Tm,Lu,Ta,Pb, Th,U

The paper presents an overview of a special field in inorganic laser induced mass spectrometry - the trace analysis of chemical elements of ceramics.

Laser ionization mass spectrometry - LIMS

All laser mass spectrometric methods are suitable for the elemental or structural analysis of different materials, but only laser ionization mass spectrometry (LIMS), resonance ionization mass spectrometry (RIMS) /18,19/ and laser ablation mass spectrometry (LAMS) /20/ have been used in the quantitative analysis of impurities in inorganic solid materials. The above mentioned techniques differ in the formation of ions in the laser ion source.

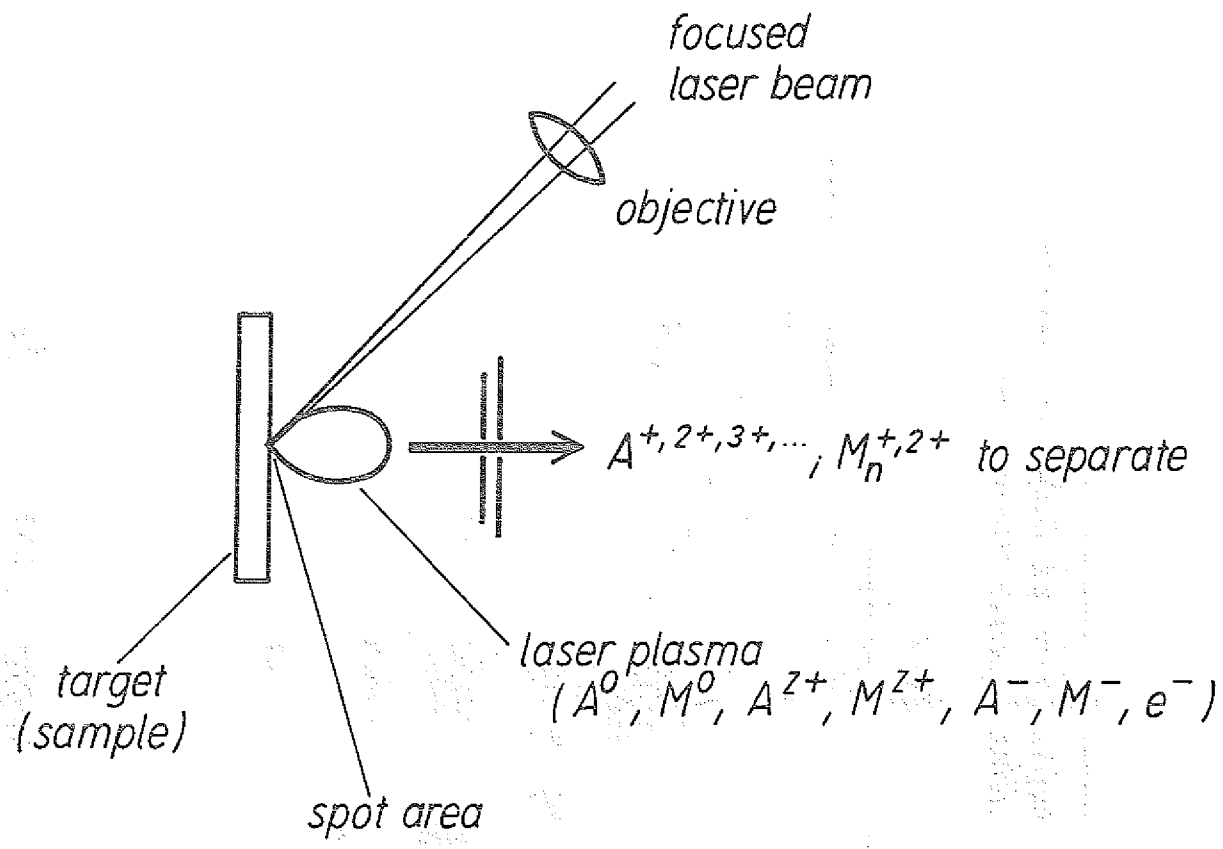

Fig. 1: Scheme of laser ionization process.
In a laser micro plasma, atoms A, molecules and clusters M, and the ionic species are present.

Laser ionization mass spectrometry is based on the evaporation and atomization of sample material by means of a focused pulsed laser beam and on the ionization of the evaporated atoms, clusters, and molecules in a laser microplasma formed in the spot area of the irradiated sample (see Fig. 1).

The efficiency of this process depends on the intensity of the laser beam, the physical and chemical properties of the sample material, and the conditions of plasma formation.

The fact that the ionization process can be influenced by the laser power density in the spot area is the great advantage of this ionization method. All types of solid materials are accessible to this ionization method, independent of their electrical conductivity, reflection properties, or types of chemical bonds.

The generation of high temperature plasmas produced by focusing laser pulses onto a solid surface -- basic principles of laser-solid interaction -- has been the subject of numerous theoretical and experimental publications /8, 21-23/.

2. Experimental conditions

The mass spectrometric trace analyses of ceramics were carried out with a double-focusing mass spectrograph (MX 3301, SKB St. Petersburg) with Mattauch-Herzog geometry with a laser ion source. A commercial russian spark source mass spectrometer has been expanded into a laser ionization mass spectrometer.

The most successful configuration used for trace analysis of inorganic sample materials (for the bulk and trace analysis of metals, semiconductors and non-conducting materials) in LIMS is the reflection mode. In Fig. 2 the scheme of laser ion source is shown. The Nd-YAG laser with a high repetition rate of laser pulse in the range from 10 Hz to a few kHz allows a high sensitive laser ionization mass spectrometry for trace analysis. With the ruby, Nd-glas or Nd-YAG impulse laser in single shot regime also a local

analysis or depth profile analysis of ceramics or thin films is possible.

The positive or negative charged ions formed in the laser plasma were accelerated into the double focusing mass spectrometer (Fig. 3). The experimental arrangement of laser ion source with a Mattauch-Herzog instrument (with a mass resolution R = m/ Δ m of about 10 000) is suitable for interference-free trace analysis and also for the study of cluster ion formation processes.
The experimental parameters of laser ionization mass spectrometry are summarized in Table 2 .

