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Heteropolyatomic Gas-Phase Species Produced by Laser Ablation of Lead Titanate Oxide, Studied by Laser Microprobe Mass Spectrometry

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Frequency tripled Nd:YAG (355 nm) laser ablations of lead titanate in a vacuum (10^{-6} mbar) have produced oxide cluster ions identified in positive and negative mode by laser microprobe mass spectrometry (LMMS). It appears that laser ablation of $PbTiO_3$ generates titanium/oxygen, lead/oxygen, and bimetallic lead/titanium/oxygen positive mixed clusters. The formation of negative clusters from $PbTiO_3$ is dominated by the aggregation of pure titanium/oxygen ions. The positive clusters are oxygen-poor as compared to the negative ones. The latter could be efficient oxygen carriers in the pulsed laser deposition of $PbTiO_3$ thin films. In addition, examining the formation process of both negative and positive clusters allowed indentification of significant neutral constituents of the plume.

Introduction

In recent years, thin films of ferroelectric materials with perovskite structure have been submitted to extensive investigation because of the numerous and important applications concerning electronic and optical devices such as nonvolatile memories, ultrasonic sensors, and infrared detectors. Among various ferroelectrics, lead titanate $PbTiO_3$ is commonly used because of its superior ferroelectric and pyroelectric properties.[1−3] A great number of techniques can be used to prepare $PbTiO_3$ films, including pulsed laser deposition (PLD). The latter is a very promising method for thin film deposition with controlled stoichiometry.[1,2,4] It is a well-known fact that $PbTiO_3$ films with perovskite structure having the same stoichiometry as the target are obtained at high substrate temperature (typically 550 °C), under conditions of controlled ambient oxygen pressure [typically $(2-3)\cdot 10^{-1}$ mbar] and appropriate laser fluence.[1−3] The partial oxygen pressure is essential to form and stabilize the targeted oxide phase. Moreover, several authors underline the problem of lead evaporation from the deposited film, due to high substrate temperature. In other words, by considering the difference of the melting point of lead (330 °C) and lead monoxide (890 °C), it can be observed that the partial oxygen pressure used contributes to maintaining the lead content in the film because of the formation of lead oxide (PbO)[5] and heavy species containing lead.[6]

The investigation of ion formation occurring in the laser plume is of fundamental interest to understand the various mechanisms of thin film deposition by PLD. The most commonly used experimental methods for plasma plume investigation are forms of optical diagnostics such as time-resolved emission spectroscopy[7] or laser induced fluorescence.[8] However, these techniques fail to characterize large species because of the difficulty in interpreting spectra and the lack of optical data. Consequently, these techniques are often limited to the analysis of atomic species and dimers.

Laser ablation sampling coupled with mass spectrometry detection, especially laser microprobe mass analysis (LAMMA), has extended the range of applications in the field of inorganic compounds.[9−11] This technique is an adequate means to investigate ablation mechanisms and plume composition, ranging from monatomic species to high-mass clusters.[12] Moreover, isotopic resolution can be easily achieved and a given peak is attributed to its correspondent ion with absolute certainty.

We have studied the formation process of positive and negative ion clusters issued from the interaction between a laser beam (frequency tripled Nd:YAG, 355 nm) and $PbTiO_3$ and some of its related monometallic compounds (lead oxides, titanium oxide). The time of flight (TOF) mass spectra of the latter compounds are used for the interpretation of lead titanate spectra. Moreover, to have a better understanding of the forma-

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tion mechanism of clusters, we correlated the relative abundance of some detected species with the thermochemical (M−O bond strength) and electronic properties of the ablated materials (ionization energy, electronic affinity).

The major goals of the work described in this paper are (1) identifying the clusters formed during the ablation of lead titanate in the negative and positive mode, (2) determining the dominant mechanism for their formation, (3) providing information about major neutral components of the plume by using the complementary information provided by both negative and positive ion TOF spectra, and (4) pointing out the contribution of neutrals and clusters in carrying oxygen from the target to the film in the PLD process.

Experimental Section

The LMMS analyses were performed in the transmission mode with the laser microprobe mass analyzer LAMMA 500 (Leybold Heraeus). The principle of the equipment can be found elsewhere.[9,10,13] We know that a frequency-tripled Nd:YAG laser [$\lambda = 355$ nm (3.5 eV), $\tau = 10$ ns, laser irradiance = 10^6-10^9 W/cm^2] was focused onto a sample. The ions emitted were separated using a time of flight mass spectrometer. The analyses were performed both in negative and positive ionization mode by simply reversing the potential of the extraction lenses.

Prior to the investigation of $PbTiO_3$ (Aldrich, 99.9%), ablation products of lead oxides PbO in the dominant β allotropic phase, Pb_3O_4 (Aldrich, 99.9%), and titanium dioxide (anatase, Aldrich, 99.9%) were characterized. Similar to the ablation performed on pure compounds, some experiments were also carried out with finely grounded PbO/TiO_2 and $Pb_3O_4/3TiO_2$ (molar) mixtures. All the samples used for the analysis were in powder form (mean grain size, 0.2 μm) and were deposited onto a TEM copper grid (400 mesh). Ten positive and negative single spectra of each compound were recorded under the same experimental conditions, allowing direct comparison. The energy deposited on the sample was about 0.5 μJ and the size of the laser spot was about 10 μm in diameter. By taking the pulse duration into account, namely 10 ns, these parameters provide a power density of about 10^8 W/cm^2. This value corresponds to the power density that we currently use to obtain good quality perovskite films and to the density that maximizes the production and detection of cluster ions.[14]

