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Novel Gaseous Polyatomic Binary and Ternary Lanthanide Oxides

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Abstract

A variety of novel gaseous polyatomic binary and ternary oxides were observed at ambient temperature arising from lanthanide (Ln) nitrate Schiff base complexes, simple salts and sesquioxides, in an FAB mass spectrometer. The new binary oxides (as singly positive ions) detected are Ln_2O_3, Ln_3O_3, Ln_3O_4, Ln_4O_4, Ln_4O_5, Ln_4O_6, Ln_5O_6, Ln_5O_7, Ln_5O_8, Ln_6O_8, Ln_6O_9, Ln_7O_{10}, Ln_8O_{11}, Ln_8O_{12} and Ln_9O_{13}; the ternary gaseous oxides are $CeEuO_2$, $CeEu_2O_3$ and Ce_2EuO_4, $LaYbO_2$, La_2YbO_4 and $LaYb_2O_4$; $NdHoO_3$, Nd_2HoO_4, and $NdHo_2O_4$; $YTmO_3$; $Y_xTm_{3-x}O_4$, $x = 1$–2; $Y_xTm_{4-x}O_6$, $x = 1$–3; $Y_xTm_{5-x}O_7$, $x = 1$–4; $Y_xTm_{6-x}O_9$, $x = 1$–5. Some of these oxides show the lanthanide cations in unusual oxidation states. Gadolinium–gallium ternary oxides, $GdGaO_2$, $GdGaO_3$ and Gd_2GaO_4 were also detected. The FAB MS environment is significantly reducing, yielding a homologous series Eu_nO_n where Eu^{2+} is dominant ($E°(Eu^{3+}/Eu^{2+}) = -0.35$ V) and no gallium or indium oxides ($E°(M^{3+}/M° = -0.34$ V (In), -0.53 V (Ga)) were formed. The stoichiometry of the polylanthanide ternary oxides formed is determined largely by the chemistry of the major metallic component. The gaseous polyatomic oxides are probably formed through a reductive condensation process involving primary species Ln^+ and LnO^+ formed when the rare earth compounds are struck by fast Xe atoms. The demonstrated possibility of double component oxide formation broadens the number and types of gaseous lanthanide oxides which are accessible.

Introduction

Solid binary and multicomponent lanthanide oxides have found extensive applications in the laser [1], electronic [2] and catalytic [3–5] areas. The excellent electronic properties of the rare earth elements which spurred the successful applications to which the rare earths and their compounds have been put are attracting interest in the development of gas phase lasing media [1] and in pioneering work on gas phase preparation techniques for new catalysts [6–9]. Despite their dominance in solid phase lanthanide applications, rare earth oxides are not being actively pursued for possible gas phase technologies, and knowledge of their gas phase chemistry is very limited. The gaseous lanthanide (Ln) oxides previously known, LnO, LnO_2, Ln_2O and Ln_2O_2, detected as singly charged cations, were in equilibrium mixtures over molten condensed systems such as rare earth metals, intermetallics, nitrides [10, 11] and sesquioxides [12] or were generated in high temperature experiments of the samarium-neodymium geochronology method [13–16], and laser ionization and spark source mass spectrometry [17]. The gaseous oxide species LnO^+ and LnO_2^+ were also observed along with Ln^+ in positive ion glow discharge mass spectrometry in a pure oxygen atmosphere [18]. The negative ion mode of this technique yielded the species, LnO_2^-, LnO_3^-, LnO_4^-, LnO_5^- and LnO_6^-, Ln = Ce, Sm [18]. But neither the positive nor the negative ion mode gave polylanthanide oxides. Similar monoanions, LaO^-, LaO_2^-, LaO_3^- and LaO_4^- were obtained from a LaB_6 ionizer at 1200 °C [19]. But there is no indication from trends in thermodynamic data [10] that the heavier unknown gaseous polyatomic oxides (especially $Ln_2O_3(g)$) are any less stable than those already known.

We report here detection of novel gaseous polyatomic lanthanide oxides, Ln_2O_3, Ln_3O_3, Ln_3O_4, Ln_4O_4, Ln_4O_5, Ln_4O_6, Ln_5O_6, Ln_5O_7, Ln_5O_8, Ln_6O_8, Ln_6O_9, Ln_7O_{10}, Ln_8O_{11}, Ln_8O_{12} and Ln_9O_{13}, each as a transient monocation in the soft ionization conditions afforded by Fast Atom Bombardment Mass Spectrometry (FAB MS). These oxides were

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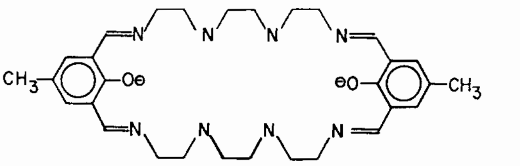
generated from homobinuclear complexes of lanthanides and the Schiff base ligand [20], $Ln_2L(NO_3)_{4-x}(OH)_x \cdot nH_2O$ ($x = 0, 1, 2$), $n = 0, 2$; as well as from lanthanide nitrates, chlorides and oxides, the latter sources yielding $Ln_3O_4^+$ and the smaller species.



