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Secondary ion mass spectrometry in the study of lanthanide compounds

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Abstract

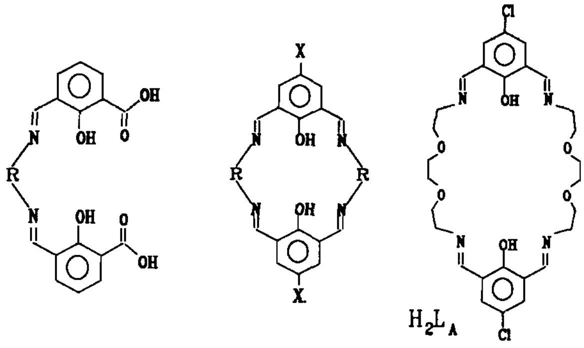
Interest in secondary ion mass spectrometry (SIMS) in the study of lanthanide compounds is rapidly growing and some results are reported here. Polynuclear complexes and mixed oxides containing 4-f ions were analyzed; in particular, the high accuracy and speed of measurements are evidenced in metal ratio determinations. The advantages of SIMS are compared with other analytical techniques and obtainable complementary results are described. Specific and sensitive responses show that rare earth elements can be detected at very low levels (ppm) and mixed oxides can be identified; in the latter case fragmentation patterns seem to be correlated with sample structures.

Introduction

In the last few years, bioinorganic chemistry, catalysis, solid state chemistry, preparation of new materials, etc. have received a new impetus from the development of knowledge of interactions between metal ions and the role played by polymetallic centres in magnetically condensed systems [1–10].

Homo- and hetero-polynuclear complexes containing rare earths are now widely studied because these metal ions, owing to their unique physico-chemical properties, are considered good candidates for the preparation of materials with particular magnetic, electric and/or optical properties [1, 3–6, 11–13].

Binuclear complexes containing rare earths are presumed to be good simple models in the study of the properties of the more complex new materials now available. In addition, homo- and hetero-dinuclear complexes have been used as useful precursors in the formation of crystallographically pure oxides, by means of their thermal decomposition [14]. Many macrocyclic and macroacyclic binucleating ligands of the type shown in Scheme 1 and related complexes containing 4f-ions have accordingly been synthesized and studied [15, 16]. We prepared the macrocycle H_2L_A by condensation of 2,6-diformyl-4-chlorophenol and 1,8-diamino-3,5-dioxaoctane. With this macrocycle, complexes formulable as $Ln_2L_A(NO_3)_4 \cdot nH_2O$ (Ln = La, Pr, Sm, Eu, Gd, Tb, Dy; $n = 1$, 2) and Ln^1_x–$Ln^2_{(2-x)}L_A(NO_3)_4 \cdot nH_2O$ ($Ln^1 \cdot Ln^2$ = La–Sm, La–Gd, La–Dy, La–Eu, Dy–Gd, Dy–Eu, Gd–Eu, Gd–Tb, Eu–Tb, La–Tb; $n = 1$, 2) were obtained and their magnetic and optical properties studied [3].



Scheme 1.

By thermal decomposition of these complexes almost the whole series of Ln_2O_3 oxides and several $Ln^1Ln^2O_3$ complexes (Ln^1Ln^2 = La–Sm, La–Gd, La–Dy, Nd–Gd, Dy–Eu, Dy–Nd) were prepared. Obviously, in these hetero-dinuclear compounds physico-chemical properties depend on the content of the two lanthanides, so that determination of the correct ratio between the two different metal centres is of primary importance. The role of mass spectrometric techniques in both inorganic and organic chemistry is rapidly growing and particularly secondary ion mass spectrometry (SIMS) is commonly used for both semiconductor and catalyst study, oxide

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layer analysis on metals, isotope measurements and for study of involatile molecules. In fact, SIMS may be considered not only a surface technique that can bombard the target in 'dynamic' (high primary beam current density) or 'static' (low primary beam current density) conditions with different destructive effects but also an analytical technique for ion compounds, metals and metal oxides, large molecules, etc. [17].

This paper reports results obtained by the SIMS technique in the analysis of polymetallic compounds and aims at showing advantages due to accuracy and speed of measurement. In particular, solutions containing lanthanide salts at ppm levels were analyzed, good calibration curves were obtained from the isotope patterns of La, Sm and Eu and mixed oxides of Eu and Dy (mechanical mixture and hetero-dinuclear oxides) were characterized.