Results and Discussion

1. Lead Oxides: PbO and Pb_3O_4. *1a. Positive Ions.* Representative positive TOF spectra of lead oxides (PbO and Pb_3O_4) are shown in Figure 1a,b. With both oxides, the most intense peak corresponds to the atomic Pb^+ ion; this peak is strongly out of scale. Two series of $Pb_xO_y^+$ cluster ions (where x and $y = 1-3$ with PbO and $1-6$ with Pb_3O_4) were identified. These ions are more abundant with Pb_3O_4. For each given value of x, the peaks detected make up groups separated by a mass of $m/z = 224$ corresponding to PbO. The main two cluster series are consistent with the following empirical formula: an oxygen deficient $[Pb(PbO)_n]^+$ series and an oxygen equivalent $[PbO(PbO)_n]^+$ series (where $n = 1-2$ with PbO and $n = 1-5$ with Pb_3O_4). The oxygen deficient series is dominant as compared to the other series, in both cases. Moreover, the dimer Pb_2^+ is detected in both spectra.

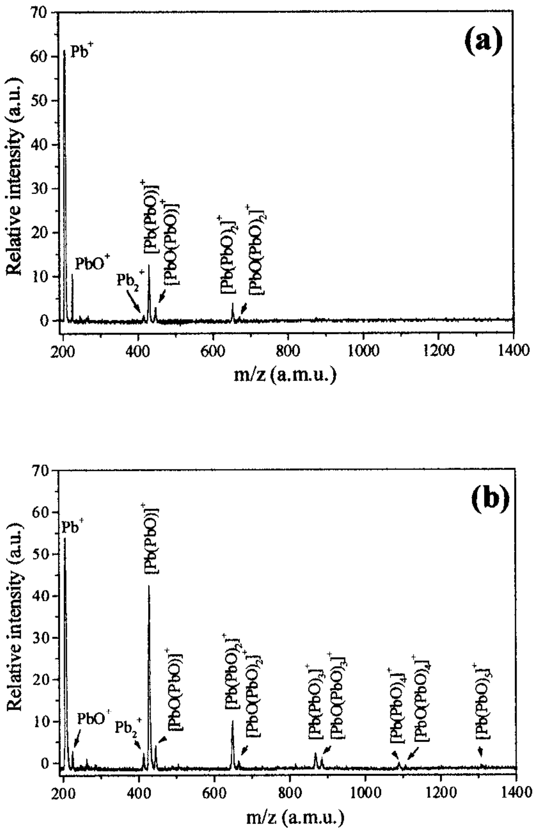

Figure 1. Time of flight mass spectra in positive mode for ablation of PbO (a) and Pb_3O_4 (b).

We can observe some reproducible differences between the spectra of the two oxides which can be related to the target stoichiometry: the sizes of the clusters formed are different ($n = 1-2$ for PbO and $n = 1-4$ for Pb_3O_4) and the relative intensity of $[Pb(PbO)_n]^+$ is much greater in the case of Pb_3O_4.

Several conclusions can be deduced from these observations. First, these clusters seem to be formed by growth from smaller entities rather than by direct emission from the target. In the case of the dominant clusters series, this observation implies the existence of a Pb^+ precursor and the sequential addition of a neutral molecule, PbO, as is shown by eq 1.

$$Pb^+ \overset{PbO}{\Longrightarrow} [Pb(PbO)]^+ \overset{PbO}{\Longrightarrow} [Pb(PbO)_2]^+ \overset{PbO}{\Longrightarrow} [Pb(PbO)_3]^+ \quad (1)$$

The second series of clusters could be obtained by considering the PbO^+ ion as the nucleus and adding subsequently PbO:

$$PbO^+ \overset{PbO}{\Longrightarrow} [PbO(PbO)]^+ \overset{PbO}{\Longrightarrow} [PbO(PbO)_2]^+ \overset{PbO}{\Longrightarrow} [PbO(PbO)_3]^+ \quad (2)$$

This mechanism has also been suggested by Gibson[15] for the ablation of several lanthanide oxides. This author has suggested that lanthanide clusters of the $Ln_xO_y^+$ type are formed by successive additions of Ln_2O_3 neutrals to a precursor ion, namely, Ln^+ and LnO^+. The stoichiometry of the neutral will be discussed later in

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Table 1. Ionization and Appearance Energies of Lead Species[a]

species	energy	species	energy
Pb^+	7.4[b]	$Pb_3O_2^+$	13.4[c]
PbO^+	9.2[b]	$Pb_3O_3^+$	9.1[c]
Pb_2O^+	10.9[c]	$Pb_4O_4^+$	8.1[b]
$Pb_2O_2^+$	8.3[b]		

[a] Data from ref 16. These value have been experimentally determined by Knudsen-cell mass spectrometry and electron impact methods. [b] Ionization energy. [c] Appearance energy.

this report. The typical way to generate clusters is postablation aggregation, using a supersonic expansion nozzle of a buffer gas. In Gibson's experiment,[15] the clusters were observed only after accumulating several laser shots on the target after the formation of a crater. This author suggested that this crater acts as a supersonic expansion nozzle in which the clusters coalesce. The transmission geometry of our equipment suggests that a similar mechanism applies, with the expansion of the plasma through microchannels between the grains of a given powder causing a similar phenomenon.

This mechanism implies that the PbO neutral might be a significant product in the plume or/and, at least, very reactive with ions. Indeed, it was observed that the PbO^+ ion is detected under low intensity. If the ionization energy is one of the main reasons for the lack of abundance, the weak intensity observed with the PbO^+ ion may be due to its high ionization potential (9.2 eV, Table 1). The wavelength used (355 nm) provides 3.5 eV photons; thus, PbO ionization requires a three-photon process, which is highly improbable in relation to the range of irradiance.