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The occurrence of the oxide species $Ln_5O_7^+$ and the smaller ones in our FAB MS experiments are discernible from the isotopic patterns when Ln is polyisotopic and higher members of the series were prominent in largely monoisotopic lanthanides.

We were also able to observe the coupling of cerium and europium, to form new ternary gaseous oxide species: $CeEuO_2^+$, $Ce_2EuO_4^+$ and $CeEu_2O_3^+$; of neodymium and holmium to yield the oxide species: $NdHoO_3^+$, $Nd_2HoO_4^+$ and $NdHo_2O_4^+$; and of lanthanum and ytterbium to give the ternary oxide species: $LaYbO_2^+$, $La_2YbO_4^+$ and $LaYb_2O_4^+$. The coupling of the monoisotopic elements yttrium and thulium revealed an extensive possibility of forming ternary oxides. The most prominent peaks in the corresponding mass spectra were those of binary oxides and the following ternary oxides: $YTmO_3^+$, $Y_2TmO_4^+$, $YTm_2O_4^+$, $Y_3TmO_6^+$, $Y_2Tm_2O_6^+$, $YTm_3O_6^+$, $Y_4TmO_7^+$, $Y_3Tm_2O_7^+$, $Y_2Tm_3O_7^+$, $YTm_4O_7^+$, $Y_5TmO_9^+$, $Y_4Tm_2O_9^+$, $Y_3Tm_3O_9^+$, $Y_2Tm_4O_9^+$ and $YTm_5O_9^+$.

In order to shed more light on the significance of low potential redox routes such as $Eu^{3+} + e^- \rightarrow Eu^{2+}$ ($E^\circ = -0.35$ V) [21, 22] contributing to the polylanthanide oxide formation process, and to see if lanthanide elements can be coupled with non-lanthanide elements to form multicomponent gaseous ternary oxides, we analyzed mixtures of lanthanide and group IIIB elements (M) by FAB MS. These elements are trivalent like rare earths and like Eu^{3+}, In^{3+} and Ga^{3+} have access to a low potential redox route: $E^\circ(In^{2+}/In^0) = -0.34$ V [23] and $E^\circ(Ga^{3+}/Ga^0) = -0.53$ V [23]. If the predominance of the stable oxidation state 2+ in europium oxides is in response to a predominantly reducing FAB MS environment, then the species formed by Ga^{3+} and In^{3+} sources should differ from those of Ln^{3+} with large Ln^{3+}/Ln^{2+} potentials for which oxidation states larger than 2 dominate the gaseous oxide systems. But since M^{3+} may be reduced to either M^0 or M^+ rather than M^{2+}, their FAB MS oxide products should differ from those of Eu^{3+} as well, which is indeed the case.

On the basis of our experimental results we tentatively conclude that the binary and ternary oxides are formed from a reductive condensation of primary species such as Ln^+ and LnO^+ which are formed when the samples are struck by fast Xe atoms, e.g. $2LnO^+ + e^- \rightarrow Ln_2O_2^+{}_{(g)}$. The reactants may be at or near the surface of sputtered material or in the gas phase. The new products are formed with an intrinsic positive charge which affords greater sensitivity for their detection in the positive ion mode of FAB MS [24].