Experimental

Homo- and hetero-dinuclear complexes were synthesized as reported elsewhere [3]. Oxides were prepared by thermal decomposition of the appropriate complex at 1200 or 1600 °C, following a procedure already published [14]. The lanthanide percentage was determined by flame emission by using a Varian AA-257 atomic absorption spectrophotometer. Sample homogeneity and lanthanide and chlorine (when present) ratios were roughly checked by electron microscopy using a methodology already published [18]. Part of the mass spectrometric measurements were performed on a double focusing instrument (Nier-Johnson E-B geometry) connected to a vacuum chamber by a custom-built ion-optic system [1] and part on a quadrupole mass analyzer equipped with a special secondary ion-optic (QMG 420, Balzers A.G.). The latter analyzer was completely computer assisted and connected to an AT class personal computer, in which a software package (QUADSTAR V.2, Balzers A.G.) allows remote control of the experiment. Positive and negative ion mass spectra were detected by an ion counting device and a floating reversible HV supply for the electron multiplier.

A primary argon ion gun (M-Minbeam I, Kratos Ltd.) bombarded the samples at energy ranging from 0.2 to 5 keV and current densities from 3 to 30 μA/cm^2; the primary beam was intentionally defocused in order to have a significant beam radius spot (2.5 mm).

Eu_2O_3, Dy_2O_3, La_2O_3, Sm_2O_3, HNO_3 and H_2SO_4 were Aldrich products (puriss. p.a.). Standard solutions of lanthanum(III), samarium(III) and europium(III) at ppm levels were prepared by dissolving the appropriate amounts of Ln_2O_3 in nitric acid and have been mixed in order to obtain the polymetallic solutions with different metal ratios. HNO_3 (2%) solutions of the complexes were prepared by digesting the appropriate amount of the complex in conc. HNO_3 up to complete mineralization and by dissolving the obtained inorganic residue in acidic water.

All dissolved compounds were deposited on a platinum support with a micro-syringe; oxide powders were put into contact with platinum or copper supports and directly adsorbed on them; ions were desorbed under Ar^+ bombardment with or without O_2 flux on the surface.

Results and discussion

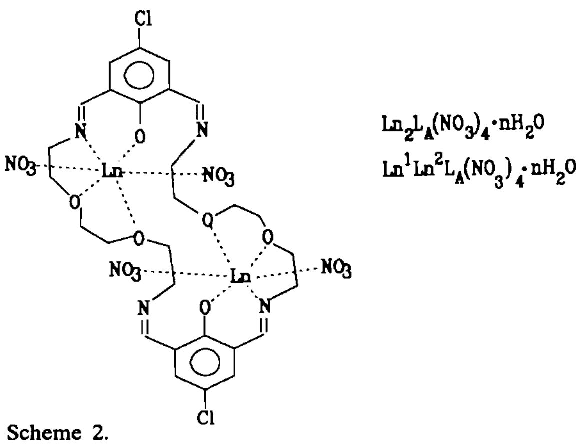
It was verified that homo- and hetero-dinuclear lanthanide(III) complexes of the type $Ln_2L_A(NO_3)_4\cdot nH_2O$ or $Ln^1Ln^2L_A(NO_3)_4\cdot nH_2O$ can be prepared. In these compounds the large macrocyclic moiety of the ligands incorporate into their coordination cavity two equal or different lanthanide ions. Two bidentate nitrate groups complete the coordination sphere about each metal ion(see Scheme 2).

Thermal decomposition of both types of complexes produces crystallographically pure oxides, according to the reactions

$$[Ln_2L_A(NO_3)_4]\cdot nH_2O \xrightarrow{1200\,°C} Ln_2O_3(\text{cubic}) \xrightarrow{1600\,°C} Ln_2O_3(\text{monoclinic})$$

$$[Ln^1Ln^2L_A(NO_3)_2]\cdot nH_2O \xrightarrow{1200\,°C} Ln^1Ln^2O_3(\text{cubic}) \xrightarrow{1600\,°C} Ln^1Ln^2O_3(\text{monoclinic})$$

The cubic and monoclinic symmetry of the oxides was determined by X-ray powder diffraction (XRD) measurements [14].