Consequently, the process described by eq 2 may be in disagreement with the lack of abundance of the PbO^+ ion. It could be assumed that the precursor ions are abundant enough to generate the PbO adducts. Consequently, it can also be assumed that the $[PbO(PbO)_n]^+$ clusters do not stem only from coalescence reactions. Moreover, the observation of this cluster series suggests that the abundance of the precursor ion is neither a necessary nor a sufficient condition for cluster growth and the reactivity of the neutral species with the ion is the dominant factor for cluster growth. The fact that $[PbO(PbO)_n]^+$ clusters are substantially less abundant than $[Pb(PbO)_n]^+$ is in agreement with the latter assumption.

Another argument for the presence of PbO in the plume is the high intensity of the $[Pb(PbO)]^+$ and $[Pb(PbO)_2]^+$ ions despite their high appearance energy (10.9 and 13.4 eV, respectively). A direct ionization process would imply a simultaneous absorption of four photons. Hence, these ions originate more probably from successive additions of PbO to a Pb^+ and $[Pb(PbO)]^+$, respectively.

Pb_3O_4 interaction with laser gives rise to a thermal decomposition reaction leading to the formation of a lower oxide and O_2 molecules:

$$Pb_3O_4 \rightarrow 3PbO + {}^1/_2O_2 \tag{3}$$

This reaction can lead to an enhancement of the concentration of PbO neutrals in the plume, as well as to a local increase of the oxygen pressure. This can be correlated with the detection of high mass species with Pb_3O_4.

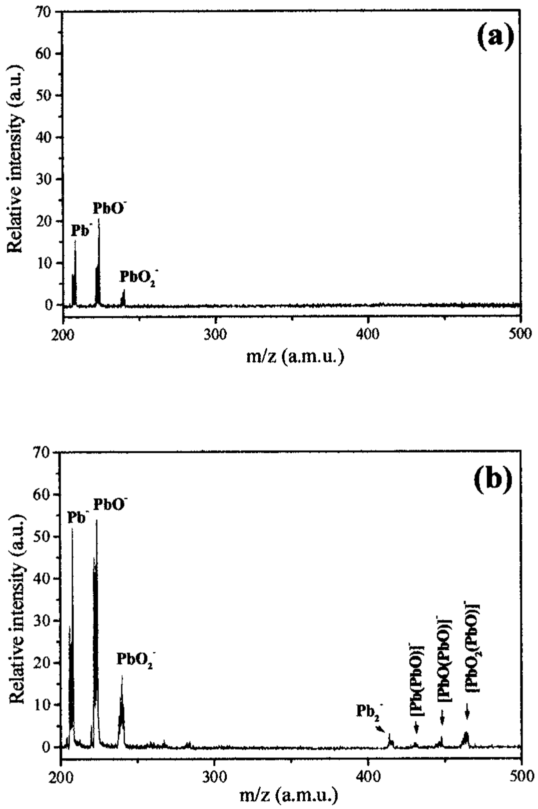

Figure 2. Time of flight mass spectra in negative mode for ablation of PbO (a) and Pb_3O_4 (b).

By ablating a $Pb(Ti_{0.48}Zr_{0.52})O_3$ target in oxygen ambient gas, Amoruso et al.[6] show that high mass clusters are more abundant in an oxygen environment as compared to high vacuum conditions. An analogy between laser ablation of Pb_3O_4 in a vacuum and PbO in an O_2 atmosphere can be suggested. Thus, ablation of Pb_3O_4 in a vacuum offers a means to approach PbO ablation in an oxygen atmosphere.

1b. Negative Ions. The negative TOF spectra of PbO and Pb_3O_4 are displayed in Figure 2a,b. Only three peaks are detected for PbO: the atomic ion Pb^- and two molecular ions, PbO^- and PbO_2^-. PbO^- is the dominant ion. The relative intensity of the three detected ions remains unchanged. The distribution of ions is wider with Pb_3O_4 and four additional high mass peaks are detected: Pb_2^-, $[Pb(PbO)]^-$, $[PbO(PbO)]^-$, and $[PbO_2(PbO)]^-$. These high mass peaks can also be caused by an addition mechanism from Pb^-, PbO^-, and PbO_2^- precursors by adding a PbO neutral molecule.

The difference in the relative intensities observed for Pb^- and PbO^- peaks $[I(Pb^-) < I(PbO^-)]$ can be linked to the electronic affinity of their corresponding neutrals (Pb and PbO) which are 0.364 and 0.722 eV, respectively[17] $(EA(Pb^-) < EA(PbO^-))$. Unfortunately, no information is available concerning the electronic affinity of PbO_2^-.