Experimental

Details of the synthesis of the lanthanide phenolate Schiff base complexes as well as details of the Fast Atom Bombardment Mass Spectrometry setup have been reported previously [20]. The samples of Nd_2O_3, $GdCl_3 \cdot nH_2O$, $Gd(NO_3)_3 \cdot 5H_2O$, basic aluminium acetate, and M_2O_3 (M = Ga, In) used to obtain $M(NO_3)_3 \cdot nH_2O$ were commercial products. The FAB MS ion source pressure was 10^{-6}–10^{-5} torr and 10^{-6}–10^{-7} torr for the analyzer. The mass spectra on which this report is based are averages of 20 to 70 successive scans in which only those peaks appearing in at least 75% of the scans with intensities of at least 1% were included. The $Y_2L(NO_3)_3(OH)$ and $Gd_2L(NO_3)_4 \cdot 2H_2O$ samples were also run in a mixture of glycerol and DMSO. In different experimental runs, three different calibration mass ranges were achieved: 250–2000, (Y, Gd samples in DMSO/glycerol matrix), 184–1953 (Dy) and 92–1785 for all other samples including the Ce/Eu, Nd/Ho, La/Yb, Y/Tm, Gd/Al, Gd/Ga, Er/In and Yb/In mixtures. Resolution was set at 1000. The double component oxides were obtained from samples containing about 1:1 molar powder mixtures of: $Ce_2L(NO_3)_4$ with $Eu_2L(NO_3)_4 \cdot 2H_2O$ (Ce/Eu); $La(NO_3)_3 \cdot nH_2O/Yb(NO_3)_3 \cdot 5H_2O$ (La/Yb); $Ln_2L(NO_3)_2(OH)_2$ (Nd/Ho); $Y_2L(NO_3)_3(OH)/Tm_2L(NO_3)_4 \cdot 2H_2O$(Y/Tm); $Ga(NO_3)_3 \cdot nH_2O/Gd(NO_3)_3 \cdot 5H_2O$ (Gd/Ga); $Gd(NO_3)_3 \cdot 5H_2O$/basic aluminum acetate (Gd/Al) and $Er_2L(NO_3)_3(OH)/InL^*(NO_3)_x$ (Er/In); $Yb_2L(NO_3)_4 \cdot 2H_2O/InL^*(NO_3)_x$ (Yb/In), where $InL^*(NO_3)_x$ = unidentified indium compound formed in the same way as the lanthanide Schiff base complexes. The presence of indium in the product was confirmed by thermogravimetry. The La/Yb, Gd/Ga and Gd/Al mixtures as well as the lanthanide chlorides and nitrates were soluble in glycerol, but the data from dry samples were the same as from solutions.

The computer program used to deconvolute isotopic patterns was our Fortran IV version of the Fortran V program obtained from C. S. Hsu of Exxon Research and Engineering Co., N.J. [25].

TABLE I. Gaseous Lanthanide Cations and Polyatomic Oxides Detected by FAB MS[a]

Gaseous species	Oxidation state of Ln	La	Ce	Pr	Nd	Sm	Eu	Gd	Dy	Ho	Er	Yb	Y
Ln^+	0	√	√	√	X	√	√	√		√	√	√	
LnO^+	2	√	√	√	√	√	√	√		√	√	√	√
LnO_2^+	4	–	√	–	–	–	–	–		–	–	–	–
$Ln(OH)_2^+$	2	√	√	√	√	–	–	√		√	√	–	√
Ln_2O^+	1	–	–	–	–	X	√	–	–	–	–	–	–
$Ln_2O_2^+$	2	√	√	√	√	X	√	√	√	√	√	√	–
$Ln_2O_3^+$	3	√	√	√	√	–	–	√	√	√	√	√	√
$Ln_3O_3^+$	2	–	–	–	–	–	√	–	–	–	–	–	–
$Ln_3O_4^+$	2 2/3	√	√	√	√	X	–	√	√	√	√	√	√
$Ln_4O_4^+$	2	–	–	–	–	–	√	–	–	–	–	√	–
$Ln_4O_5^+$	2 1/2	–	–	–	–	–	–	√	–	–	–	–	√
$Ln_4O_6^+$	3	√	√	√	√	–	–	√	√	√	X	–	√
$Ln_5O_6^+$	2 2/5	√	–	–	–	–	–	–	–	–	–	–	√
$Ln_5O_7^+$	2 4/5	√	√	√	√	–	–	X	X	√	–	–	√
$Ln_5O_8^+$	3 1/5	√	–	–	–	–	–	–	–	–	–	–	√
$Ln_6O_8^+$	2 2/3	√	√	√	–	–	–	X	–	√	–	–	√
$Ln_6O_9^+$	3	√	–	√	–	–	–	X	–	√	–	–	√
$Ln_7O_{10}^+$	2 6/7	√	–	√	–	–	–	X	–	√	–	–	√
$Ln_8O_{11}^+$	2 3/4	√	–	–	–	–	–	–	–	–	–	–	√
$Ln_8O_{12}^+$	3	√	–	–	–	–	–	X	–	√	–	–	–
$Ln_9O_{13}^+$	2 8/9	√	–	–	–	–	–	X	–	√	–	–	√

[a] Blank = out of calibration range; √= observed and calculated isotopic intensity pattern matched well; X = observed and calculated isotopic intensity pattern matched unsatisfactorily; – = no peak (clustering) was observed for the species.

Results

Bombardment of lanthanide phenolate Schiff base complexes with fast xenon atoms in a FAB source leads to the formation of a variety of gaseous polyatomic oxides listed in Table I. The observed and calculated isotopic patterns for some gadolinium species detected are shown in Fig. 1. While most of the lanthanides formed gaseous oxides from LnO to Ln_5O_7 (Table I), the nearly monoisotopic elements lanthanum, praseodymium, holmium, and yttrium gave additional peaks corresponding to *m*/*z* for the positive ions of Ln_5O_6, Ln_5O_8, Ln_6O_8, Ln_6O_9, Ln_7O_{10}, Ln_8O_{11}, Ln_8O_{12}, and Ln_9O_{13} (Fig. 2). Close proximity of the FAB gun to the off-white $Gd_2L(NO_3)_4 \cdot 2H_2O$ sample enhanced the intensity of the heavy species of gadolinium oxides showing poorly defined intensity patterns. (See the crosses in Table I).