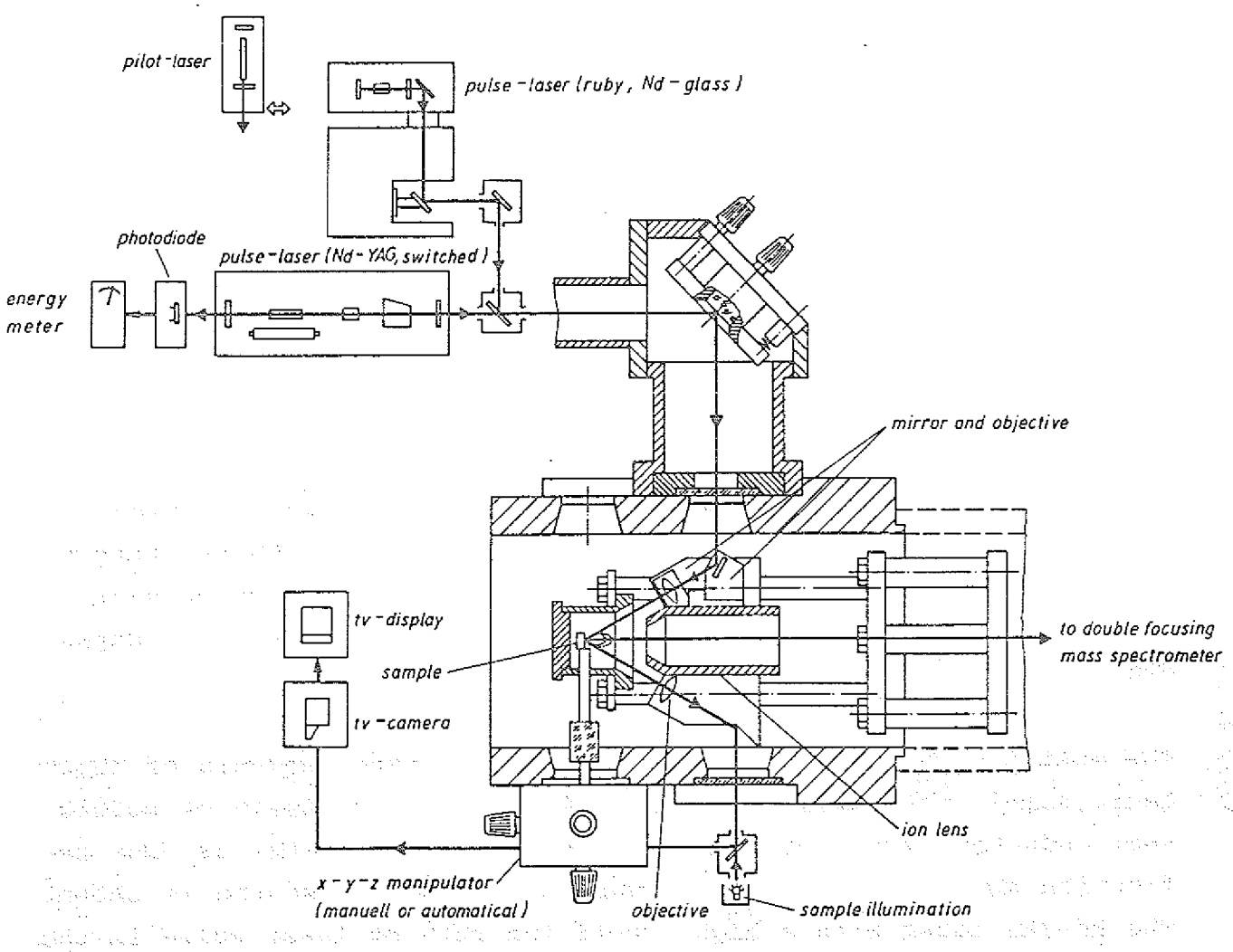

Fig. 2: Scheme of a laser ion source

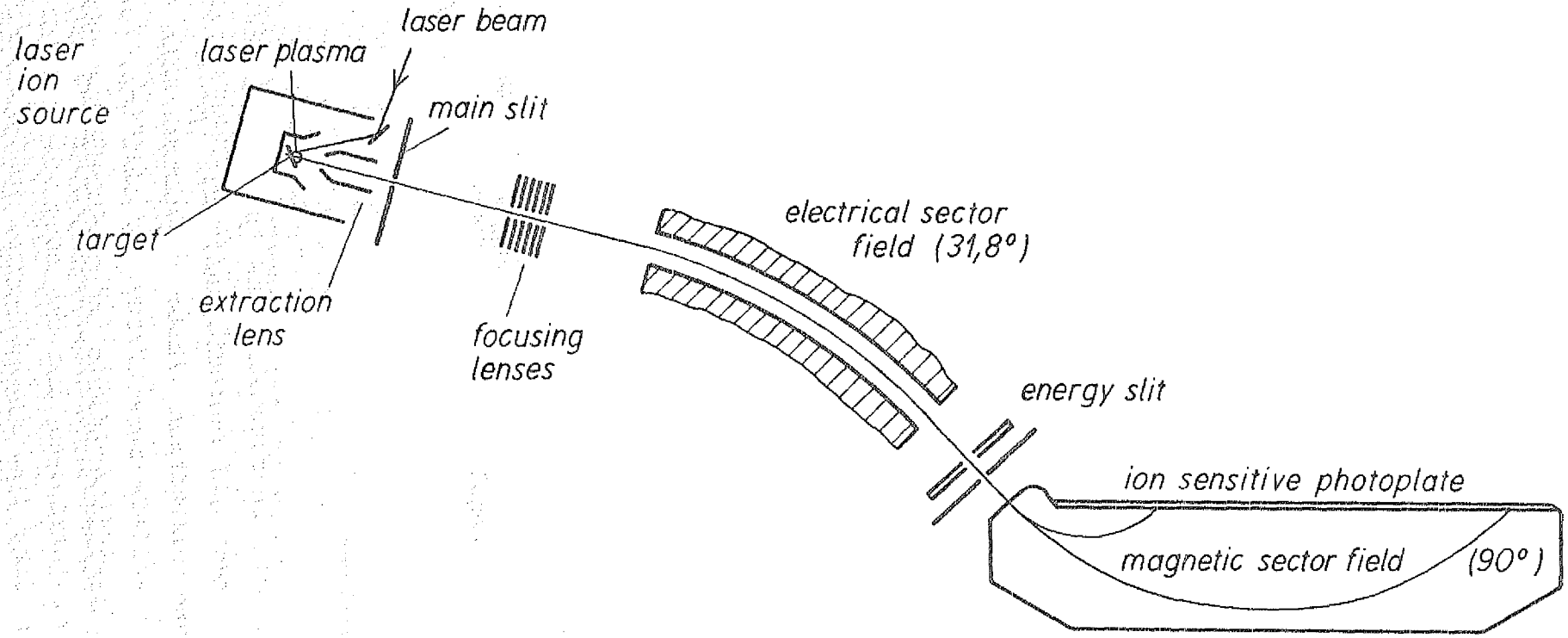

Fig. 3: Schematic diagram of laser ionization mass spectrograph

Table 2: Experimental parameters of LIMS

ion source:		
Nd-YAG laser		
wavelength	-	1064 nm
pulse width	-	100 ns or 15 ns
repetition frequency	-	5 kHz or 100 Hz
acceleration voltage	-	15 kV to 25 kV
ion separation:		
main slit	-	10 µm
electrostatic analysator	-	31.8° sector field
magnetic analysator	-	90° sector field
registrable mass range	-	1:36,e.g. 8 a.u. - 288 a.u.
ion detection:		
ion sensitive photoplate	-	Ilford Q2 photoplate
range of exposition	-	10^{-14} - $3*10^{-7}$ C
mass resolution	-	10 000
vacuum condition:		
ion source		10^{-6} - 10^{-7} Torr
analyzers		10^{-7} - 10^{-8} Torr
analytical results:		
detection limit	-	10 ppb - 100 ppb
reproducibility of results	-	10 - 20%

3. Analytical features

Laser ionization mass spectrometry has become attractive for very sensitive multielement and isotopic analysis. Due to its high rate of evaporation and ionization, laser ionization mass spectrometry offers a high and uniform sensitivity. In addition, low background facilitates low detection limits of the chemical elements. The mass separation of laser ions and the easy identification of trace elements even at very low concentration levels - in the ppm or

sub-ppm range - are characteristic features of laser ionization mass spectrometry.