Furthermore, the quantitative density of neutral precursors in the plasma should be taken into account to explain the relative intensity of the species detected. In fact, when considering a process that involves

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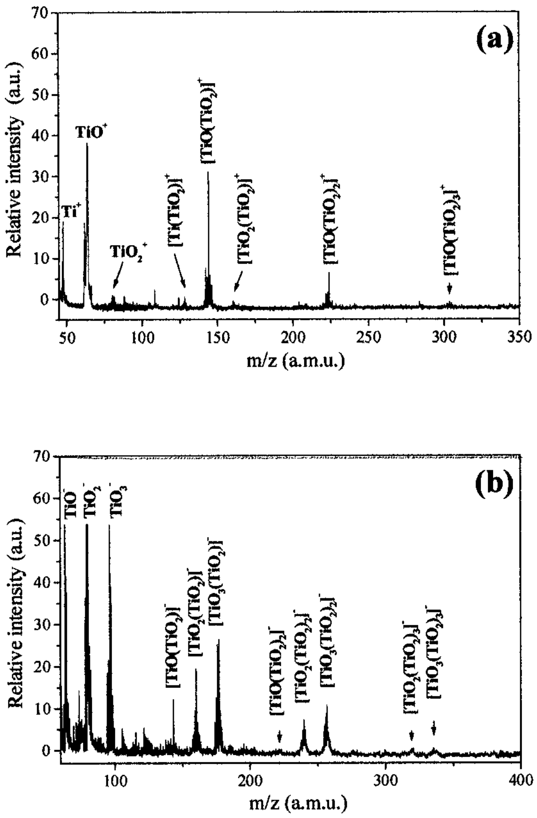

Figure 3. Time of flight mass spectra for ablation of TiO_2 in the positive mode (a) and in the negative mode (b).

electrons and neutrals in a three-body collision,[18] formation of negative ions can be primarily attributed to the two following equations:

$$e^- + e^- + A^0 \rightleftharpoons A^- + e^- \qquad (4)$$

$$e^- + A^0 + A^0 \rightleftharpoons A^- + A^0 \qquad (5)$$

These processes are reversible and obviously occur in a high-density region of the plume. For their "survival", the negative ions that have just been formed should have a velocity that is high enough to escape the dense plasma without being destroyed.

Such a process also involves a high density of neutral precursors in the plume. It is likely that PbO neutrals (as well as Pb) are a significant component in the plasma plume issued from solid PbO (and obviously from Pb_3O_4 ablation), as already suggested in the case of the positive ions. It is worth noting that the presence of Pb^0 and Pb^+ is well evidenced by applying optical emission spectroscopy to a KrF laser plume of a PbO target, performed in an oxygen atmosphere.[7] However, the presence of neutral PbO is not observed with certainty, due to interferences with other spectral lines.

2. Titanium Dioxide. *2a. Positive Ions.* The positive TOF spectrum of TiO_2 (Figure 3a) is characterized by two dominant peaks from Ti^+ and TiO^+ and by peaks from $Ti_xO_y^+$ clusters (where $x = 1-4$ and $y = 1-7$). These clusters make up several three-peak groups separated by 80 mass units corresponding to TiO_2. In analogy to the case of lead oxides, cluster growth from smaller entities by a sequential addition of the neutral TiO_2 (and not TiO) to precursor ions (Ti^+, TiO^+, TiO_2^+) is also suggested. Thus, the cluster distribution can be completely described by three series of clusters: $[TiO(TiO_2)_n]^+$ (where $n = 1-3$), which is largely dominant, $[Ti(TiO_2)_n]^+$, and $[TiO_2(TiO_2)_n]^+$, the latter two being detected at low intensity.

Table 2. Ionization and Appearance Energies of Titanium Species[a]

species	energy	species	energy
Ti^+	6.83[b]	$Ti_2O_3^+$	8.3[b]
TiO^+	6.82[b]	$Ti_2O_4^+$	10.5[c]
TiO_2^+	9.5[b]		

[a] Data from ref 19. These value have been experimentally determined by Knudsen-cell mass spectrometry and electron impact methods. [b] Ionization energy. [c] Appearance energy.

The ionization energy of Ti^+ and TiO^+ is respectively 6.83 and 6.82 eV (Table 2). This energy level is lower than that brought about by two 355 nm photons. Hence, their respective intensity levels are in reasonable agreement with their ionization energy levels. This holds true for the TiO_2^+ ion (IP = 9.5 eV) which requires a rather improbable three-photon process to be ionized. This fact provides an explanation for the low intensity observed with TiO_2^+. As additional proof, Lobstein et al.,[13] using a 266 nm (4.7 eV) laser (frequency-quadrupled Nd:YAG) coupled with mass spectrometry, have obtained TOF spectra corresponding to TiO_2 for which the TiO_2^+ ion was relatively more abundant than what we had observed. The ionization energy values fall in agreement with the lack of abundance of the $[TiO_2(TiO_2)_n]^+$ series, if we assume the application of the addition mechanism. Moreover, it can be noted that the Ti_mO_{2m} (see Table 2) species have high ionization energy. Therefore, $[TiO_2(TiO_2)_n]^+$ clusters are weakly detected, first, due to high ionization energy levels for the precursor ion and, second, because of a high ionization potential of Ti_mO_{2m} species, if we assume direct ejection/ionization of these kinds of clusters.

Despite an appearance energy value of 8.3 eV, involving a three-photon ionization process, the $Ti_2O_3^+$ ($[TiO_2(TiO_2)_n]^+$) ion is surprisingly abundant. This can be regarded as an additional argument for a mechanism calling for a reaction between a TiO^+ ion (IE = 6.82 eV) and TiO_2:

$$TiO^+ \overset{TiO_2}{\Rightarrow} [TiO(TiO_2)]^+ \qquad (6)$$

Yu et al.[20] have investigated the fragmentation mechanisms of titanium/oxygen positive clusters using FAB mass spectrometry and collision-induced dissociation. The experiment performed on TiO_2 powder gave results which are in good agreement with the addition mechanism hypothesis. Notwithstanding the different experimental conditions,[21] FAB experiments allow the same type of clusters as those observed in our work to

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(21) Michiels, E.; Celis, A.; Gijbels R. In *Microbeam Analysis*; Washington, DC, 1982. The authors have shown that despite quantitative difference between LMMS and SIMS spectra, the general features are similar. It has been also suggested that SIMS litterature can be consulted for the LMMS technique.