Samarium was the poorest gaseous polyatomic oxide-former studied, as it exhibited only one oxide (SmO) with a well-defined intensity pattern and complex peak clusters at *m*/*z* values for Sm_2O^+, $Sm_2O_2^+$ and $Sm_3O_4^+$. Europium samples preferred formation of a homologous series: Eu_nO_n, with n = 1, 2, 3, 4 and a suboxide Eu_2O. The ytterbium sample gave an intense cluster at *m*/*z* corresponding to Yb_2O_2 and a less intense one for Yb_2O_3 and like

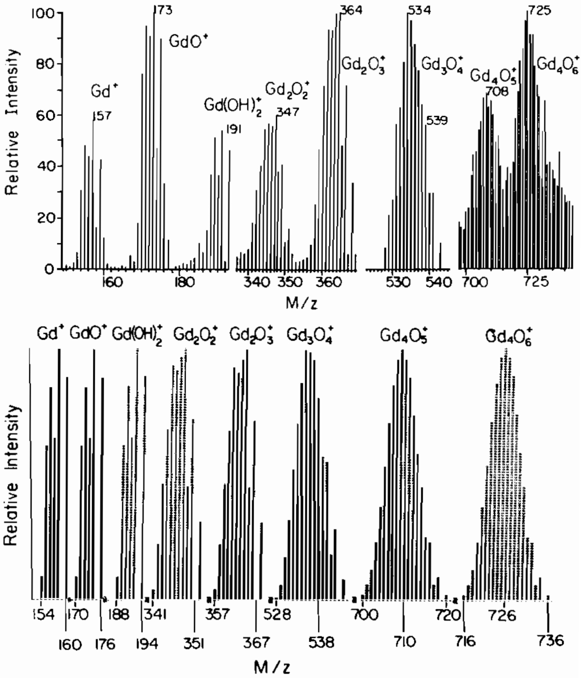

Fig. 1. Isotopic patterns for a series of gaseous species of gadolinium as found by FAB MS of the $Gd_2L(NO_3)_4 \cdot 2H_2O$ complex in glycerol. The peak intensities in each fraction of the mass spectrum are normalized to the most intense peak in that fraction. Upper lines, observed; lower lines, calculated.

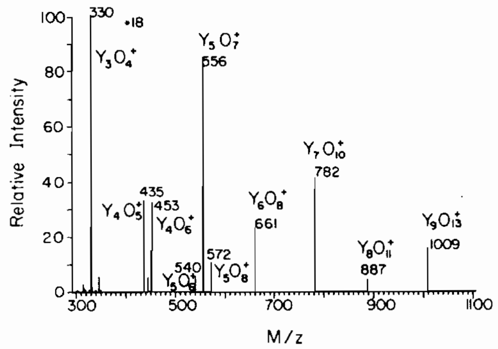

Fig. 2. The average FAB MS spectrum of $Y_2L(NO_3)_3(OH)$ in DMSO/glycerol. Peaks at *m/z* greater than 400 have intensities increased by a factor of 18.

other lanthanides it also yielded Yb_3O_4, but like europium it also gave the oxide Yb_4O_4. The gadolinium sample run in a DMSO/glycerol matrix had peak clusters of comparable intensity at *m/z* for Gd_2O_2 (80%) and Gd_2O_3 (100%) but no oxides heavier than Gd_3O_4; however, matrices without DMSO gave much more intense Gd_2O_3 peaks relative to those of Gd_2O_2 and also yielded heavier oxides. On the contrary the yttrium sample in DMSO/glycerol gave many oxides (Fig. 2) heavier than Y_3O_4 with clusters containing odd numbers of yttrium atoms being more prominent than those containing even numbers. The cerium sample gave a doublet at 172, 174 for CeO_2 as expected, but other lanthanides gave $Ln(OH)_2$. Samples of $Gd(Cl_3)_3 \cdot nH_2O$, $Gd(NO_3)_3 \cdot 5H_2O$ and Nd_2O_3 gave the gaseous oxides LnO to Ln_3O_4 demonstrating that the sources of these oxides is more general. Lanthanide oxyglycolate species $Ln_2O(gly)^+$ and $Ln_3O(gly)^+$ were formed along with the glycolate species $Ln(gly)^+$. A sample of $GdCl_3 \cdot nH_2O$ gave the species $GdCl^+$ and $Gd_2O_2Cl^+$.

