# Composition and local bonding in RE–Si–M–O–N (M = Mg, Al ; RE = La, Lu) glasses

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## Abstract

Two series of oxynitride glasses, RE–Si–Mg–O–N (M = Mg, Al ; RE = La, Lu), have been studied by X-Ray photoelectron spectroscopy (XPS). The oxygen 1s photoelectron lineshape reveals a striking difference depending on the rare earth, both in the Mg series and in the Al series. Specifically, the oxygen 1s photoelectron lines of the La doped glasses are broader than the ones of the Lu doped glasses. This result is an experimental evidence that Lu has a larger affinity for oxygen versus nitrogen than La, as theoretically predicted by the first-principles calculations by Painter et al.

## 1. Introduction

Oxynitride glasses have attracted interest during the last two decades because of two principal reasons. First, mechanical, rheological, optical and other properties of these glasses can be tailored by changes in nitrogen content and additions of various rare-earth elements (RE) [1–6]. As an example, it has been shown that the indentation moduli and microhardness of RE–Si–Mg–O–N glasses (RE = Y, Sc, and lanthanides La, Sm, Yb, Lu) containing 20–24 eq% of nitrogen depend on RE type and nitrogen content as well. The Lu-containing glasses exhibit microhardness significantly higher than that of La-glasses with the same nitrogen content, whereas a 4% increase in nitrogen content results only in a few % increase of microhardness [3].

A second reason motivating the study of oxynitride glasses is that such glassy phases are present at the grain boundaries of silicon nitride ceramics, in the form of thin intergranular films

(IGF) of nanometer thickness. These oxynitride glassy films are known to effectively control high temperature mechanical properties of the polycrystalline ceramics. In order to understand and control the different properties of these ceramics as a function of the IGF, recent studies have been undertaken on oxynitride glasses considered as model glasses of these intergranular films [6]. The purpose was to understand the effect of rare-earth elements and nitrogen on microhardness, indentation modulus, fracture toughness and viscosity of model glasses with the same composition as the IGF. A conclusion of this work is that the usual cationic field strength (CFS) concept seems to be insufficient to describe all the effects of rare-earth dopants on the properties of oxynitride glasses.

The present work is devoted to an XPS study of four RE–Si–M–O–N glasses (M = Mg, Al ; RE = La, Lu). A detailed analysis of the XPS photoelectron lineshapes and binding energies was performed in order to get insight into the bonding in these glasses as a function of the rare earth. The striking difference occurs in the oxygen photoelectron line, the shape of which is very different when comparing the La glasses and the Lu glasses. We explain this difference as due to a change in the

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glass structure and interpret it in the frame of a recent theoretical work by Painter et al. [7], where the differential binding energies are calculated so as to measure the rare earth's preference for bonding with O over N, compared to that of silicon.

## 2. Experimental methods

### 2.1. Glass preparation

Four glass formulations have been prepared in the same way as in references [2] and [3] for RE–Si–Al–O–N and RE–Si–Mg–O–N (RE = La, Lu) glasses, respectively. The compositions of the individual powder mixtures in equivalent % and atom % are given in the two first columns of the Table 1.

Samples were cleaned ultrasonically in ethanol, then rinsed in distilled water and dried under dry nitrogen before loading in the ultra high vacuum chamber for XPS analysis. No other heat treatments were performed, in order to avoid a modification of the surface composition.

### 2.2. X-ray photoelectron spectroscopy

The XPS analyses were carried out in a VG Escalab Mark II. X-ray photoelectron spectra were produced using a non-monochromatized X-Ray source ($h\nu = 1486.6$ eV) and a hemispherical analyzer fitted with a five-channeltron multi-detection system. Pressure in the sample chamber was less than $2.10^{-10}$ mbar. Calibration of the spectrometer was such that the Ag3d5/2 photoelectron line had a binding energy of 368.35 eV and a Full Width at Half Maximum (FWHM) of 0.85 eV, with a 20 eV pass energy. Wide scans were recorded in the 50–1250 eV energy range to determine the elements present in the sample and to check for surface contamination. Then the O1s, N1s, Si2p/Si2s, Mg2p, Al2p, La3d/La4d and Lu 4d photoelectron lines were recorded separately.