Table 3. Collision-Induced Dissociation Experiments Results Performed with FAB-Induced Titanium/Oxygen Clusters[a]

clusters before CID	fragment ions	neutral fragments	relative abundance
$Ti_4O_7^+$	$Ti_3O_5^+$	TiO_2	100
	TiO^+	$(TiO_2)_3$	25
$Ti_3O_5^+$	$Ti_2O_3^+$	TiO_2	25
	TiO^+	$(TiO_2)_2$	100
$Ti_2O_3^+$	TiO^+	TiO_2	100

[a] Data from ref 20.

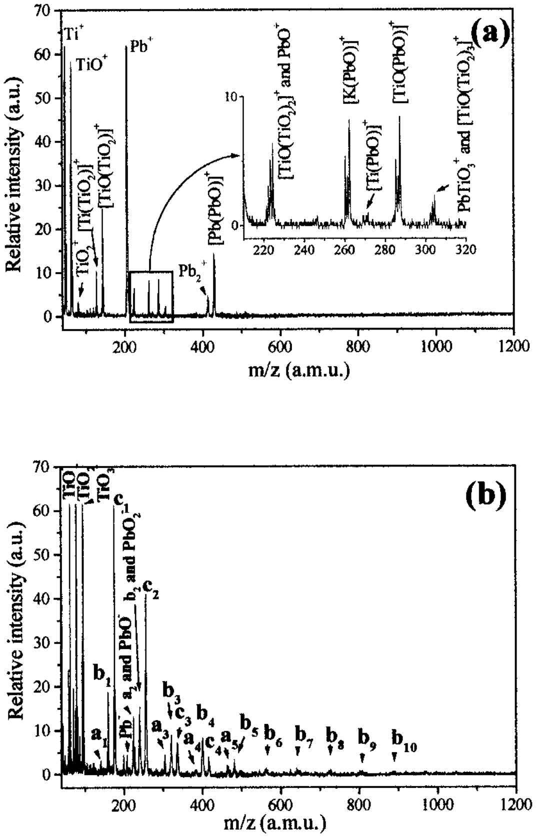

Figure 4. Time of flight mass spectra for ablation of $PbTiO_3$ (or PbO/TiO_2 mixture) in the positive mode (a) and in the negative mode (b). In the negative mode, a_n, b_n, and c_n are respectively $[TiO(TiO_2)_n]$, $[TiO_2(TiO_2)_n]$, and $[TiO_3(TiO_2)_n]$.

be obtained. Each of these clusters has been isolated and dissociated. The neutral fragments obtained are consistent with the formula $(TiO_2)_n$ (Table 3).

2b. Negative Ions. A negative ion TOF spectrum of TiO_2 is shown in Figure 3b. It can be seen that Ti^- is not detected. This can be related to the low value of its electron affinity (0.079 eV). The dominant peak is TiO_2^-; TiO^- and TiO_3^- are also very abundant. Therefore, it is not surprising to observe that TiO_2 adducts to these ions are also abundant: $[TiO(TiO_2)_n]^-$, $[TiO_2(TiO_2)_n]^-$, and $[TiO_3(TiO_2)_n]^-$, where $n = 0-4$. For $n > 1$, $[TiO_2(TiO_2)_n]^-$ and $[TiO_3(TiO_2)_n]^-$ clusters are predominant in relation to $[TiO(TiO_2)_n]^-$. In contrast to the positive spectra, the dominant clusters have the same stoichiometry as the target.

3. $PbTiO_3$ and PbO/TiO_2 Equimolar Mixture. *3a. Positive Ions.* A representative positive ion mass spectrum of $PbTiO_3$ is shown in Figure 4a. This spectrum is similar to those obtained with a PbO/TiO_2 equimolar mixture (spectrum non displayed here). The characteristic peaks detected in the spectra of pure PbO and TiO_2 are also observed: Ti^+, TiO^+, $[Ti(TiO_2)_n]^+$, and $[TiO(TiO_2)_n]^+$ (where $n = 1-3$) and Pb^+, Pb_2^+, $[Pb(PbO)]^+$, and $[PbO(PbO)]^+$.

Table 4. The Peaks Concerned by Isobaric Interferences

ions	calculated masses	ions	calculated masses	resln[a]
$[Ti(TiO_2)_2]^+$	207.822952	Pb^+	207.976078	1400
$[TiO(TiO_2)_2]^+$	223.817867	PbO^+	223.970993	1500
$[TiO(TiO_2)_3]^+$	303.755644	$PbTiO_3^+$	303.908770	2000

[a] Minimal resolution needed to distinguish the two peaks.

In the two compounds analyzed, Pb^+ ion is dominant relative to Ti^+; conversely, PbO^+ is less abundant than TiO^+. Their corresponding intensity levels are in agreement with the ionization energy and the bond strength of TiO (6.96 eV) and PbO (3.95 eV). In other words, the fact that PbO^+ is weakly detected relative to TiO^+ could be explained either by the tendency of neutral PbO to be easily broken or the difficulty for it to be ionized.

Some peaks cannot be identified with certainty because of isobaric interferences. However, the contribution of each one can be estimated on the basis of the theoretical isotopic distribution and/or by using information taken from the spectra of the pure compounds. Table 4 displays the peaks affected by this phenomena, the corresponding calculated masses, and the mass resolution required to distinguish the two species. For instance, the peak labeled PbO^+ could also be $[TiO(TiO_2)_2]^+$, and the resolution necessary to separate these two peaks must be at least 1500.