The FAB MS of a powder mixture of 1:1 (molar) cerium and europium Schiff base complexes gave new double component oxides $CeEuO_2$, $CeEu_2O_3$ and Ce_2EuO_4 (Fig. 3) in addition to the binary oxides observed in separate pure samples (Table I). The region in which Eu_3O_3 and $CeEu_2O_4$ peaks are expected is cluttered and it is not possible to say with certainty whether the species $CeEu_2O_4^+$ was observed or not.

The powder mixture of $Nd_2L(NO_3)_2(OH)_2$ and $Ho_2L(NO_3)_2(OH)_2$ gave the double component gaseous oxides $NdHoO_3$, Nd_2HoO_4 and $NdHo_2O_4$ besides the binary oxides observed in separate samples (Table I and Fig. 4). Although the peaks due to $NdHoO_2^+$ are expected to overlap with the upper end of the peak cluster due to Nd_2O_3, a comparison of the observed and calculated intensity patterns does not suggest interference from $NdHoO_2^+$ peaks in the area $m/z = 339$–347. The $La(NO_3)_3 \cdot nH_2O$/$Yb(NO_3)_3 \cdot 5H_2O$ sample gave the ternary oxides

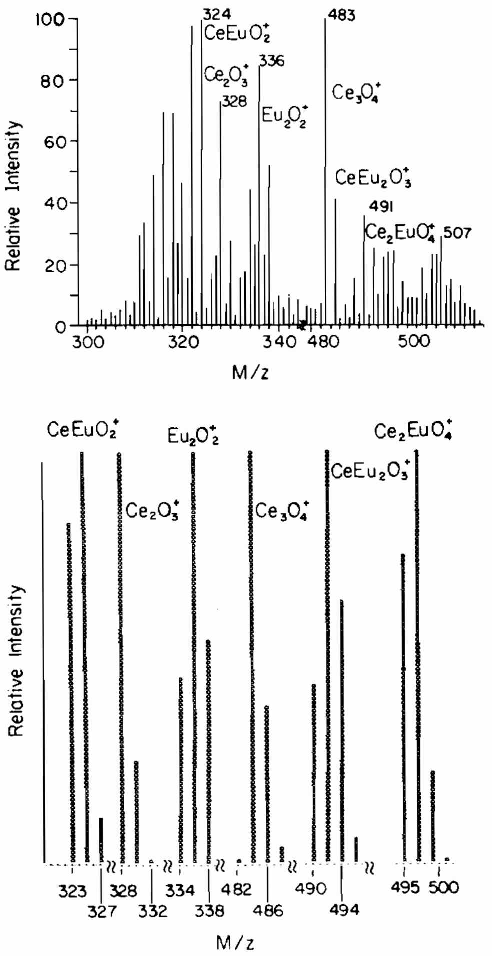

Fig. 3. Isotopic patterns for the gaseous double component oxides of cerium and europium as found in FAB MS of a mixture of $Ce_2L(NO_3)_4$ and $Eu_2L(NO_3)_4 \cdot 2H_2O$ in glycerol. Upper lines, observed; lower lines, calculated.

$LaYbO_2$, La_2YbO_4 and $LaYb_2O_4$ in addition to the binary oxides (Table I) showing satisfactory calculated and observed isotopic patterns, and $LaYbO_3$ with a poorly defined intensity pattern.

The $Y_2L(NO_3)_3(OH)$/$Tm_2L(NO_3)_4 \cdot 2H_2O$ mixture extended the types of ternary oxide species detected. Because of similarities in the chemistry of Y^{3+} and Tm^{3+} and their monoisotopic nature, a statistical combination of Tm and Y, e.g. $Y_3O_4^+$, $Y_2TmO_4^+$, $YTm_2O_4^+$, $Tm_3O_4^+$, $Y_4O_6^+$, $Y_3TmO_6^+$, $Y_2Tm_2O_6^+$, $YTm_3O_6^+$ and $Tm_4O_6^+$ accounts for all the major peaks observed. The value $m/z = 612$ for the species $Y_2Tm_2O_6^+$ corresponds to $Tm_3O(gly)^+$ as well, so peaks due to these species, which are intense, are expected to overlap. Additional ternary oxides observed are: Y_4TmO_7, $Y_3Tm_2O_7$, $Y_2Tm_3O_7$, YTm_4O_7, Y_5TmO_9, $Y_4Tm_2O_9$, $Y_3Tm_3O_9$, $Y_2Tm_4O_9$ and YTm_5O_9, all of which exhibit calculated and observed *m/z* values within a mass unit of each other.