An important advantage of laser ionization mass spectrometry is that this analytical method does not require any sample preparation, because the laser ionization is applicable for all materials without limitation.

The identification of trace elements is very simple and is accomplished by way of a qualitative analysis of their isotopes at given masses. An orientation in the mass spectra is easy, since the lines of different charged states (z) of atomic ions of major elements of the sample material appear at the corresponding m/z ratio. A mass spectrum of the sample to be analyzed can be predicted exactly if the atomic molecular and cluster ions of the major, minor and trace elements formed in the laser plasmas are known. Thus, all line interferences appearing between the analysis ions -- usually these are single charged atomic ions of the chemical element to be determined -- and the disturbed ions -- e.g. molecular and cluster ions formed in the laser plasma, charge exchange lines, and others -- can also be determined. In a quantitative trace analysis of inorganic sample material, all line interferences must be detected unambiguously. A mathematical correction of the line interferences is possible only in a some cases.

The quantitative mass spectrometric analysis is carried out by measuring the ion currents -- these are proportional to the element concentration c_x of trace element x -- mostly by means of an internal standard element with well-known concentration c_v. A bulk element (e.g. in the analysis of high purity metals or semiconductors) can be used as an internal standard or an internal standard may be admixed to the powdered sample material. The following analytical equation is applied for the evaluation of the concentration of chemical elements:

$$c_x = c_v \cdot \frac{I_x}{I_v} \cdot \frac{S_v}{S_x} \cdot \frac{A_v}{A_x}$$

I_v and I_x are the ion currents (or the numbers of ions) measured from the internal standard v and trace element x; A_v and A_x are the respective isotopic abundances; and S_v and S_x are the respective relative element sensitivities. The relative sensitivity coefficient (RSC) - S_x/S_v - is a function of the physical and chemical properties of the sample (e.g. ionization potential, melting point of the trace element, dissociation energy of analyzed compounds, sample composition, etc.) and of the laser ion source parameters (e.g. laser power density, ion focusing conditions, initial energy of ions). By applying RSC's, all these effects can be considered indirectly and the accuracy of the analytical results can be improved.

The *absolute sensitivity* of a laser ionization mass spectrometry using a classical static ion separation system varies between 10^{-8} g and 10^{-12} g. The *relative sensitivity* of a laser ionization mass spectrometer using a Mattauch-Herzog configuration is usually somewhat better in comparison to a time-of-flight mass spectrometer and is about 10 ppb because the possibility of the integration of exposition with the photoplate detection. In general, the element-specific relative sensitivity of laser ionization mass spectrometry varies between 10 ppb and 1 ppm. Laser ionization mass spectrometry features a variation of the sensitivity between elements and also a matrix dependent variation of sensitivity.

The *accuracy* of laser ionization mass spectrometry depends on the calibration procedure used. From measurements of standard samples, it is possible to obtain relative sensitivity coefficients (RSC's). The RSC(x) of a chemical element (x) is determined by dividing the measured value c_x by the certified value c_s of a standard samples. Usually, relative sensitivity coefficients are defined on the basis of a matrix and are applicable only to a particular analysis technique with specified analytical parameters. Correcting the concentration measured with an RSC provides analytical results with improved accuracy. The RSC's can also be applied in trace analyses in ultrasensitive mass spectrometry, provided the RSC's have been determined on the basis of relatively higher concentrations of the chemical element in the calibration sample. An influence of the matrix needs to be factored in, but

homogeneous standard reference materials are not available for many matrices. In such a case the preparation of a mixed synthetic standard using suprapure chemicals with given element concentrations is necessary in order to determine chemical elements in a special matrix. The maximum differences of experimental RSC's using different matrices are no greater than 10. The *precision* of the analytical results of laser ionization mass spectrometry using RSC's is, on an average, 25% to 30% relative standard deviation.

In the range of laser power density of 10^9 to 10^{10} W/cm^2, the most RSC's are nearly around 1 /24-26/. This range of laser power density is favourable for mass spectrometric analysis, there is no fractional evaporation of chemical elements or compounds in the ion source. The ion beam composition corresponds to the composition of the analyzed target material.

Table 3 summarizes the experimental LIMS results of a zirconium standard (Zr-NBS SRM 1235) and the resulting RSC values at different laser power densities (I - $5*10^8$ W/cm^2/27/ and II - $5*10^9$ W/cm^2). An increase of laser power density results in a changing of the RSC's values.

The critical factor responsible for the *sensitivity*, *accuracy*, and *precision* of the analytical method is that of a constant ion formation rate in the laser ion source. This can be influenced by varying of the laser parameters, e.g. of the laser power density during the interaction of the laser beam with the sample. The reasons for the inconstancy of ion currents in laser ionization mass spectrometry are the change of the interaction conditions of photons with the solid surface in the spot area and the inhomogeneity of the sample material. The problems of inhomogeneities are greater in laser ionization mass spectrometry than in spark source mass spectrometry because with the laser a smaller sample volume is evaporated and ionized. To reduce analytical errors in mass spectrometric measurements, mass spectrometric trace analysis by means of laser excitation is carried out by scanning the target surface with the laser beam or by movement of the target (e.g. rotation). On the other hand, inhomogeneities can be reduced by good powdering and mixing of the sample material, e.g. in the

Table 3: Mass spectrometric results of the zirconium-standard NBS 1235 and the RSC values

chem. element	concentration /ppm/		NBS-value /ppm/	RSC	
	I	II		I	II
B	-	4	2	-	2
C	-	220	170	-	1.3
F	-	15	-	-	-
Na	270	125	-	-	-
Mg	8	1	-	-	-
Al	(810)[1)]	420	105	(7.7)	4
Si	96	100	95	1.01	1.05
P	42	46	44	0.95	1.04
S	46	40	-	-	-
Cl	9	5	-	-	-
K	(1000)[1)]	152	-	-	-
Ca	70	17	-	-	-
Ti	230	160	-	-	-
V	(90)[1)]	32	10	(9)	3.2
Cr	(340)[1)]	135	60	(5.7)	2.3
Fe	930	857	850	1.1	1.0
Mn	26	28	25	1.04	1.1
Ni	70	67	65	1.07	1.03
Co	-	18	20	-	0.90
Cu	44	75	80	0.55	0.94
Zn	-	2.5	-	-	-
As	-	0.8	-	-	-
Sr	-	1.7	-	-	-
Y	-	0.4	-	-	-
Nb	210	298	200	1.05	1.5
Mo	38	41	40	0.95	1.03
Sn	25	23	25	1	0.9
Ba	-	0.3	-	-	-
Hf	52	100	95	0.55	1.05
Ta	70	240	280	0.25	0.86
W	114	49	50	0.28	0.98

1) possible inhomogeneities

trace analysis of geological samples. Inhomogeneities can also be avoided by dissolving the sample. The sample must be handled very carefully since a contamination of the sample material with impurities is always possible. The sensitivity is also increased significantly by additional chemical separation of the matrix elements.