One of the most interesting characteristics of the mass spectra is the detection of mixed clusters: $PbTiO^+$ and $PbTiO_2^+$. The second one is significantly more abundant than the first one. The peak at $m/z = 304$ (see Table 4) could be $[TiO(TiO_2)_3]^+$ as well as $PbTiO_3^+$ or a superposition of both. The $[TiO(TiO_2)_2]^+$ ion is detected together with the theoretical isotopic distribution of the two peaks. It follows that the peak at $m/z = 304$ is a combination of $[TiO(TiO_2)_3]^+$ and $PbTiO_3^+$. Moreover, mass peaks at $m/z = 39$ and 41 of the alkali ion K^+ are also frequently observed for the two compounds. The presence of this ion is due to adventitious impurities in the samples. Its presence in the plasma plume allows detection of the $[K(PbO)]^+$ ion. The formation of the bimetallic clusters from the two compounds ($PbTiO_3$ and PbO/TiO_2) indicates that the mixed clusters are formed in the gas phase or/and, most probably, in a liquid phase (by surface fusion).[22] Ti^+ and TiO^+, as well as K^+, are major components of the ion population in the plume. The series $[Pb(PbO)_n]^+$ and $[PbO(PbO)_n]^+$ are detected in both spectra. This observation indicates that PbO and TiO_2 neutrals are present in the plume. By considering, first, that $PbTiO^+$ and $PbTiO_2^+$ are detected in both $PbTiO_3$ and PbO/TiO_2 mixture and, second, that the $[K(PbO)]^+$ ion is detected, the most probable formation process of the $PbTiO^+$ and $PbTiO_2^+$ clusters must be a three-body interaction involving an ionic titanium species, neutral PbO , and a buffer species (B, ion or

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[22] Musselman, I. H.; Linton, R. W.; Simons, D. S. *Anal. Chem.* **1988**, *60*, 110

neutral), according to the following equations:

$$Ti^+ + PbO + B \Rightarrow PbTiO^+ + B \qquad (7)$$

$$TiO^+ + PbO + B \Rightarrow PbTiO_2{}^+ + B \qquad (8)$$

Alkali metal ions are the most common impurities detected in inorganic compounds because of their low IP (about 5 eV). The detection of their PbO adducts can be regarded as additional proof for the cluster growth mechanism. Considering reactions 7 and 8, it can be seen that the mixed clusters originate from monometallic titanium ions (Ti^+ and TiO^+), and subsequently, their PbO adducts can be written as $[Ti(PbO)]^+$ and $[TiO(PbO)]^+$. It is also interesting to note that the addition mechanism assumed still occurs with both purely titanium/oxygen and lead/oxygen species. Initial laser heating could result in a decomposition of $PbTiO_3$ into Pb and Ti oxide: $PbTiO_3 \rightarrow PbO + TiO_2$. This equation is in agreement with the similarity between the lead titanate and the PbO/TiO_2 mixture spectra.

3b. Negative Ions. There is also a great similarity between the fingerprint spectra of $PbTiO_3$ and PbO/TiO_2 mixture in the negative mode. A representative spectrum of $PbTiO_3$ and PbO/TiO_2 in the negative mode is shown in Figure 4b. Again, the ions observed earlier in the spectra of the pure compounds (TiO_2, PbO) are detected: $[TiO(TiO_2)_n]^-$, $[TiO_2(TiO_2)_n]^-$, and $[TiO_3(TiO_2)_n]^-$, where $n = 1-5$, and Pb^-, PbO^-, and $PbO_2{}^-$.

The peak labeled $PbO_2{}^-$ can also be attributed to $[TiO_2(TiO_2)_2]^-$, and making a distinction between the isobars requires a minimal resolution of 1500. However, when considering the spectra of pure substances and the theoretical isotopic distribution, it can be concluded that the peak intensity is to be attributed mostly to $[TiO_2(TiO_2)_2]^-$. It can also be observed that titanium clusters are dominant as compared to lead clusters. Moreover, it appears again that the addition mechanism occurs only with Ti species. This is in good agreement with the spectra of pure PbO, where no clusters with more than one Pb atom have been observed. Moreover, in contrast to the spectra recorded in the positive mode, there is no clear evidence of the formation of bimetallic clusters. The main components of the spectra are supposed to be titanium/oxygen species.

4. $Pb_3O_4/3TiO_2$ Molar Mixtures. The molar ratio between the two oxides was selected in order to study mixtures with Pb/Ti =1 as in the $PbTiO_3$ compound. In positive mode, the Pb_3O_4 oxide has given an enhancement of the yield of cluster formation relative to PbO. It has been shown that an enhancement of neutrals and oxygen density in the plasma could account for the greater yield of clusterization. Thus, the ablation of the $Pb_3O_4/3TiO_2$ mixture allows examination of the effect of the (Pb + Ti)/O molar ratio on cluster formation.