As these glass samples are highly insulating, all the photoelectron lines are shifted towards higher binding energies. No electron flood gun was used to compensate for the surface charge. The electron binding energies were corrected for charging effect by setting the C1s peak of contamination carbon at 284.6 eV. For this correction to be reliable, one had to be sure that the C1s has not been shifted with time. So the carbon photoelectron line was recorded before and after measuring each given photoelectron line (O1s, Si2p...) so as to assure that

there was no C1s shift with time. We have also checked that the C1s photoelectron line of our four samples had similar shape and width (2.4 eV). The adventitious carbon was therefore of the same type on all the samples, ensuring therefore the reliability of the calibration method.

## 3. Results

### 3.1. Composition determined from XPS

An estimate of the elemental composition (at%) of the glasses was obtained from the intensities of O1s, N1s, Si2p/Si2s, Mg2p, Al2p, La3d/La4d and Lu 4d photoelectron lines, using a standard quantitative XPS analysis. Results are shown in the third column of Table 1. The atomic concentrations were derived from the areas of the characteristic photoelectron lines after substraction of Shirley background, divided by the ionisation cross-section [8]. The precision in the derived concentration is of the order of 10%. When comparing with the nominal composition, we find slightly more Si and O than expected and less N and Mg (or Al) . The RE concentration for La–Si–Mg–O–N glass (La27) is the one expected, while that for Lu–Si–Mg–O–N (Lu20), ornlLa (ornlLa) O–N (ornlLa) and Lu–Si–Al–O–N (ornlLu) and samples are slightly less. As this analysis probes only a 5 nm surface layer of the glass, it is likely that the composition in the surface layers is slightly different from that of the bulk. In addition, we carefully checked that the amount of carbon was the same on the La–Si–Mg–O–N (La27) and Lu–Si–Mg–O–N (Lu20) samples, on the one hand, and on the La–Si–Al–O–N (ornlLa) and Lu–Si–Al–O–N (ornlLu) samples on the other hand. This ascertains that differences observed in the photoelectron lineshapes of the La and Lu glasses are not due to an artefact coming from the carbon contamination.

### 3.2. Photoelectron lineshapes and binding energies of silicon

We first focus on the Si2p photoelectron line, shown in Fig. 1.The measured binding energies are reported in Table 2 along with that of $SiO_2$ for comparison [9]. The Si2p photoelectron lines of La glasses overlap the La4d 5/2 photoelectron lines, so that they can not easily be compared with those of the two other glasses. The binding energies of Si2p photoelectron lines in Lu glasses are very close to $102.1 \pm 0.1$ eV, with a FWHM of about 2.5 eV. These binding

Table 1
Nominal (in equivalent % and in atom %) and measured compositions (in atom %) and of RE–Si–Mg,Al–O–N (RE = La, Lu) glasses

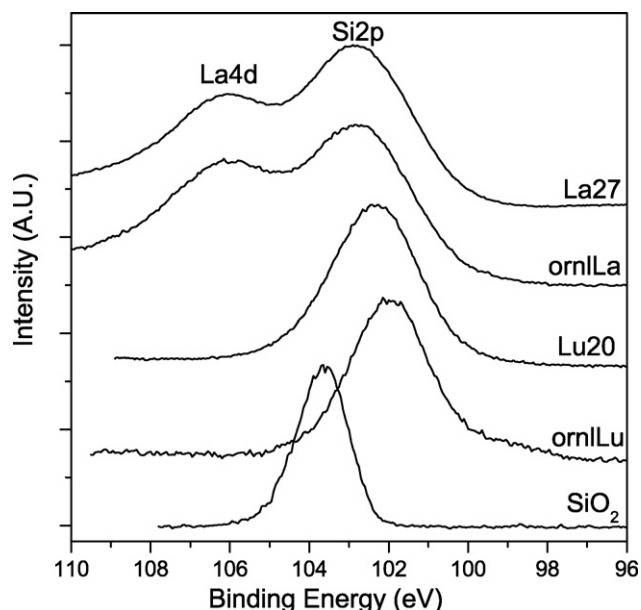| Glass system | Eq% | | | | | (Nominal composition (at%) | | | | | Measured composition (at%) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Si | RE | Mg | O | N | Si | RE | Mg | O | N | Si | RE | Mg | O | N |
| La27 | 60 | 20 | 20 | 73 | 27 | 19.4 | 8.6 | 13.0 | 47.3 | 11.7 | 24.9 | 8.5 | 10.2 | 50.0 | 6.4 |
| Lu20 | 60 | 20 | 20 | 80 | 20 | 19.2 | 8.5 | 12.8 | 51.0 | 8.5 | 26.2 | 6.0 | 10.3 | 52.5 | 5.0 |
| | | | Al | | | | | Al | | | | | Al | | |
| ornlLa | 45 | 30 | 25 | 70 | 30 | 14.3 | 12.7 | 15.9 | 44.4 | 12.7 | 15.6 | 4.1 | 14.3 | 59.8 | 6.2 |
| ornlLu | 45 | 30 | 25 | 70 | 30 | 14.3 | 12.7 | 15.9 | 44.4 | 12.7 | 20.0 | 5.9 | 12.7 | 55.4 | 6.0 |