A further improvement of trace analysis can be attained by application of the powerful isotope dilution technique (ID-MS), but ID-MS is expensive because of extensive sample preparation processes. The method of isotope dilution mass spectrometry has long been used as a single or multielement analytical method in combination with thermal ionization /28/, laser ionization /29/, or spark ionization /30/. Sample preparation is similar in all cases. The sample material is completely dissolved in acids, an isotope spiked solution is added and, in laser ionization mass spectrometry, a small amount thereof is dried on a target surface (e.g. high purity Ag metal). To avoid matrix effects, the matrix elements can also be separated before adding the spiked solution. An accuracy of 2 - 5% can be expected in this case. The isotope spikes can also be used as an internal standard in trace analysis.

4. Appearance of molecular and cluster ions in laser mass spectra

The existence of molecular and cluster ions is well known in laser ionization mass spectrometry and their intensities are a function of the laser plasma parameters. Mostly, the clusters play a subordinate role in ordinary element analysis because of their minor intensities. In trace analysis of inorganic sample materials, the molecular and cluster ions M_n^+ (and also the multiple charged ions M^{z+}) formed in the laser plasma disturb the atomic analysis ions by interferences. A mass resolution of up to 10 000 requires the separation of all of these interfering ions from the atomic ions M^+. A systematic study of the types of clusters formed in a laser plasma is useful for estimating mass spectral interferences of cluster and atomic ions of the same mass. Therefore, knowledge of cluster formation and abundance distribution is of considerable importance for mass spectrometric analysis as well as for our

understanding of the chemical and physical processes in laser plasmas.

The problem of interferences of atomic ions with cluster ions for trace analysis should be explained on the example of boron nitride. A characteristic feature of the mass spectrometric analysis of boron compounds is a high cluster formation rate in laser plasmas. At a laser power density of about $5*10^8$ W/cm^2 positively and negatively charged $B_nN_m^+$ cluster ions with well known abundance distributions were formed. For several B_nN_m clusters in laser plasmas the following sequence of ion intensities was found for positively and negatively charged cluster ions /31/:

$$B_nN_{n-1} > B_nN_{n-2} > B_nN_n.$$

Together with the B_nN_{n-2} and with the B_nN_n clusters the B_nN_{n-1} clusters give a typical alternating abundance distribution (for positively charged cluster ions see Fig. 4).

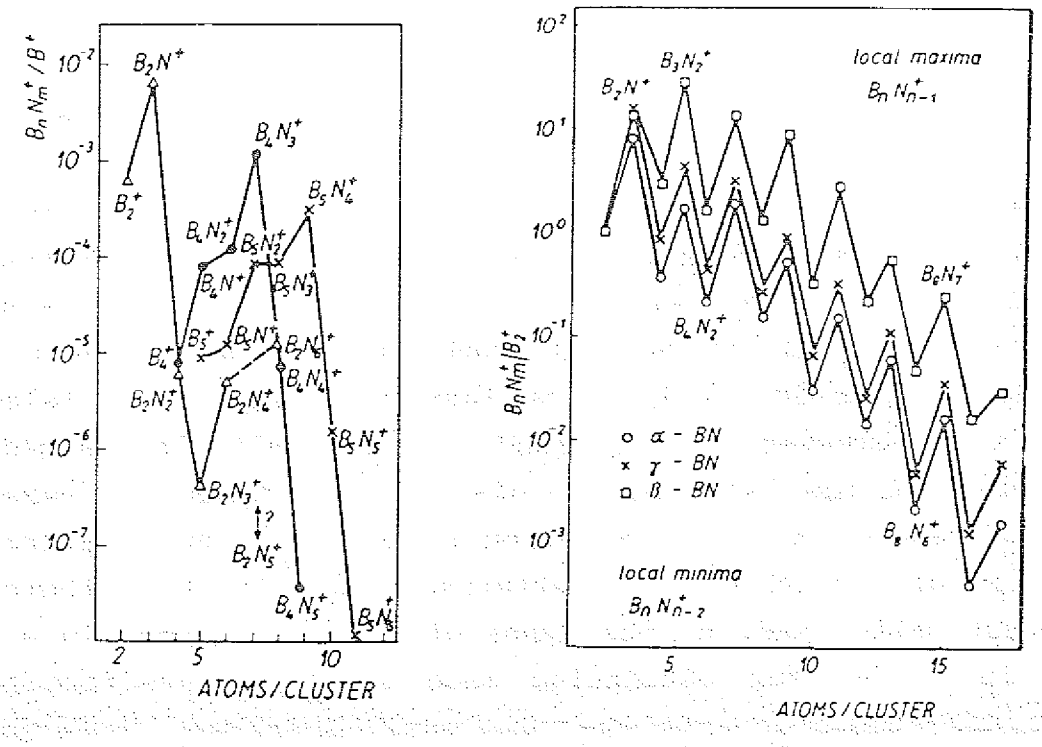

Fig. 4: Distribution of boron nitride clusters in a laser plasma

Table 4: Possible line interferences in the laser mass spectrum of a boron nitride sample in the trace analysis of magnesium and zinc and necessary mass resolution to separate the interferences (mass resolution: $R = m/\Delta m$), abundance of cluster ions relative to B^+

analyzed ion	mass /m/	cluster ion	mass /m/	R	abundance of cluster
$^{24}Mg^+$	23.9850	$^{10}B^{14}N^+$	24.0160	770	$4.7*10^{-4}$
$^{25}Mg^+$	24.9858	$^{11}B^{14}N^+$	25.0124	940	$1.9*10^{-3}$
		$^{10}B^{15}N^+$	25.0130	39000	$1.4*10^{-6}$
$^{26}Mg^+$	25.9826	$^{11}B^{15}N^+$	26.0094	970	$5.7*10^{-6}$
$^{32}S^+$	31.9721	$^{10}B^{11}B_2^+$	32.0316	540	$2.3*10^{-2}$
$^{33}S^+$	32.9715	$^{11}B_3^+$	33.0279	580	$9.2*10^{-2}$
$^{34}S^+$	33.9679	$^{10}B_2{}^{14}N^+$	34.0289	560	$1.4*10^{-1}$

Possible line interferences in the laser mass spectra of boron nitride for the trace analysis of magnesium, sulfur and zinc are summarized in Tables 4 and 5.