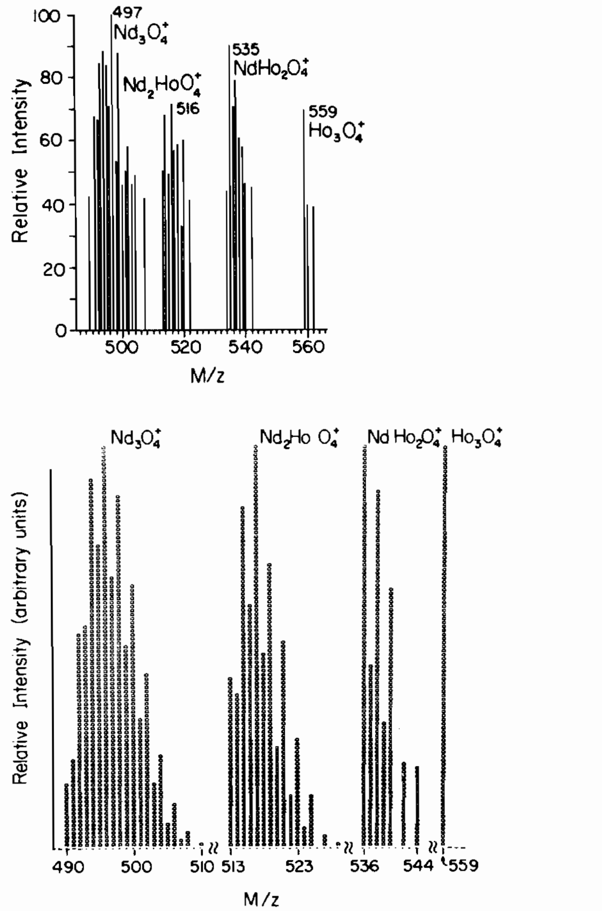

Fig. 4. Isotopic patterns of ternary neodymium–holmium oxides obtained from FAB MS of a mixture of $Ln_2L(NO_3)_2(OH)_2$ (Ln = Nd, Ho) complexes in glycerol. Upper lines, observed; lower lines, calculated.

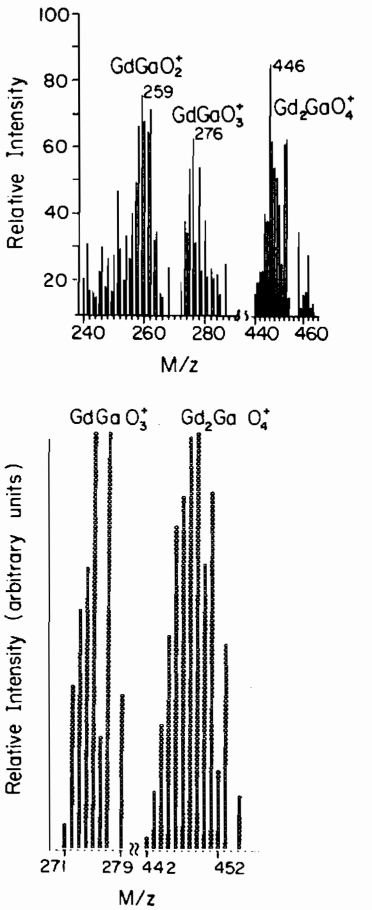

Fig. 5. Isotopic patterns of ternary gadolinium gallium oxides generated from a mixture of gadolinium and gallium nitrates in glycerol. Upper lines, observed; lower lines, calculated.

The Gd/Al mixture afforded the species Gd^+, GdO^+, $Gd_2O_2^+$, $Gd_2O_3^+$ and $Gd_3O_4^+$. No evidence of binary or ternary aluminium oxide formation was discernible in the calibration range studied.

The mixture of $Gd(NO_3)_3 \cdot 5H_2O/Ga(NO_3)_3 \cdot nH_2O$ gave the gallium hydroxide $Ga(OH)_2^+$ at m/z = 103, 105, (lighter species Ga^+, GaO^+ being out of our calibration range) as well as the gadolinium species: Gd^+, GdO^+, $Gd(OH)_2^+$, $Gd_2O_2^+$, $Gd_2O_3^+$ and $Gd_3O_4^+$. In addition to these oxides, the ternary oxide species $GdGaO_3$ (Fig. 5) showed a good calculated and observed intensity pattern. The ternary oxides $GdGaO_2$ and Gd_2GaO_4 show peak clusters at the correct positions but the clusters are of poorly matched calculated and observed intensity patterns.

The Er/In and Yb/In mixtures gave only In^+, Ln^+, LnO^+ and $Ln(OH)_2^+$ species. No InO^+ species was detected despite an intense In^+ peak and no polylanthanide oxide species were detected either.