4a. Positive Ions. A positive TOF spectrum of the $Pb_3O_4/3TiO_2$ mixture is shown in Figure 5a. The spectrum is qualitatively similar to that of the above-mentioned compounds, but there are differences in the yield of cluster formation. $[Pb(PbO)_n]^+$ and $[PbO(PbO)_n]^+$ clusters are identified up to a mass of 1100 (n = 4). The mixed clusters ($[Ti(PbO)]^+$, $[TiO(PbO)]^+$, and $[TiO_2(PbO)]^+$) are detected, and moreover, PbO adducts of the ions $[TiO(PbO)_n]^+$ and $[TiO_2(PbO)_n]^+$ or $[TiO(TiO_2)_3(PbO)_n]^+$ have been identified up to a mass of 1000 (n = 4). Cluster formation is more efficient with this mixture. This can be interpreted as being caused by an increasing number of PbO neutrals in the plume, as suggested in the case of the ablation of pure Pb_3O_4. This is in good agreement with the enhancement of $[K(PbO)]^+$, if we assume its formation as a reaction between an alkali ion and a neutral PbO . Cluster formation occurs also with $[K(PbO)]^+$ considering that $[K(PbO)_2]^+$ has been detected. Another characteristic of these mixed clusters is the decreasing yield of cluster formation in pure lead/oxygen species relative to the yield observed with pure compounds. This could be linked to a competition between the aggregation of pure lead/oxygen species and mixed species. This feature has been observed by Mele et al.[12] in the case of a mixture of CuO and $SrCO_3$; the mixed species detected were consistent with the empiric formula $[Cu(SrO)_n]^+$.

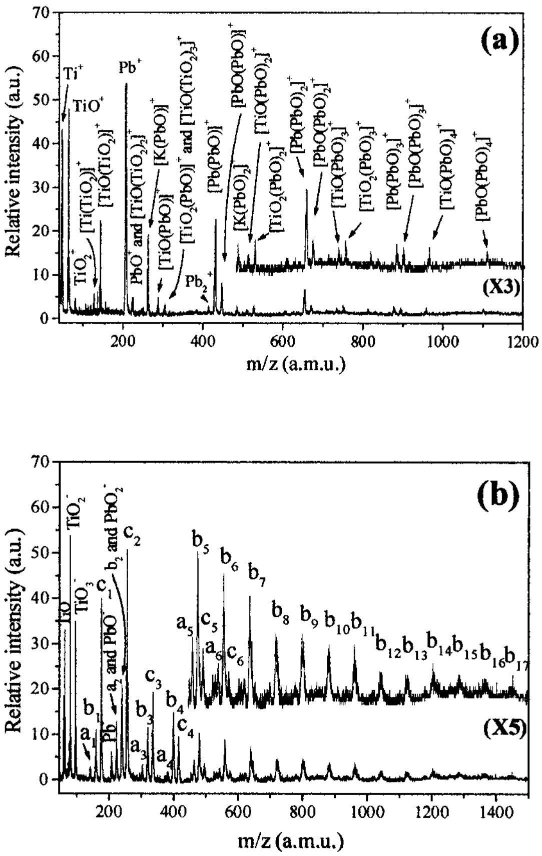

Figure 5. Time of flight mass spectra for ablation of a $Pb_3O_4/3TiO_2$ mixture in the positive mode (a) and in the negative mode (b). In the negative mode, a_n, b_n, and c_n are respectively $[TiO(TiO_2)_n]$, $[TiO_2(TiO_2)_n]$, and $[TiO_3(TiO_2)_n]$.

4b. Negative Ions. With the $Pb_3O_4/3TiO_2$ molar mixture (Figure 5b), TiO_2 adducts are identified up to a mass of 1600. $[TiO(TiO_2)_n]^+$ clusters with n up to 17 are also clearly evidenced. The major enhancement of cluster formation achieved by this compound is additional proof of a high concentration of neutral TiO_2 in the plume. However, in comparison with the spectra of the pure titanium oxides, the yield of titanium/oxygen aggregation has dramatically increased. It can be suggested that the Pb species plays the role of a third body which absorbs the surplus energy of the titanium/oxygen species which have just formed in a three-body collision process, as described by eqs 7 and 8.

Table 5. Detected Species in Negative and Positive Mode[a]