Scheme 2.

In the complexes and related oxides sample homogeneity and the lanthanide (and chlorine, when present) ratios were roughly determined by a scanning electron microprobe [18].

Secondary ion mass spectrometry can also be used to obtain useful information on the composition of involatile inorganic samples. In particular its specificity and sensitivity can unequivocally identify elements and molecules or molecular fragments at very low levels. Aqueous solutions of the dissolved complexes exposed to a primary ion beam of 2.5 keV gave positive ion mass spectra revealing the behaviour of La(III), Sm(III) and Eu(III) salts deposited on a Pt support: the isotope relative abundances of interest are shown in Table 1. The ion species La^+, LaO^+, $LaOH^+$, $La(OH)_2{}^+$, Sm^+, SmO^+, $SmOH^+$, Eu^+, EuO^+ and $EuOH^+$ are clearly recognizable: some of the relative peaks are partially superimposed and an isotope pattern simulation programme allows the Ln oxide and hydroxide ion intensities to be estimated. It should be noted that the $LaOH^+$ peak ($m/z = 156$) is very low, while those of $SmOH^+$ ($m/z = 161, 164, 165, 166, 167, 169, 171$) and $EuOH^+$ ($m/z = 168, 170$) are much higher than the respective SmO^+ ($m/z = 160, 163, 164, 166, 168, 170$) and EuO^+ ($m/z = 167, 169$).

TABLE 1. Relative abundances of peaks obtained by 2.5 keV Ar^+ bombardment of lanthanide solutions on platinum[a]

m/z	Ion species	Relative abundance (%)		
		La(III)	Sm(III)	Eu(III)
138	La	<0.5		
139	La	39		
144	Sm		12	
147	Sm		57	
148	Sm		42	
149	Sm		53	
150	Sm		28	
151	Eu			94
152	Sm		100	
153	Eu			100
154	LaO, Sm	<0.5	85	
155	LaO	100		
156	LaOH	2		
160	SmO		4	
161	SmOH		7	
163	SmO		13	
164	SmO, SmOH		45	
165	SmO, SmOH		38	
166	SmO, SmOH		39	
167	SmOH, EuO		17	13
168	SmO, EuOH		23	52
169	SmOH, EuO		62	14
170	SmO, EuOH		20	20
171	SmOH		55	
173	$La(OH)_2$	2		

[a] Ln(III) solution obtained by dissolving pure Ln_2O_3 in nitric acid.

The presence of specific ions and the stability of their ion yield ratios (Fig. 1) versus time confirm the ability of the SIMS technique to determine metal concentrations or ratios in homo- and hetero-polynuclear complexes.

Figure 2 shows the positive mass spectra of solutions containing different concentrations of the three lanthanide salts. The more significant peaks can be used to obtain calibration curves; base peaks $m/z = 152$ (Sm^+), $m/z = 153$ (Eu^+) and $m/z = 155$ (LaO^+) (Fig. 2(a)) or peaks $m/z = 169$, 171 ($SmOH^+$) and $m/z = 168$, 170 ($EuOH^+$) (Fig. 2(b)) appropriately estimated, were selected (see Table 1).

Standard solutions with the following metal concentrations (ppm) were analyzed.

	Samples			
	1	2	3	4
La(III)	0.5	1	1.5	2
Sm(III)	1	1	1	1
Eu(III)	1	1	1	1

Calibration curves with 99% confidence limits (Fig. 3) give as correlation coefficients 0.9987 for the La(III), Eu(III) solutions and 0.9993 for the La(III), Sm(III) solutions.

The figures also show data obtained for $LaEuL_A(NO_3)_4 \cdot nH_2O$ and $LaSmL_A(NO_3)_4 \cdot nH_2O$ dissolved in aqueous solutions. The data are given in Table 2. These results were confirmed by calibration curves obtained from other isotope peaks, and the method allows a direct check of the calculation of metal ratios with the same analysis time.

The second part of this work aimed at testing the ability of SIMS to discriminate between the thermal decomposition products of EuDy polynuclear complexes and the mechanical mixture of Eu_2O_3 and Dy_2O_3. The positive and negative ions ejected from the Cu support for pure Eu_2O_3 and Dy_2O_3 under 3 kV primary ion impact are shown in Table 3. The presence of Ln^+, LnO^+ and $LnOH^+$ in the positive mass spectra and of LnO^- and $LnO_2{}^-$ in the negative mass spectra confirms that complementary information can be obtained by working in positive and negative modes.