Discussion

The experiments described above have revealed accessibility of a variety of novel gaseous polyatomic lanthanide oxides at relatively low temperatures. These oxides are available from many compounds containing the rare earths, for example condensed systems (such as oxides), simple salts and complexes such as those of the ligand L. Since mass spectrometric techniques employing large ionization energies have not yielded these heavy polyatomic gaseous oxides even in cases where a variable oxygen atmosphere was used [18], use of low energies such as those afforded by FAB MS seems to be essential for the observation of these oxo clusters. This is supported by the observation that increased ionization temperature reduced the oxide to metal ion ratio (NdO^+/Nd^+) of a nitrate sample [26].

The apparent inability of samarium to form the oxides is difficult to explain. Perhaps there will be an explanation when more light is shed on the mechanism and type of chemistry involved in the condensation process leading to the polyatomic oxides. The dominance of the 2+ oxidation state in europium oxides, which is in good agreement with the large $E^\circ(Eu^{3+}/Eu^{2+})$ value of −0.35 V, [compared to $E^\circ(Ln^{3+}/Ln^{2+}) = -2.8$ V (Nd), −4.9 V (Gd)] [21, 22], and the limited occurrence of the 4+ oxidation state in cerium oxides suggest that reductive processes are significant in the mechanism by which the polyatomic oxides are formed. This is supported by the results obtained from experiments employing group IIIB elements. The redox potentials $E^\circ(Ga^{3+}/Ga^0) = -0.53$ V and $E^\circ(In^{3+}/In^0) = -0.34$ V are rather comparable to $E^\circ(Eu^{3+}/Eu^{2+}) = -0.35$ V and since Eu^{2+} features prominently in the observed dominant homologous series $Eu_nO_n^+$ for Eu^{3+} samples, a different chemistry is expected for M^{3+} (M = Ga, In) speciation in FAB MS. Indeed, Ga^{3+} yielded $Ga(OH)_2^+$ as the heaviest single metal component species but despite its inability to form polygallium oxides it couples with Gd^{3+} to yield the ternary oxides $GdGaO_2^+$, $GdGaO_3^+$ and $Gd_2GaO_4^+$. The decisive influence of gadolinium(III) chemistry on gallium(III) is therefore likely to be a key feature of the process leading to these ternary oxides. Indium(III) with a rather larger $E^\circ(In^{3+}/In^0)$ value is unable to form any indium oxides and it somehow also inhibits the formation of polylanthanide oxides. Experiments are planned to explore the manner in which this inhibitory effect of indium towards polylanthanide oxide formation occurs. Aluminium with a much lower $E^\circ(Al^{3+}/Al^0) = -1.66$ V does not form polyaluminium oxides (to be found in our calibration range) or ternary oxides with rare earths, but neither does it inhibit the formation of polylanthanide oxides. It will be interesting to see how trivalent d-block elements and divalent s-block elements behave in the FAB MS when coupled to lanthanides. FAB MS experiments directed to d- and s-block elements are planned.

The solid compound Eu_3O_4 is known but similar compounds of other rare earths are unknown [27]. Under the FAB MS conditions the gaseous Ln_3O_4 compounds are formed by all rare earths except europium which prefers a further reduced oxide Eu_3O_3.

We do not have explanation for the absence of $Ln(OH)_2^+$ species in samples of samarium, europium, and ytterbium or their mixtures with other rare earth samples, but it is interesting to note that these elements have relatively low $E^\circ(Ln^{3+}/Ln^{2+})$, −0.35 V (Ln = Eu), −1.1 V (Ln = Yb) and −1.5 V (Ln = Sm) compared to values of −2 to about −4 V for other rare earths.

The significance of the prominence of the intensity, hence relative abundance, of yttrium oxides containing odd numbers of yttrium atoms compared to those oxides with even numbers of yttrium atoms is also not clear. This behavior is not shown in lanthanum and holmium oxides as explicitly as it is in yttrium oxides. Whether this difference in behavior is of structural, thermodynamic or kinetic importance to the polylanthanide oxide formation process will be investigated.