Measured compositions are determined from XPS.

Fig. 1. Si2p photoelectron lines in La–Si–Mg–O–N (La27), La–Si–Al–O–N (ornlLa), Lu–Si–Mg–O–N (Lu20), Lu–Si–Al–O–N (ornlLu) glasses and in $SiO_2$.



Fig. 2. La3d photoelectron lines in La–Si–Al–O–N (ornlLa) and La–Si–Mg–O–N (La27) glasses.

energy values are lower than in pure $SiO_2$ (103.1 eV), as expected in silicates and glasses.

### 3.3. Photoelectron lineshapes and binding energies of rare earths

#### 3.3.1. Lanthanum

Now we draw our attention to the photoelectron lines characteristic from the rare earths. The La3d photoelectron lines of La–Si–Al–O–N (ornlLa) and La–Si–Mg–O–N (La27) glasses are shown in Fig. 2. They overall display the same features, with a splitting of La3d3/2 and La3d5/2 into two peaks corresponding to the two different final states characteristic of trivalent La.

The shape of the La3d photoelectron line in $La_2O_3$ has been described on the basis of electronic structure calculations by Kotani and Ogasawara [10]: two electronic configurations
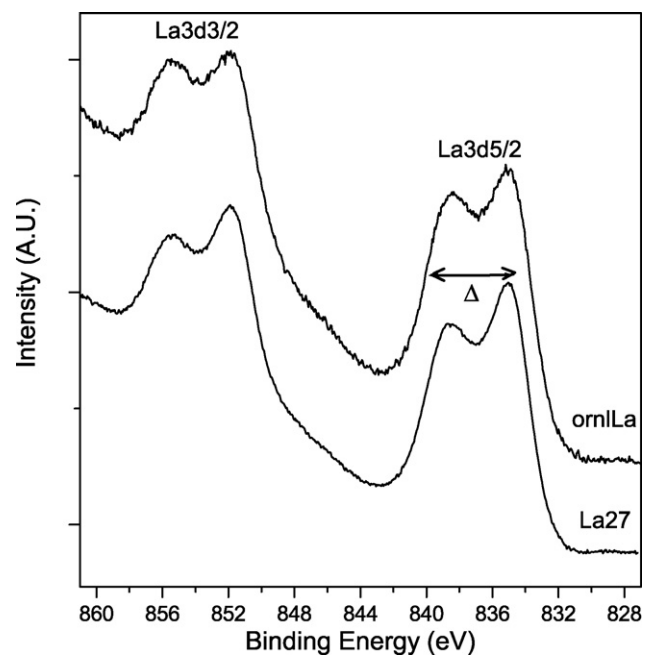
hybridize and as a result there are two final states for each of the La3d3/2 and La3d5/2 components. The binding energy of the La3d5/2 line is 833.5 eV and the two final states are 4.4 eV apart [11]. Measured binding energies of the La3d5/2 photoelectron lines and the energy differences between the two final states ($\Delta$) in our La glass samples are reported in Table 2 along with that of $La_2O_3$ for comparison [11]. The binding energy of the La3d5/2 lines in La glasses is $835.1 \pm 0.1$ eV, so there is a 1.4 eV shift towards higher binding energy in the glasses compared to the pure oxide. In addition the energy differences between the two final states are lower than in $La_2O_3$ (3.6 eV instead of 4.4 eV).