The isotope patterns of the compounds allow the immediate identification of the ion species; a partial overlap of DyO^+ and $DyOH^+$ peaks is evident and the contributions of the different ions are easily estimated.

In the same conditions, the mechanical mixture of Eu_2O_3 and Dy_2O_3 and $EuDyO_3$ obtained from

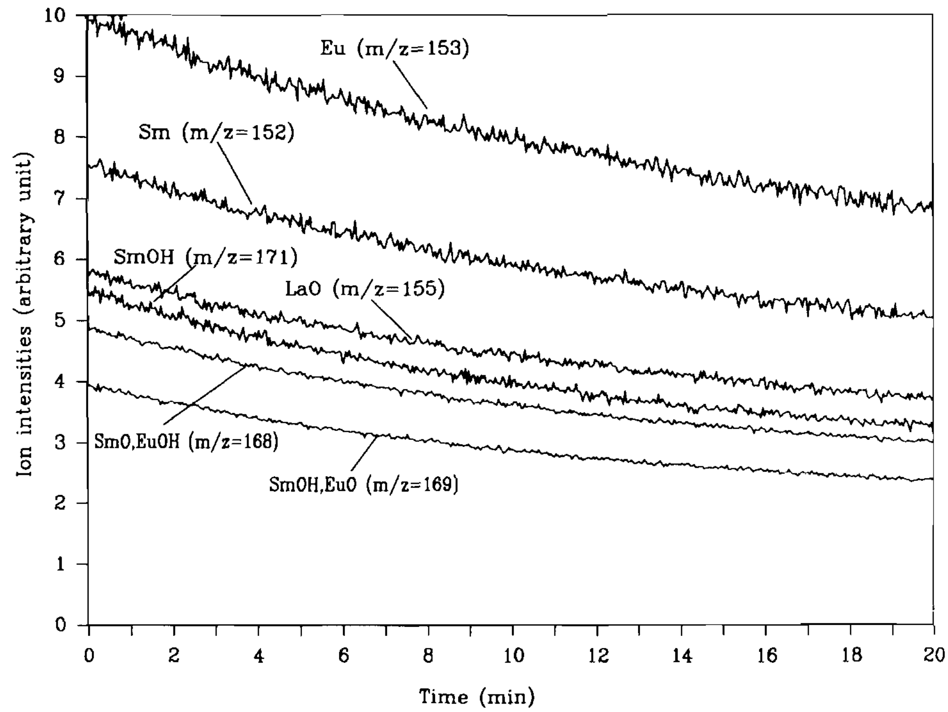


Fig. 1. Ion intensities vs. time of isotopes suitable for quantitative determinations.

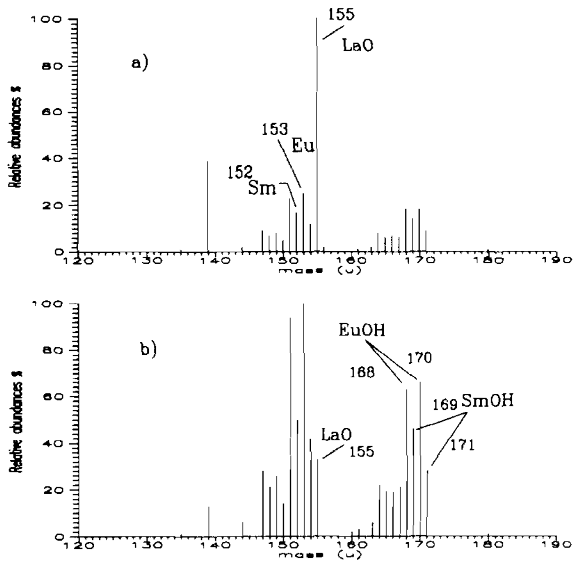


Fig. 2. Positive SIMS spectra (2.5 keV, Ar^+ primary beam) of solutions containing different concentration of La(III), Eu(III), Sm(III) salts.

thermal decomposition of $EuDyL_A(NO_3)_4 \cdot nH_2O$ at 1200 and 1600 °C, respectively were bombarded. The secondary ions produced from Cu are shown in Table 4.