In experiments in which double component oxides were obtained both glycerol soluble and insoluble mixtures were used. In the case of glycerol insoluble mixtures the cations were trapped in different matrices: therefore the successful formation of the ternary oxides from such systems is an indication that condensations leading to polylanthanide oxides take place after the metal ions have left their original environments, probably at the surface of the sputtered particulates, and/or in the gas phase. The nature of products formed are as statistically expected and in accord with the chemistry of the two elements, so that the species $CeEuO_2^+$ was formed in the same manner that the corresponding $Ce_2O_2^+$ and $Eu_2O_2^+$ species were formed from separate cerium and europium compounds, whereas $CeEuO_3^+$ was not observed. Although such a species is favored by cerium, as in $Ce_2O_3^+$, it is not favored by europium, which did not form the $Eu_2O_3^+$ species. Also the gaseous oxide species $Ce_2EuO_4^+$ and $CeEu_2O_3^+$ were formed in good agreement with the occurrence of both $Ce_3O_4^+$ and $Eu_3O_3^+$ from separate cerium and europium samples, showing respectively, the dominant influence of the major metallic component on the nature of the ternary oxide formed. Consistent with this, $Ce_2EuO_3^+$ was not observed even though it might have been expected from the chemical behavior of europium (Table I), but it is not favored by cerium which would be the major metallic component. The region in which the peaks due to $Eu_3O_3^+$ and $CeEu_2O_4^+$ are expected is too cluttered. Thus, the quartet due to $Eu_3O_3^+$ is expected in the region m/z = 501–507, whereas the quartet due to $CeEu_2O_4^+$ is expected to be found in the m/z = 506–512 region; and there are peaks in the whole region m/z = 501–514, but the observed pattern cannot be disentangled to fit well the double quartet pattern. Since there are peaks in this region it is not prudent to conclude that the species $CeEu_2O_4^+$ did not form. However, if it did form, then cerium must have influenced the chemical behavior of europium and this may have interesting implications for the study and applications of these materials; but if it did not form then the chemistry of europium was decisive and consistent with other observations. The double component oxides formed when lanthanum and ytterbium or neodymium and holmium are coupled, are also consistent with the chemistry of the coupled rare earth elements (Table I).

We now tentatively propose that once process (1) has been initiated, a series of rapid reductive condensations follow leading to the variety of polyatomic gaseous oxides we have observed.

$$\text{(glycerol)} + \text{lanthanide compound} \xrightarrow[\text{Xe atoms}]{\text{Fast}} Ln^+ + LnO^+ \quad (1)$$

(glycerol or water is needed if the counter anion does not contain oxygen)

Illustrating this conclusion with some of the elementary processes which may lead to binary and double component oxides of cerium and europium we have:

$$2CeO^+ + e^- \longrightarrow Ce_2O_2^+ \quad (2)$$

$$CeO^+ + CeO_2^+ + e^- \longrightarrow Ce_2O_3^+ \quad (3)$$

$$EuO^+ + Eu^+ + e^- \longrightarrow Eu_2O^+ \quad (4)$$

$$2EuO^+ + e^- \longrightarrow Eu_2O_2^+ \quad (5)$$

$$CeO^+ + EuO^+ + e^- \longrightarrow CeEuO_2^+ \quad (6)$$

$$CeO_2^+ + Eu^+ + e^- \longrightarrow CeEuO_2^+ \quad (7)$$

$$Ce_2O_3^+ + CeO^+ + e^- \longrightarrow Ce_3O_4^+ \quad (8)$$

$$Ce_2O_2^+ + CeO_2^+ + e^- \longrightarrow Ce_3O_4^+ \quad (9)$$

$$Eu_2O_2^+ + EuO^+ + e^- \longrightarrow Eu_3O_3^+ \quad (10)$$

$$Ce_2O_3^+ + EuO^+ + e^- \longrightarrow Ce_2EuO_4^+ \quad (11)$$

$$CeO^+ + Eu_2O_2^+ + e^- \longrightarrow CeEu_2O_3^+ \quad (12)$$

Such a mechanism can explain why large oxo clusters, e.g. Gd_9O_{13}, have poorly defined intensities, since a large number of reactions involving different isotopes has to occur to lead to a well defined isotopic pattern.

Besides shedding some light on the possible condensation mechanism, the coupling experiments have demonstrated the possibility of preparing gaseous polyatomic multicomponent oxides thereby enlarging enormously the range of possible oxides that are accessible at relatively low temperature. If this is found to be more general so that lanthanides can be coupled with more p- and d-block elements the scientific and technological potential of the gas phase lanthanide oxide system may be vast. This optimism is reinforced by the unusual oxidation states of lanthanides associated with some of the oxides e.g. Ln_3O_4, Ln_4O_5, Ln_5O_6, Ln_5O_7, Ln_5O_8, Ln_7O_{10}, Ln_8O_{11} and Ln_9O_{13} (Table I), evoking the possibility that there may be some direct Ln–Ln bonding.

Conclusion

Although there are several important experiments that need to be done to shed more light on the gaseous lanthanide oxide systems, the experiments we have described have shown that interesting binary and ternary lanthanide and lanthanide–p-block element oxides in the gas phase are accessible at relatively low temperatures and that the processes leading to their formation most probably occur among species present on or near the surfaces of sputtered particulates or in the gas phase. The unusual oxidation states associated with some of the oxides, the demonstrated possibility of synthesizing multicomponent oxide systems in the gas phase as well as the challenge of trapping and characterizing the observed oxides, should make investigation of gaseous lanthanide oxides more attractive.

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