#### 3.3.2. Lutetium

The Lu4d photoelectron lines in Lu–Si–Al–O–N (ornlLu) and Lu–Si–Mg–O–N (Lu20) are shown in Fig. 3. The lineshape

Table 2
Measured binding energies of the Si2p, O1s, La3d5/2 and Lu4d5/2 photoelectron lines in $La_2O_3$, La–Si–Mg–O–N (La27), La–Si–Al–O–N (ornlLa), $SiO_2$, Lu–Si–Mg–O–N (Lu20), Lu–Si–Al–O–N (ornlLu) and $Lu_2O_3$

| Glass | $La_2O_3$ [11] | La–Si–Mg–O–N (La27) | La–Si–Al–O–N (ornlLa) | $SiO_2$ [9] | Lu–Si–Mg–O–N (Lu20) | Lu–Si–Al–O–N (ornlLu) | $Lu_2O_3$ [12] |
|---|---|---|---|---|---|---|---|
| $E_{b(Si2p)}$ | | 102.8 | 102.7 | 103.1 | 102.2 | 102.0 | |
| FWHM | | (.) | (.) | 2.0 | 2.6 | 2.4 | |
| $E_{b(O1s)}$ | 529.1 | 531.5 | 531.3 | 532.7 | 531.1 | 531.0 | 529.0 |
| FWHM | | 3.5 | 3.0 | 2.0 | 2.9 | 2.7 | |
| $E_{b(La3d5/2)}$ | 833.5 | 835.0 | 835.1 | | | | |
| $\Delta$ | 4.4 | 3.6 | 3.6 | | | | |
| $E_{b(Lu4d5/2)}$ | | | | | 197.5 | 197.2 | 194.7 |
| $E_{b(N1s)}$ | | 397.1 | 396.9 | | 397.3 | 396.9 | |
| FWHM | | 2.7 | 2.8 | | 2.5 | 2.5 | |

FWHM is the full width at half maximum of the Si2p and O1s photoelectron lines. $\Delta$ is the energy difference between the two final states of La3d5/2 photoelectron lines. All values are in eV.
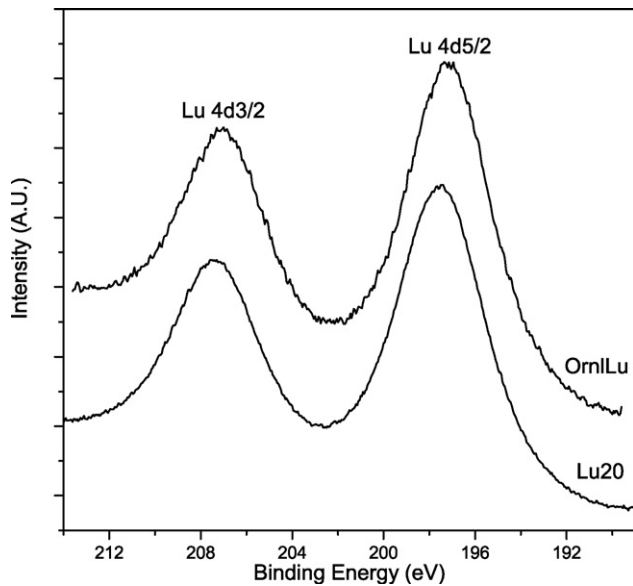
Fig. 3. Lu4d photoelectron lines in Lu–Si–Al–O–N (ornlLu) and Lu–Si–Mg–O–N (Lu20) glasses.
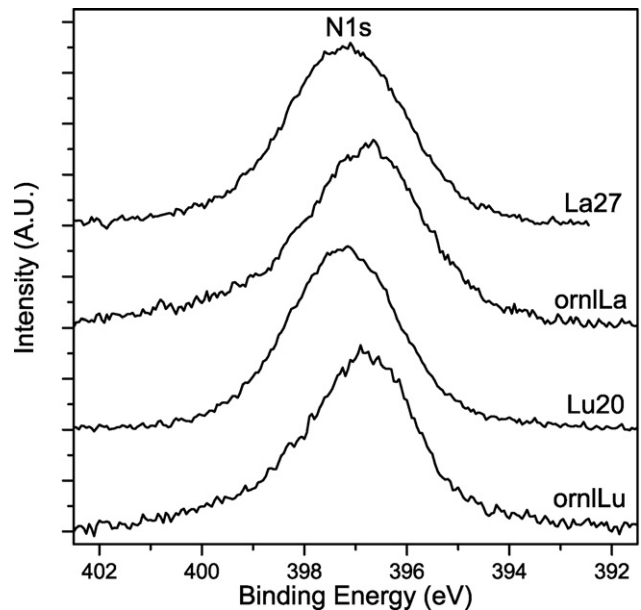