It should be noted that:

(i) The mechanical mixture gives a positive ion mass spectrum that corresponds to the addition of Eu_2O_3 and Dy_2O_3 mass spectra and, particularly, $LnOH^+/Ln^+$ peak intensity ratios maintain the same value as in the pure oxides.

(ii) Eu^+ ($m/z = 151$, 153) and $EuOH^+$ ($m/z = 168$, 170) peaks are much higher than Dy^+ ($m/z = 160$, 161, 162, 163, 164) and $DyOH^+$ ($m/z = 177$, 178, 179, 180, 181) peaks. This may be explained by the different secondary ion yields also shown in Ca–Al–silicate glass matrix with O^- ion primary beam [19].

(iii) $EuDyO_3$ obtained at 1600 °C gives the same positive ion isotope patterns observed in the mechanical mixture and only small differences of peak relative abundances can be noted; results do not allow the polymetallic compounds to be discriminated from homometallic ones.

(iv) The $EuDyO_3$ produced at 1200 °C has a spectrum that shows new ion species as $Eu(OH)_2{}^+$, $Dy(OH)_2{}^+$, $DyO(OH)_2{}^+$ partially overlapping with oxide ions facilitating oxide identification.

(v) Molecular ions and dinuclear fragment ions (Eu_2O^+, $Eu_2O_2{}^+$, $EuDyO_2{}^+$, $EuDyO_3{}^+$, $Dy_2O_2{}^+$, $Dy_2O_3{}^+$) in the mass range higher than 300 μ can be detected at high sensitivity conditions. Some part of them are probably due to primary ion impact on the target; the same isotope pattern groups were obtained for the three compounds.

(vi) Clusters $Cu_3{}^+$, $EuCu^+$ and $EuCuO^+$ are generated after a long bombardment time.

TABLE 2. Sample ion intensity ratio

Complex	Ion species	1	2	3	4	Average	Calculated metal ratio
$LaEuL_A(NO_3)_4 \cdot nH_2O$	$^{139}LaO/^{153}Eu$	6.04	6.06	5.98	6.14	6.05	9.79 ± 0.0412
$LaSmL_A(NO_3)_4 \cdot nH_2O$	$^{139}LaO/^{152}Sm$	1.32	1.24	1.25	1.30	1.28	1.026 ± 0.041

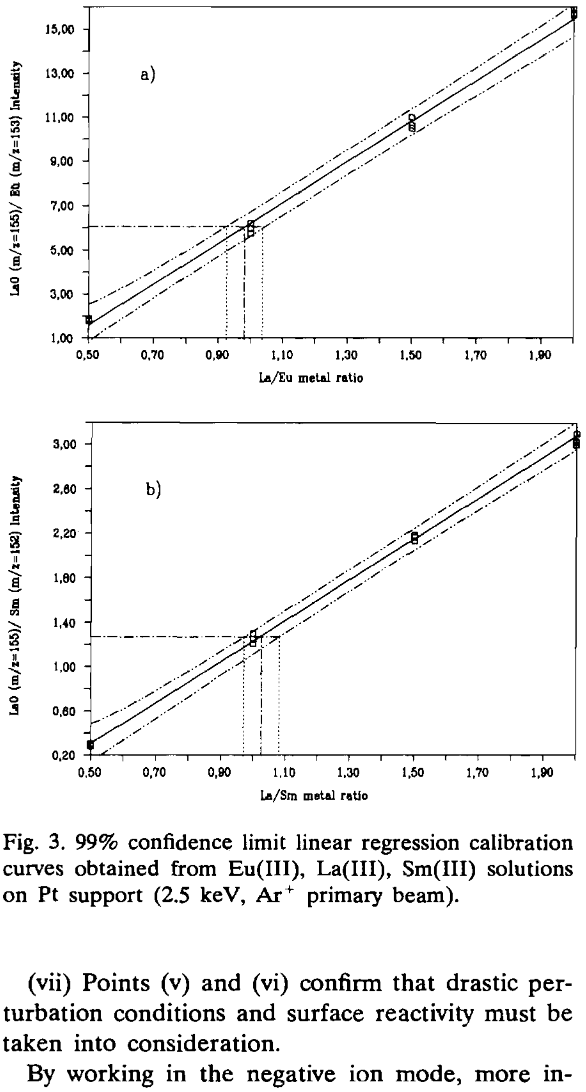


Fig. 3. 99% confidence limit linear regression calibration curves obtained from Eu(III), La(III), Sm(III) solutions on Pt support (2.5 keV, Ar^+ primary beam).