PbO	Pb$_3$O$_4$	TiO$_2$	PbTiO$_3$	PbO/TiO$_2$	Pb$_3$O$_4$/3TiO$_2$
Positive Ions					
Pb$^+$	**Pb$^+$**	**Ti$^+$**	**Ti$^+$**	**Ti$^+$**	**Ti$^+$**
PbO$^+$	*PbO$^+$*	**TiO$^+$**	**TiO$^+$**	**TiO$^+$**	**TiO$^+$**
[Na(PbO)]$^+$	*[Na(PbO)]$^+$*	*[Ti(TiO$_2$)$_n$]$^+$*	[Ti(TiO$_2$)]$^+$	[Ti(TiO$_2$)]$^+$	[Ti(TiO$_2$)]$^+$
[K(PbO)]$^+$	*[K(PbO)]$^+$*	**[TiO(TiO$_2$)$_n$]$^+$** (c)	[TiO(TiO$_2$)$_n$]$^+$ (e)	[TiO(TiO$_2$)$_n$]$^+$ (e)	[TiO(TiO$_2$)$_n$]$^+$ (i)
Pb$_2^+$	*Pb$_2^+$*	*[TiO$_2$(TiO$_2$)$_n$]$^+$*	*[TiO$_2$(TiO$_2$)$_n$]$^+$*	*[TiO$_2$(TiO$_2$)$_n$]$^+$*	*[TiO$_2$(TiO$_2$)$_n$]$^+$*
[Pb(PbO)$_n$]$^+$ (a)	**[Pb(PbO)$_n$]$^+$** (b)		**Pb$^+$**	**Pb$^+$**	**Pb$^+$**
[PbO(PbO)$_n$]$^+$ (a)	*[PbO(PbO)$_n$]$^+$* (b)		*PbO$^+$*	*PbO$^+$*	*PbO$^+$*
			[K(PbO)]$^+$	*[K(PbO)]$^+$*	[K(PbO)$_n$]$^+$
			[Ti(PbO)]$^+$	*[Ti(PbO)]$^+$*	*[Ti(PbO)]$^+$*
			[TiO(PbO)]$^+$	*[TiO(PbO)]$^+$*	*[TiO(PbO)$_n$]$^+$* (j)
			[TiO$_2$(PbO)]$^+$	*[TiO$_2$(PbO)]$^+$*	*[TiO$_2$(PbO)$_n$]$^+$* (k)
			Pb$_2^+$	*Pb$_2^+$*	*Pb$_2^+$*
			[Pb(PbO)]$^+$	[Pb(PbO)]$^+$	[Pb(PbO)$_n$]$^+$ (l)
			[PbO(PbO)]$^+$	[PbO(PbO)]$^+$	[PbO(PbO)$_n$]$^+$ (m)
Negative Ions					
Pb$^-$	**Pb$^-$**	**TiO$^-$**	**TiO$^-$**	**TiO$^-$**	TiO$^-$
PbO$^-$	**PbO$^-$**	**TiO$_2^-$**	**TiO$_2^-$**	**TiO$_2^-$**	**TiO$_2^-$**
PbO$_2^-$	PbO$_2^-$	**TiO$_3^-$**	**TiO$_3^-$**	**TiO$_3^-$**	TiO$_3^-$
	[Pb(PbO)]$^-$	*[TiO(TiO$_2$)$_n$]$^-$*	*[TiO(TiO$_2$)$_n$]$^-$* (f)	*[TiO(TiO$_2$)$_n$]$^-$* (f)	*[TiO(TiO$_2$)$_n$]$^-$* (n)
	[PbO(PbO)]$^-$	[TiO$_2$(TiO$_2$)$_n$]$^-$ (d)	[TiO$_2$(TiO$_2$)$_n$]$^-$ (g)	[TiO$_2$(TiO$_2$)$_n$]$^-$ (g)	[TiO$_2$(TiO$_2$)$_n$]$^-$ (o)
	[PbO$_2$(PbO)]$^-$	[TiO$_3$(TiO$_2$)$_n$]$^-$ (d)	**[TiO$_3$(TiO$_2$)$_n$]$^-$** (h)	**[TiO$_3$(TiO$_2$)$_n$]$^-$** (h)	**[TiO$_3$(TiO$_2$)$_n$]$^-$** (p)
			Pb$^-$	**Pb$^-$**	**Pb$^-$**
			PbO$^-$	**PbO$^-$**	**PbO$^-$**
			PbO$_2^-$	PbO$_2^-$	PbO$_2^-$

[a] The ions labeled in bold are the dominant ions and those in italic are weakly detected. n values: (a) 1−2, (b) 1−4, (c) 1−3, (d) 1−3, (e) 1−3, (f) 1−3, (g) 1−9, (h) 1−4, (i) 1−3, (j) 1−4, (k) 1−3, (l) 1−3, (m) 1−4, (n) 1−6, (o) 1−17, (p) 1−6.

Conclusions

The heavy ionized species (clusters) created under vacuum during the ablation of lead titanate and lead and titanium oxides were characterized by laser microprobe mass spectrometry. The ions and clusters detected for each compound in the positive and the negative mode have been summarized in Table 5. Our results suggest that these species are formed by an addition mechanism rather than by direct ejection from the target. An interesting feature is the formation of positive mixed clusters containing both lead and titanium (and oxygen). In the negative mode, no mixed clusters are observed, but the high mass clusters are oxygen rich and are therefore good oxygen carriers. This point has to be underlined in relation to the role of oxygen in PLD experiments.

Currently, in the PLD process, crystallized PbTiO$_3$ films are deposited at high substrate temperatures under optimized oxygen pressure. The similarity between PbO/TiO$_2$ and PbTiO$_3$ TOF spectra is in agreement with the possibility of obtaining PbTiO$_3$ thin films, from either the PbTiO$_3$ target[1] or the alternative laser ablation of TiO$_2$ and PbO.[23] The various laser-induced clusters and neutrals are responsible for the stoichiometry obtained in the PbTiO$_3$ structure. On one hand, pure metallic clusters have various M/O ratios: positive clusters are rather oxygen deficient, whereas negative clusters are rather oxygen rich. Globally, purely metallic positive and negative clusters can be regarded as nearly stoichiometric with regard to oxygen. However, the laser ablation of Pb−Ti−O compounds induced specific mixed species and it can be suggested that the latter are appropriate precursors for the growth of PbTiO$_3$ films. On the other hand, neutral species (mainly PbO and TiO$_2$, as shown by the aggregation reactions) are important oxygen carriers and their behavior could be similar to what we have with ablation when performed on monometallic oxides (PbO or TiO$_2$). Actually, the transfer of TiO$_2$ in a vacuum is nearly stoichiometric.[13] Though this observation also applied to the laser ablation of lead oxide, PbO films are generally oxygen deficient due to the loss of lead induced by the high-temperature substrate.[5]

A low oxygen background introduced into the ablation cell during PLD experiments implies a high level of stoichiometry stability in oxide clusters and/or neutral species. Considering that the oxygen−lead binding is weak and removing lead is easy due to high substrate temperature, we can assume that oxygen enhances cluster formation, as suggested by our experiments performed on a Pb$_3$O$_4$/3TiO$_2$ mixture. Nevertheless, the role of the oxygen coming respectively from the target and the oxygen introduced in the gaseous phase has not been clearly established yet. This is currently one of the fields of investigation for our research team, using ^{18}O tracer as ambient gas for PbTiO$_3$ thin films deposition, and will be the subject of a forthcoming paper.

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