Fig. 4. N1s photoelectron lines in La–Si–Mg–O–N (La27), La–Si–Al–O–N (ornlLa), Lu–Si–Mg–O–N (Lu20) and Lu–Si–Al–O–N (ornlLu) glasses.

is similar for the two samples. Each Lu4d3/2 and Lu4d5/2 is a single peak because trivalent Lu in the ground state has a filled 4f shell with 14 electrons. So no final state effects are expected.

Measured binding energies of the Lu4d5/2 photoelectron line are reported in Table 2 along with that of $Lu_2O_3$ for comparison [12]. The Lu4d5/2 binding energy is $197.3 \pm 0.2$ eV in the Lu glasses and 194.7 eV in $Lu_2O_3$. There is a 2.6 eV shift towards higher binding energy in the glass compared to the pure oxide.

### 3.4. Photoelectron lineshapes and binding energies of nitrogen

The N1s photoelectron lines of the four glass samples are shown in Fig. 4 and measured binding energies are reported in Table 2. The binding energy of the N1s photoelectron line is $397.1 \pm 0.2$ eV whatever the glass may be. This value is very close to 397.4 eV, found for $Si_3N_4$[13].

The N1s binding energy in the Al glasses is slightly larger than the one in the Mg glasses (by 0.2 eV for La, by 0.4 eV for Lu). However no difference in the N1s lineshape could be evidenced as a function of the rare earth.

### 3.5. Photoelectron lineshapes and binding energies of oxygen

Now we focus on the O1s photoelectron lines of the four glasses. Their FWHM, reported in Table 2, are larger than in the simple oxide $SiO_2$. This is due to the fact that there are several oxygen environments in the glasses, oxygen being bonded with different cations.

The O1s photoelectron lines of the RE–Si–Mg–O–N and RE–Si–Al–O–N samples are shown on Figs. 5 and 6 respectively. An asymmetry of the high binding energy side of the O1s photoelectron line is clearly observed for La glasses,

while the lines of Lu glasses are symmetric and narrower, with a FWHM of $2.8 \pm 0.1$ eV.

Then, if we assume that in the Lu glasses the O1s photoelectron line consists of only one component (O1) centered at 531.1 eV, then the O1s photoelectron lines of La glasses do contain another smaller component (O2) at 532.8 eV. The results of decomposition in terms of contribution of O1 type and O2 type oxygen atoms in the different glasses are summarized in Table 3. The decomposition indicates that Lu containing oxynitride glasses mostly consist of O1 type oxygen atoms and the contribution of O2 is very small compared to this.
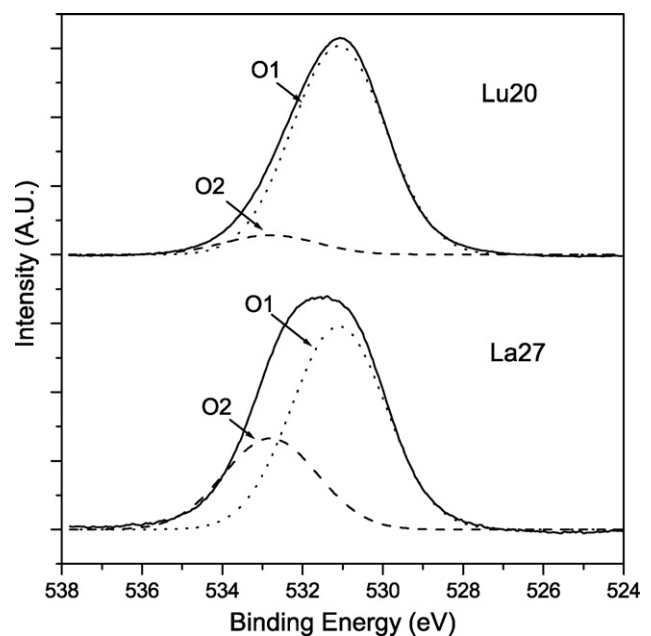