TABLE 3. Relative abundances of positive and negative ions obtained from pure homometallic oxides on copper support (3 keV, Ar^+ primary beam)

m/z	Ion species	Relative abundance (%)	
		Eu_2O_3	Dy_2O_3
151	Eu^+	93	
153	Eu^+	100	
160	Dy^+		8
161	Dy^+		67
162	Dy^+		91
163	Dy^+		88
164	Dy^+		100
167	EuO^+	4	
	EuO^-	48	
168	$EuOH^+$	85	
169	EuO^+	5	
	EuO^-	52	
170	$EuOH^+$	91	
176	DyO^+		3
	DyO^-		9
177	DyO, $DyOH^+$		28[a]
	DyO, $DyOH^-$		66[b]
178	DyO, $DyOH^+$		54[a]
	DyO, $DyOH^-$		91[b]
179	DyO, $DyOH^+$		60[a]
	DyO, $DyOH^-$		87[b]
	DyO, $DyOH^+$		64[a]
180	DyO, $DyOH^-$		100[b]
181	$DyOH^+$		29
183	EuO_2^-	92	
185	EuO_2^-	100	
192	DyO_2^-		8
193	DyO_2^-		64
194	DyO_2^-		88
195	DyO_2^-		83
196	DyO_2^-		96

[a] Relative abundance is due to DyO^+ and $DyOH^+$.
[b] Relative abundance is due only to DyO^-.

(vii) Points (v) and (vi) confirm that drastic perturbation conditions and surface reactivity must be taken into consideration.

By working in the negative ion mode, more interesting mass spectra allow discrimination of the different oxides and specific fragmentations can be immediately evidenced (Fig. 4). Marked differences in the relative abundances of the fragment ions appear at first sight; the base peaks correspond to different ion species. In particular Fig. 4(a) (mechanical mixture) shows $m/z = 185$ as the more intense peak, corresponding to EuO_2^- ion species, while Figs. 4(b) and (c) ($EuDyO_3$ synthesized at 1200 and 1600 °C, respectively) show $m/z = 213$ and $m/z = 196$ as the base peaks. The latter peaks correspond to significant dysprosium oxide or hydroxide ion fragment and their ion yields seem to be determinant for identification of the analysed compounds. The other isotope patterns shown in Fig. 4, also reveal characteristic ion intensities for the different samples.

As expected, comparison of the negative and positive ion mass spectra reveals that negative secondary ion yields are higher for fragments containing dysprosium, while positive secondary ion yields are higher

TABLE 4. Ion relative abundances obtained from oxide mechanical mixture and mixed oxides on copper support (3 keV, Ar^+ primary beam)

m/z	Ion species	Relative abundance (%)		
		Eu_2O_3 + Dy_2O_3	$EuDyO_3$	
			1200 °C	1600 °C
151	Eu	94	36	75
153	Eu	100	39	79
160	Dy	1	1	<0.5
161	Dy	9	10	5
162	Dy	12	13	8
163	Dy	11	12	7
164	Dy	13	14	9
167	EuO	11	42	13
168	EuOH	87	96	90
169	EuO	12	41	12
170	EuOH	96	100	100
176	DyO	1	1	<0.5
177	DyO, DyOH	5	22	6
178	DyO, DyOH	8	43	9
179	DyO, DyOH	9	41	8
180	DyO, DyOH	11	40	7
181	DyOH	5	10	
185	$Eu(OH)_2$		6	
187	$Eu(OH)_2$		7	
195	$Dy(OH)_2$		11	
196	$Dy(OH)_2$		9	
197	$Dy(OH)_2$		12	
198	$Dy(OH)_2$		5	
199	$DyO(OH)_2$		6	
211	$DyO(OH)_2$		3	
212	$DyO(OH)_2$		3	
213	$DyO(OH)_2$		9	
214	$DyO(OH)_2$		4	
215	$DyO(OH)_2$		8	

Very small ion intensities of Eu_2O^+, $Eu_2O_2^+$, $EuDuO_2^+$, $EuDyO^+$, $Dy_2O_2^+$, $Dy_2O_3^+$ are present in all compounds.

for ion fragments containing europium. This result may be due to the different electronegativity of the elements and confirms the importance of obtaining complementary information from the detection of all ion species.