Table 5: Possible line interferences in the laser mass spectrum of a boron nitride sample in the trace analysis of zinc and necessary mass resolution to separate the interferences (mass resolution: R = m/Δ m); abundance of cluster ions relative to B^+

analyzed ion	mass /m/	cluster ion	mass /m/	R	abundance of cluster
$^{64}Zn^+$	63.9291	$^{11}B_2{}^{14}N_3{}^+$	64.0278	650	$2.4*10^{-4}$
		$^{11}B^{10}B^{14}N_2{}^{15}N^+$	64.0285	91000	$1.8*10^{-6}$
		$^{10}B_2{}^{11}B_4{}^+$	64.0631	1800	$1.2*10^{-4}$
		$^{10}B_5{}^{14}N^+$	64.0678	14000	$1.9*10^{-6}$
$^{66}Zn^+$	65.9261	$^{10}B^{14}N_4{}^+$	66.0252	670	$3.5*10^{-3}$
		$^{11}B_6{}^+$	66.0558	2200	$2.0*10^{-3}$
		$^{10}B_3{}^{11}B_2{}^{14}N^+$	66.0605	14000	$3.0*10^{-8}$
		$^{10}B_4{}^{11}B^{15}N^+$	66.0612	99000	$2.0*10^{-11}$
$^{67}Zn^+$	66.9271	$^{11}B^{14}N_4{}^+$	67.0216	710	$1.4*10^{-2}$
		$^{10}B_2{}^{11}B_3{}^{14}N^+$	67.0569	1900	$1.2*10^{-7}$
		$^{10}B_3{}^{11}B_2{}^{15}N^+$	67.0575	105000	$9.0*10^{-11}$
$^{68}Zn^+$	67.9249	$^{10}B^{11}B_4{}^{14}N^+$	68.0532	530	$4.8*10^{-7}$
		$^{10}B_2{}^{11}B_3{}^{15}N^+$	68.0539	97000	$3.0*10^{-10}$
		$^{10}B_4{}^{14}N_2{}^+$	68.0579	17000	$2.9*10^{-4}$
$^{70}Zn^+$	69.9253	$^{11}B_5{}^{15}N^+$	70.0466	580	$6.0*10^{-9}$
		$^{10}B_2{}^{11}B_2{}^{14}N_2{}^+$	70.0506	17500	$1.2*10^{-5}$
		$^{10}B_3{}^{11}B^{14}N^{15}N^+$	70.0513	99000	$3.5*10^{-6}$
		$^{10}B_7{}^+$	70.0906	1800	$1.2*10^{-7}$

It is shown that the mass resolution for the mass separation of the atomic ion and the neighbouring cluster ion at the same mass is in each case lower than 1000. In contrast the line interferences between the different cluster ions of boron nitride require a significantly higher mass resolution. The necessary mass resolution is especially high for the separation of clusters with the isotop ^{15}N of the neighbouring cluster ions. But these cluster species were expected with very low intensities since the abundance of the natural isotope ^{15}N is 0.365%.

In Fig. 5 a part of a laser mass spectrum of boron nitride is present.

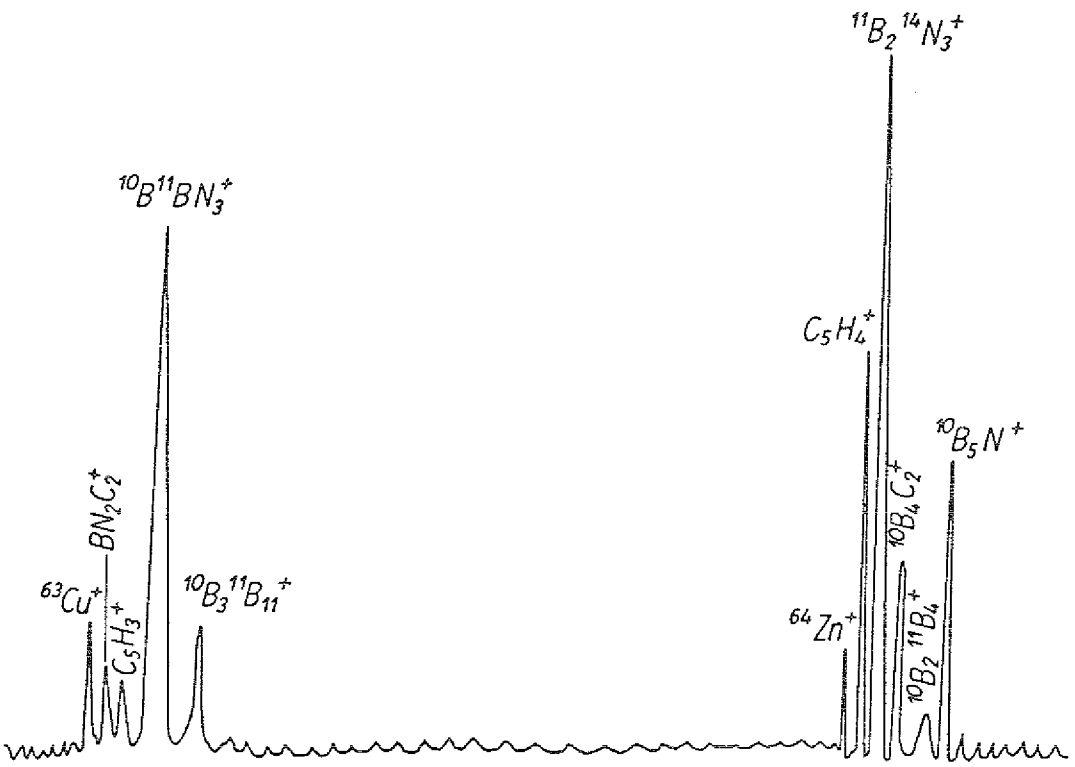

Fig. 5: Part of a laser mass spectrum of a boron nitride sample (with carbon impurities)

In spite of the multitude of cluster ions of boron nitride in laser mass spectra the trace analysis is practicable.

The necessary mass resolution for boron nitride clusters as a function of the mass of the analysed ions is shown in Fig. 6.