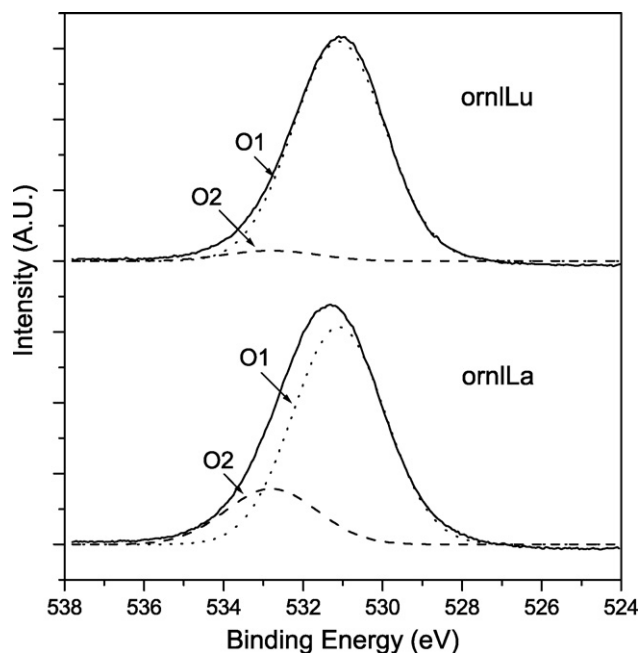Fig. 5. O1s photoelectron lines in Mg glasses: Lu–Si–Mg–O–N (Lu20) and La–Si–Mg–O–N (La27).

Fig. 6. O1s photoelectron lines in Al glasses: Lu–Si–Al–O–N (ornlLu) and La–Si–Al–O–N (ornlLa).

However, for La-containing glasses, the ratio of the O1 oxygen component to the O2 oxygen one is smaller.

## 4. Discussion

### 4.1. Relationship between binding energy and atomic charge for Si and RE

The binding energies of Si2p photoelectron lines in the glass samples are found lower than in $SiO_2$ and the binding energies of RE photoelectron lines are found higher than in $RE_2O_3$ oxides. Such binding energy shifts are common in mixed oxides [14]. Due to the presence of cations like Mg, Lu or La which are less electronegative than Si, there is a charge transfer from these cations towards the silicon atoms via the oxygen and nitrogen atoms. Hence the positive charge on Si will be smaller in the glass than in pure $SiO_2$ and the positive charge on the RE atoms is larger in the glass than in the pure RE oxide. If we make the assumption that the binding energy shifts are driven by the charge transfer, then the decrease of the positive charge on Si atoms will entail a decrease of the binding energy of the Si2p photoelectron line and in the same way the increase of the positive charge on RE atoms will entail an increase of the binding energies of the RE photoelectron line, which is what we get indeed, both for La and Lu.

This explanation can be only qualitative especially for La glasses for which the situation is complicated by the final state effects. However it is striking that as soon as more electronegative elements than La, like Si are involved in the compounds, then there is an overall shift of all the La3d photoelectron lines towards higher binding energies. In addition, the energy separation between the components corresponding to the two final states is lower than in pure $La_2O_3$ oxide. This decrease of the energy separation likely comes from the slight increase of the positive charge on the La atoms in the glass compared to pure $La_2O_3$, which might induce changes in the energy levels, in the hybridization strength, and in the value of the interaction potential between the core hole and the 4f electrons. However it is not possible to go further into a discussion without electronic structure calculations of the La3d shape, as such calculations were reported, to the best of our knowledge, only for pure oxides and not on glasses or complex compounds [10].