It should also be noted that:

(i) $LnOH^+/LnO^+$ ion intensity ratios are higher in the positive mass spectra, while $LnOH^-$ ions are practically absent in the negative ion mass spectra.

(ii) $Ln(OH)_2^+$, $LnO(OH)_2^+$, $Ln(OH)_2^-$ and $LnO(OH)_2^-$ ion species are present;

(iii) Metal ion species with negative charge are practically absent, while the LnO_n^- ($n = 1$–3) ions are well stabilized.

(iv) Non-diagnostic ions present in the higher mass range (300–400 μ) related to polymetallic fragments or molecules are also detected in negative mode conditions.

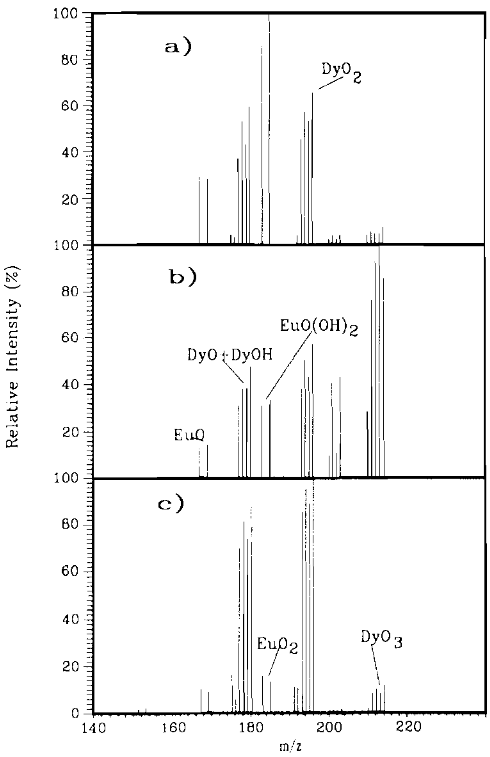


Fig. 4. Negative SIMS mass spectra (3 keV, Ar^+ primary beam) of: (a) mechanical mixture of Eu_2O_3 and Dy_2O_3; (b) $EuDyO_3$ produced at 1200 °C; (c) $EuDyO_3$ produced at 1600 °C.

Some experiments carried out using the Pt target confirm the presence of isotope patterns ejected from the Cu support, but secondary ion yields are higher and some other ion species (DyO_3^-, DyO_4^-) may be present. This is particularly evident if the primary Ar^+ beam hits the target with high energy or is contemporary with an oxygen flux: variations of the relative abundances of the ions occur and the more oxidized species prevails.

From these data it may be argued that modification of experimental condition may give new possibilities for sample discriminations. In any case, the satisfactory results obtained here and the need to use very clean targets in order to avoid matrix effect suggest systematic study with Cu supports and without oxygen flux: the lower cost means that a new support can be used for every analysis and simpler conditions guarantee more reproducible data.

Conclusions

Secondary ion mass spectrometry is increasingly used, not only as a surface technique but also as an analytical technique in the inorganic field. This work reveals its ability to give interesting information on involatile rare earth element compounds. Its speed of response allows the contemporary analysis of several elements in numerous samples in a very short time, and its high sensitivity allows their detection at trace level.

The positive and negative secondary ions ejected from the bombarded target show the presence of specific molecular or fragment ions for different samples, and confirm the possibility of analyzing compound mixtures or discriminating polymetallic mixed oxides. In particular the isotope patterns obtained from lanthanide compounds give immediate and definite answers and allow semiquantitative evaluations based on different isotope ions of the same sample: the validity of semiquantitative data is also confirmed by the stability of ion signals and particularly of ion signal ratios.

Comparison with other analytical techniques generally used for analogous compounds show some advantages of the SIMS technique, mainly linked to the wealth of obtainable complementary information. This suggests that the role of SIMS in the characterization of innovative inorganic compounds may increase; its systematic application may be particularly useful in the study of new materials.

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