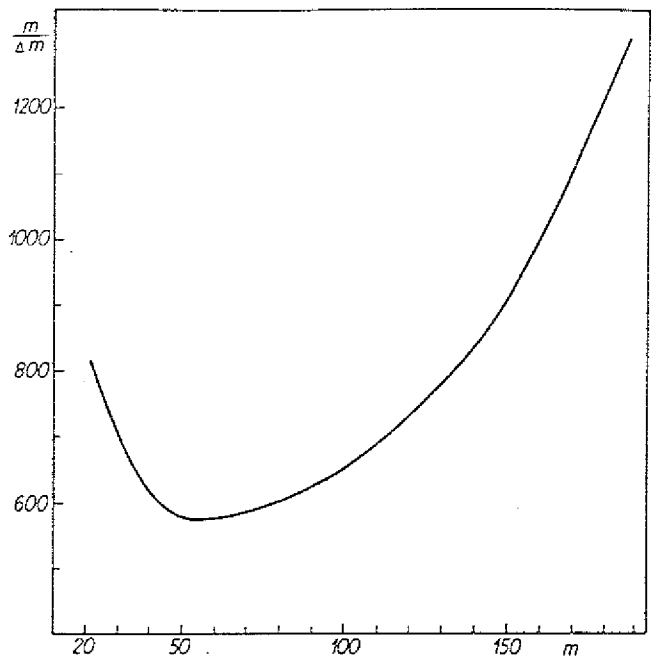

Fig. 6: Necessary mass resolution for the separation of boron nitride clusters and atomic ions of the analyte

Similar to boron nitride the trace analysis of silicon nitride is limited by disturbed cluster ions. In the laser mass spectra of silicon nitride detected line interferences of atomic and cluster ions in trace analysis on Si_3N_4 by LIMS are summarized in Table 6.

Table 6: Interferences of atomic and cluster ions in laser mass spectra of Si_3N_4

cluster ion (M^+)	mass /u/	rel. intensity (M^+/Si^+)	atomic ion	$m/\Delta m$
SiN^+	41.98	$2.1*10^{-6}$	$^{42}Ca^+$	2 000
Si_2^+	55.95	$2.5*10^{-3}$	$^{56}Fe^+$	2 950
Si_2N^+	69.96	$1.3*10^{-3}$	$^{70}Ge^+$	2 200
$Si_2N_2^+$	83.96	$4.7*10^{-5}$	$^{84}Sr^+$	1 680
$Si_2N_2B^+$	94.97	$5.5*10^{-5}$	$^{96}Mo^+$	1 480
$Si_3N_2^+$	111.94	$4.4*10^{-5}$	$^{112}Cd^+$	3 284
$Si_4N_2^+$	139.92	$4.6*10^{-5}$	$^{140}Ce^+$	9 330
$Si_5N_2^+$	167.89	$5.4*10^{-5}$	$^{168}Er^+$	3 830

Clusters are also of interest for several practical purposes. For example, clusters can be synthesized via laser-induced reactions of atomic and molecular species which, possibly due to their deposition on substrates, can result in thin films with new and interesting properties /32-34/. An example of this is the deposition of boron nitride clusters and investigation of laser-induced plasma deposition of boron nitride by LIMS as described in /35/.

For inorganic trace analysis by laser ionization mass spectrometry, experimental conditions are of interest under which the cluster formation rate is minimal. A maximum of the cluster formation rate of carbon clusters using a graphite target /36/ and carbide clusters using a rare earth oxide and graphite mixture target /32/ is observed at ϕ 10^8 W/cm^2. At this laser power density, the intensity of the cluster ions are higher than those of the atomic ions to be analyzed. At a high laser power density, $\phi > 10^{10}$ W/cm^2, cluster formation is negligible because of the high dissociation rate of possible clusters formed in the laser plasmas. In laser mass spectra using a graphit target at a laser power density of about 10^{10} W/cm^2 Bykovskii et al. /37/

observed only C_2^+ and C_3^+ clusters with intensities of 10^{-5} and 10^{-7}, relative to the atomic ions. From the point of view of the cluster formation rate and the constancy of relative sensitivity coefficients of chemical elements this laser power density is most suitable for inorganic trace analysis.

5. Results of Trace Analysis on Ceramics by LIMS

5.1 Nitride

5.1.1 *Boron Nitride*

In following, the application of laser ionization mass spectrometry by the trace analysis of boron nitride is discussed.

In order to demonstrate the efficiency of LIMS in the analysis of ceramics two boron nitride samples with different concentrations of trace impurities were investigated. In the case of trace analysis in the 10 - n*100 ppm concentration range LIMS can be applied without difficulties (Table 7, sample I). With boron nitride samples of high purity the trace analysis is more complicated.

Table 7: Trace element analysis on boron nitride by LIMS in comparison with SSMS

chemical element	concentration /ppm/		
	sample I	sample II	
	LIMS	LIMS	SSMS
F	35	< 2	0.32
Na	590	18	37
Mg	90	2.4	n.d.[1)]
Al	280	6.9	6.3
P	240	< 2	3.4
S	160	< 3	(80)
Cl	240	< 5	5.7
K	300	5.3	3.5
Ca	210	9.0	14
Ti	490	-	6
Fe	920	-	2.5
Co	30	-	1
Zn	110	< 10	0.5
Cu	195	-	0.6

1) Interferences of Mg^+ ions with cluster ions of high intensity, the concentration of Mg in boron nitride could be not determined by reason of a high background in this mass range.

For the determination of the concentration of trace elements in the ppb-range it is necassary to expose the photoplate of 100 nC and more. This is not possible with LIMS using an Nd-YAG laser at a wavelength of 1064 nm and a relatively low laser energy (1 mJ), long laser pulses (100 ns) and a low laser power density of $5*10^8 W/cm^2$. Under these experimental conditions the photons are reflected and a sligth plasma formation is observed. As a result, low ion currents were measured.

With our experimental conditions we only reached a detection limit in the ppm range. For an ultrasensitive trace analysis of boron nitride samples of high purity by laser ionization mass spectrometry a laser system with a short wavelength (in the range of visi-

ble light) - using a frequency multiplier - using a frequency multiplier and higher laser energy must be applied.

A comparison of the results of LIMS and SSMS shows the efficiency of the SSMS. Because of the higher exposition of the ion sensitive photoplate by SSMS (factor 10) higher concentrations of chemical elements could be determined.

5.1.2 *Silicon Nitride*

The analytical results of survey analysis of silicium nitride by LIMS are summarized in Table 8.

Table 8: Trace element analysis on Si_3N_4 by LIMS

chem. element	concentration /ppm/	chem. element	concentration /ppm/
B	1 600	Mn	370
C	1 170	Co	200
Na	500	Ni	250
Mg	13 600	Cu	105
Al	320	Zn	6
P	3	Sr	12
S	16	Zr	40
Cl	280	Mo	100
K	1 000	Ba	130
Ca	1 260	La	1
V	10	Rb	2
Ti	370	Cs	0.1
Cr	850	W	680
Fe	3 650	Sc	0.1

The investigated silicon nitride was a technical product with high concentrations of impurities. This can demonstrated by LIMS.

5.2 Carbide

5.2.1 *Silicon Carbide*

Compact silicon carbide was analysed using a focused Nd-YAG laser at a pulse width of 15 ns and a repetition frequency of 80 Hz. The trace analysis of some chemical elements is difficult due to many line interences. Measured intensities of cluster ions ($Si_nC_m^+$) are given in Table 9.