### 4.2. Bonding of RE atoms with oxygen and nitrogen

We have decomposed the oxygen 1s line of the four samples into two components, O1 and O2, with a binding energy difference of 1.7 eV. The binding energy of the O1 component is 531.1 eV and is between the values of the O1s lines in rare earth oxides (529.0 eV) and $SiO_2$ (532.7 eV). This contribution can likely be attributed to RE–O–Si or M(Al,Mg)–O–Si environments. The additional peak at 532.8 eV has a binding energy close to that of oxygen in pure $SiO_2$ so the O2 component can be assigned to Si–O–Si bonds.

The attribution of the difference in the O2 component between the La and the Lu glass samples to some additional C–O bond can be discarded. We have checked indeed that the amount of carbon contamination was the same on both La–Si–Mg–O–N (La27) and Lu–Si–Mg–O–N (Lu20), and on both La–Si–Al–O–N (ornlLa) and Lu–Si–Al–O–N (ornlLu) as well. Moreover the shape of the carbone C1s photoelectron line was the same on the four samples, so that the carbon contamination was of the same type. We can therefore deduce that the difference in the O2 component is a genuine effect of the rare earth (La or Lu).

The two types of oxygen environments O1 and O2 can be related to non bridging and bridging oxygens occurring in oxide glasses [15]. The decomposition analysis, reported in Table 3, shows that:

- in both the La and Lu glasses, more oxygen atoms are involved in RE–O–Si bonds (O1 type) than in Si–O–Si bonds (O2 type), whatever M is Al or Mg,
- the ratio O2/O1 is about four times larger in the La glasses than in the Lu glasses, while the RE and M concentrations are very close (Table 1).

We can interpret these changes in the glass structure in the framework of the differential binding energy (DBE) model,

Table 3
Summary of the deconvolution analysis on O1s photoelectron lines

| Glass system | RE–O–Si, M–O–Si (O1) (531.1 eV) | Si–O–Si (O2) (532.8 eV) |
|---|---|---|
| La27 | 70% | 30% |
| ornlLa | 80% | 20% |
| Lu20 | 90% | 10% |
| ornlLu | 95% | 5% |

developed to explain the different grain growth aspect ratios in silicon nitride ceramics with rare earth oxide additions [7]. Rare earth elements in oxynitride glasses have a different local chemistry in O, N environment, and the DBE provides a second-difference measure of relative site stabilities of RE versus Si atoms in regions of variable O/N content. It measures the RE's preference for bonding with O over N compared to that of silicon. Lu has an oxyphilic character and the Lu's preference for bonding with O over N exceeds that of Si, which means that the Lu competes with Si for O-rich environment. On the contrary, the La's preference for bonding with O over N is lower than that of Si. More nitrogen containing units (Si–RE–N) than oxygen containing units (Si–RE–O) are therefore expected to form in the glass with La, than in the glass with Lu with the same amount of nitrogen. In the same way the strongest bonding of La with N might involve a lower proportion of RE–O–Si bonds in La glass, bonding with O turning to the advantage of Si. Due to the oxyphilic character of Lu, the proportion of Si–O–Si bonds is expected to be lower in the Lu glass, which is indeed what we get.

## 5. Conclusion

Two series of oxynitride glasses, RE–Si–M–O–N (M = Mg, Al ; RE = La, Lu), have been studied by XPS. A detailed analysis of the photoelectron lineshapes and binding energies was performed in order to get insight into the bonding in these glasses as a function of the rare earth.

The measured binding energies of Si2p and RE3d lines were compared with those of silicon oxide $SiO_2$ and rare earth oxide $RE_2O_3$ and binding energy shifts were explained by charge transfer effects.

The oxygen 1s photoelectron lineshape reveals a striking difference depending on the rare earth, both in the Mg series and in the Al series. We explain this difference as due to a change in the glass structure, and interpret it in the framework of the differential binding energy model, which measures the RE's preference for bonding with O over N compared to that of silicon. A lower proportion of RE–O–Si bonds is observed in the La glasses, compared to the Lu glasses, while the oxyphilic character of Lu leads to a lower proportion of Si–O–Si bonds in the Lu glasses, compared to the La glasses. This result is an experimental evidence that Lu has a larger affinity for oxygen versus nitrogen than La.

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