Table 9: Relative intensities of $Si_nC_m^+$ cluster ions [$Si_nC_m^+/Si^+$]

cluster Ion	ion intensity
SiC^+	$5.1 * 10^{-6}$
SiO^+	$3.0 * 10^{-6}$
SiC_2^+	$5.2 * 10^{-5}$
Si_2^+	$1.6 * 10^{-5}$
SiC_3^+	$1.9 * 10^{-7}$
Si_2C^+	$3.1 * 10^{-5}$
$Si_2C_2^+$	$1.4 * 10^{-4}$
$Si_2C_3^+$	$6.2 * 10^{-7}$
Si_3C^+	$1.6 * 10^{-6}$
$Si_3C_2^+$	$8.0 * 10^{-7}$

A determination of concentration of Cr, in the 10 ppm-range is impossible (line interference with SiC_2^+).

Table 10 summarizes the experimental LIMS results of trace analysis of a compact silicon carbide sample by laser ionization mass spectrometry.

Table 10: Trace element analysis of compact silicon carbide by LIMS

chem. element	concentration
F	0.1
Na	9
Mg	7
Al	290[1)]
P	3.5
S	0.5
K	260[1)]
Ca	35
Ti	138
V	70
Cr	n.d[2)]
Fe	260
Cu	<1.5
Mo	<2.5
Zr	49

1) inhomogeneities

2) line interference with SiC_2^+

5.2.2 *Tungsten Carbide*

The results of trace analysis of tungsten carbide by LIMS are summarized in Table 11. In earlier experiments we found, the formation rate of cluster ions in the laser plasma of tungsten carbide is lower than in a tungsten oxide-graphite mixture /38/. For the trace analysis of tungsten carbide the cluster formation is of no importance.

Table 11: Trace element analysis of wolfram carbide by LIMS

chem. element	concentration /ppm/	chem. element	concentration /ppm/
Na	58	Cu	10
Mg	16	Zn	1.7
Al	75	As	1.8
P	0.7	Y	0.9
S	1	Zr	10
K	620	Mo	2 680
Ca	830	Ag	1.8
Sc	0.9	Ba	31
Ti	120	La	3.4
V	12	Ce	3.5
Cr	730	Pr	0.6
Mn	24	Nd	4
Fe	15 000	Sm	1.2
Ni	27	Gd	0.8
Co	10	Ta	5

The detection limit is about 50 ppb. An increase of relative sensitivity can be reached by use of a laser with a shorter wavelength, with shorter pulses and higher laser energy. The trace analysis of silicon nitride and tungsten carbide were carried out with a Nd-YAG laser (1064 nm) with higher pulse energy (12 mJ) and shorter laser pulses (15 ns). The application of a laser system with shorter wavelength was in these trace analyses not possible owing to lack of a suitable laser system.

5.2.3 *Boron Carbide*

Boron carbide was used for the preparation of thin films by laser induced plasma deposition. In Table 12 the results of trace element analysis on boron carbide are summarized.

Table 12: Trace element analysis on boron carbide by LIMS

chemical element	concentration /ppm/
Na	190
Mg	80
Al	2 600
Si	1 600
P	0.4
K	560
Ca	1 780
Ti	220
V	8
Cr	340
Fe	580

The cluster distribution of boron carbide in laser plasma investigated by LIMS is discussed in /38/.

5.3 Oxide

5.3.1 *Aluminium Oxide*

Aluminium oxide ceramics are widely used in industry. We investigated polycrystalline Al_2O_3 ceramics of a high purity. The ceramic was applied as substrate material for the preparation of thin high-T_c superconducting Bi-Sr-Ca-Cu-O films by laser induced plasma deposition.

The results of trace analysis of Al_2O_3 substrates are given in Table 13.

Table 13: Results of trace analysis on Al_2O_3

chemical element	concentration /ppm/
B	1.1
F	2.2
Na	90
Mg	100
P	0.4
S	30
K	11
Ca	17

The alkali and earth alkali elements were measured with high sensitivity by laser ionization mass spectrometry (high RSC's), the true concentrations of these elements are something lower.

5.3.2 *Zirconium Oxide*

Sintered polycrystalline ZrO_2 ceramics were used directly by preparation of a thin buffer layer on silicon wafer with laser deposition and as substrates for thin high-T_c superconducting films. A silicon contamination during the sinter process of the Y_2O_3-stabilized ZrO_2 ceramic is possible.

The LIMS results are summarized in Table 14.

Table 14: Trace element analysis on a polycrystalline ZrO_2 pellet

chemical element	concentration /ppm/
Na	65
Mg	10
Al	58
Si	500
K	115
Ca	40
Ti	58
Cr	4
Fe	8
Y	5.2 %
Hf	620

With LIMS it is also possible to analyse ceramic powders. In this case the sample was homogenized and pressed in targets.

The LIMS-results of trace analysis of (Zr, Y) O_2 powder are shown in Table 15.

Table 15: Results of trace analysis of (Zr, Y)O_2 powder by LIMS

chemical element	concentration /ppm/
Mg	14
Al	520
Si	36
P	0,2
U	50
Ca	335
Ti	275
C	0.1
Cr	6.2
Fe	28
Mn	0.5
Cu	4.1
Mo	1.5
Nb	0.7
Hf	1.83 %

All determined concentrations of chemical elements in Tables 7 - 16 are uncorrected by Relative Sensitivity Coefficients (RSC's) of chemical elements, because ceramic standards with certified element concentrations are unknown. Without the correction of analytical results with Relative Sensitivity Coefficients of chemical elements the accuracy of concentration is about a factor 2-3. That means that the real concentration of Y in ZrO_2 the compact polyxrystalline pellet (Table 14) is perhaps higher than measured.

5.4 Glass Ceramics

Laser ionization mass spectrometry can be used for the survey analysis of ceramics unknown composition.
The results of mass spectrometric analysis of a glass ceramic sample are summarized in Table 16. The matrix element silicon with known concentration was used as an internal standard for the quantification.

Table 16: Mass spectrometric analysis of a glass ceramic sample

chemical element	concentration /ppm/
B	147
C	750
F	1.6 %
Na	2.7 %
M	8.5 %
Al	17.7 %
S	30
P	25
C	1885
K	3.7 %
Ca	180
Ti	35
Cr	0.5
Fe	42
Ni	5
Co	2
Ba	35

5.5 High-T_c Superconducting Ceramics

For the preparation of high-T_c superconducting ceramics (HTSC) and thin films the purity of the chemical substances and the exactness of all preparation steps were of high significance.

Usually, for the preparation of superconducting ceramics chemical substances with impurities in the ppm range were applied. The total concentration of impurities in ceramics or films with good superconducting properties should be no more than a few hundred ppm. The concentration of different trace elements in superconducting materials is of particular interest. Whereas low concentrations of some chemical elements, e.g. Ag (in the Y-Ba-Cu-O system) or Pb (in the Bi-Sr-Ca-Cu-O system) improve the superconducting properties, other chemical elements (e.g. Zn, Cd, Hg, Fe, Al) deteriorate the superconduction, so it is desirable to suppress these contaminations.

By laser ionization mass spectrometry the impurities of the of high-T_c superconducting $YBa_2Cu_3O_x$ and Bi-Sr-Ca-Cu-O ceramics were investigated. Using elemental spikes the *Relative Sensitivity Coefficients (RSC's)* were determined to improve the analytical results.

An improvement of precision and accuracy of analytic methods is the application of an internal standard element (e.g. Re) and elemental spikes in order to determine the *Relative Sensitivity Coefficients (RSC's)* using synthetic standards.

The experimental details of determination of RSC's on high T_c superconducting ceramics are described in /40/.

The results of mass spectrographic analysis of a high-T_c superconducting $YBa_2Cu_3O_x$ pellet are summarized in Table 17.

The analytical results of a high-T_c superconducting $Bi_2Sr_2Ca_2Cu_3O_x$ target prepared via the known solid state reaction from a stoichiometric mixture of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO are shown in Table 18.

The analytical values without correction by RSC's are signed by 1).

An increase of the concentrations of trace impurities in superconducting ceramics causes a deterioration of the superconducting properties. At a total concentration of impurities > 1 % semiconducting properties of ceramics at 77K were observed.

6. Conclusion

The great analytical potential of laser ionization mass spectrometry is based on its capability of a simultaneous determination of all chemical elements and their isotopes in solid samples, the possibility of a direct analysis of any kind of solids, its high efficiency for evaporation and ionization, its high absolute and relative sensitivity, and its applicability to microlocal and depth profile analysis. Furthermore, laser ionization mass spectrometric methods can be used in materials research, the semiconductor industry, microelectronics, atomic physics, geology, chemical analysis, biomedicine, environmental research, etc. In comparison to other spectrometric techniques for trace analysis laser ionization mass spectrometry can also be applied to the multielement analysis of both minor and major components in inorganic materials with similar accuracy and precision. In the described laser ionization mass spectrometry a double-focusing mass spectrometer with a Mattauch-Herzog geometry has been coupled with a laser ion source for the trace analysis of ceramics. In general, a disadvantage of laser ionization mass spectrometry is the high cost of mass spectrometers. Nevertheless, the development of laser ionization mass spectrometry will continue to make progress.

7. References

1. Honig RE, Woolston JR (1963) Appl Phys Lett 2: 138-139
2. Honig RE (1963) Appl Phys Lett 3: 8-11
3. Dumas JL (1967) Method Phys Anal 64: 47-49
4. Ban VS, Knox BE (1969) Int J Mass Spectrom Ion Phys 3: 131-141
5. Beam EC (1973) An Investigation of the Laser Source Mass Spectrometer, Thesis, Pennsylvania State University, University Microfilms Order No. 74-4215
6. Dietze H-J, Zahn H (1972) Exp Techn Phys 20: 389-400
7. Maksimov GA and Larin NV (1976), Usp Khim (USSR) 45: 2121-2125
8. Kovalev ID, Maksimov GA, Suchkov AI, Larin NV (1978) Int J Mass Spectrom Ion Phys 27: 101-137
9. Concemius RJ, Capellen JM (1980) Int J Mass Spectrom Ion Phys, 34: 197-271
10. Becker JS, Dietze H-J (1991) Proceedings SPIE's Technical Symposium on Microelectronic Processing Integration '91, 9-13 September 1991, San Jose, CA, USA
11. Eloy JF (1984) J de Physique 45: C2 265-269
12. Bingham RA, Salter PZ (1976) Anal Chem 48: 1735-1740
13. Surkyn P, Adams FJ (1982) Trace and Microprobe Technique, 1: 79-114
14. Spurny KR, Schörmann J, Kaufmann R (1981) Fresenius Z Anal Chem 308: 274-279
15. Leybold-Hereaus GmbH (1982), Köln, FRG, Application, 12-18
16. Sanderson TK (1985) Anal Proceed 22: 118-119
17. Michiels E, Van Vaeck L, Gijbels R (1984) Scann Electr Micros III: 1111-1128
18. Hurst GS, Payne MG, Kramer SD, Young JP (1979) Rev Mod Phys 51: 767-819
19. Smith DH, Young JP and Shaw RW (1989 Mass Spectrometry Reviews 8: 345
20. Phipps CR, Dreyfus RW in Laser Ionization Mass Analysis Ed. John Wiley & Sons, New York in press
21. Demtröder W, Jantz W (1970) Plasma Physics 12: 691-703

22. Shibanov AN (1985) in V.S. Letokhov (Ed), Laser Analytical Spectrochemistry, Adam Hilger, Bristol 353-376

23. Zahn H, Dietze HJ (1976) Int J Mass Spectrom Ion Phys 22: 111-120

24. Jansen JAJ, Witmer AW (1982) Spectrochim Acta 3B: 483-491

25. Bykovskii YuA, Schuralev GI, Belousov VI, Gladskoi VM, Degtjarev VG, Kolosov YuN, Nevolin VN (1978) Fiz Plasm 4 : 323-331

26. Matus L, Seufert M, Jochum KP (1988) Int J Mass Spectrom Ion Proc 84: 101-111

27. Dietze H-J, S. Becker JS (1987) Fresenius Z Anal Chem 302: 490-492

28. Heumann KG (1988) in Inorganic Mass Spectrometry, John Wiley & Sons, New York 301-348

29. Jochum KP, Matus L, Seufert HM (1988) Fresen Z Anal Chem 331: 136-139

30. Dietze H-J, Opauszky I (1979) Isotopenpraxis 15: 309-312

31. Becker JS, Dietze H-J (1986) Int J Mass Spectrom Ion Proc 73: 157-166

32. Dietze H-J, Becker JS (1987) "Beiträge zur Clusterforschung" ZfI-Mitt 134: 5-174

33. Martin TP (1986) Angew Chem 98: 197-212

34. Duncan MA, Rouvray DH (1989) Scientific American 60: 60-65

35. Becker JS, Dietze H-J, Keßler G, Bauer H-D, Pompe W (1990) Z Phys B-Condensed Matter 81: 47-51

36. Seifert G, Becker JS, Dietze H-J (1988) Int J Mass Spectrom Ion Proc 84: 121-133

37. Bykovskii YuA et al. (1978) Zh Tekn. Fiz (USSR) 48: 382-385

38. Dietze H-J, Becker JS (1988) Int J Mass Spectrom Ion Proc 82: 47-53

39. Becker JS, Dietze H-J (1988) Int J Mass Spectrom Ion Proc 82: 287-289

40. Becker JS, Dietze H-J (1991) 12 th International Mass Spectrometry Conference 26 - 30 August 1991, Amsterdam

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