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## Spectroscopic analysis of “MgAlON” spinel powders: influence of nitrogen content

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### Abstract

The thermoluminescence (TL) and fluorescence spectra of magnesium aluminium oxynitride “MgAlON” and magnesium aluminate  $\text{MgAl}_2\text{O}_4$  spinel powders have been analysed. Two broad peaks at about 100 and 300 °C appear in the TL spectra of  $\text{MgAl}_2\text{O}_4$  and seem to be related to electron and hole release from  $[\text{Al}_{\text{Mg}}^\vee]$  and  $[\text{Mg}_{\text{Al}}^\cdot]$  traps, respectively. The intensity of each peak strongly depends on the nature of the annealing atmosphere (neutral, oxidizing or reducing). TL spectral analyses have shown the presence of two intense emissions at 520 and 690 nm attributed to the  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  emitting centers, respectively. A study on  $\text{MgAl}_2\text{O}_4$  is used as a reference for MgAlON powders, which can be considered as a solid solution derived from magnesium aluminate. Disturbance in the emission spectrum of  $\text{Cr}^{3+}$  is clearly observed with the nitrogen/oxygen substitution.

### Keywords:

*MgAlON; Thermoluminescence; Fluorescence;  $\text{MgAl}_2\text{O}_4$*

### I. Introduction

A solid solution containing magnesium, aluminium, oxygen and nitrogen elements has been for the first time observed on the SiAlON system [1]. More recently, Sun *et al.* [2] extended the knowledge of the system Mg–Al–O–N. Magnesium aluminium oxynitride can be easily synthesised by solid state reaction between AlN, MgO and  $\alpha\text{-Al}_2\text{O}_3$ , and such a solid solution has been previously obtained by Willems [3] at 1400 °C. Granon *et al.* [4] have given some details on the reactivity in this system. In our case, single MgAlON phase was obtained after an appropriate thermal treatment of these mixed starting powders at 1450 °C for 9 h under static atmosphere of nitrogen (grade U) at 0.1 MPa.

The study of the MgAlON compounds must be completed by the study of  $\text{MgAl}_2\text{O}_4$  and  $\gamma\text{AlON}$  materials, which are the two limits for the MgAlON solid solution.

A commercial  $\text{MgAl}_2\text{O}_4$  powder (%N=0) was selected as a reference material. This powder (labelled S30Cr from Baikowski) obeys the formula  $\text{Mg}_{0.969}\text{Al}_{2.021}\text{O}_4$ , which is very close to the ideal stoichiometric composition. Point defects in  $\text{MgAl}_2\text{O}_4$  have been widely studied [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 and 18] either by thermostimulated methods such as

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thermoluminescence (TL) and thermally stimulated conductivity (TSC) or by spectroscopic techniques such as electronic spin resonance (ESR) and UV fluorescence. No data have been published on MgAlON compounds. As a result, this study is firstly focused on MgAl<sub>2</sub>O<sub>4</sub> in order to disregard the influence of the nitrogen content in the MgAlON derived solid solution. By comparing the results obtained for MgAl<sub>2</sub>O<sub>4</sub> and MgAlON, we will try to understand the evolution of point defects according to the nitrogen content.

γAlON material was also studied. In this material, all the cationic sites of the spinel solid solution are occupied by Al<sup>3+</sup> ions [19]. γAlON compounds are obtained by reaction between AlN and Al<sub>2</sub>O<sub>3</sub> at 1700 °C under static nitrogen (grade U) at atmospheric pressure.

## II. Crystallochemical properties of the spinel structure

One of the particular characteristics of the MgAl<sub>2</sub>O<sub>4</sub> spinel structure (*Fd3m* space group) is the possible existence of a disorder in the cationic lattice. This disorder is due to permutation between some of Mg<sup>2+</sup> cations and some of Al<sup>3+</sup> ions which normally are located in tetrahedral and octahedral sites, respectively. As a result, some divalent Mg<sup>2+</sup> ions are present in sites of octahedral symmetry, whereas some of trivalent Al<sup>3+</sup> ions are in tetrahedral position. The ideal structure, obtained when there is no permutation, is called “normal spinel” and can be observed from natural MgAl<sub>2</sub>O<sub>4</sub> materials [20]. On the other hand, a certain degree of disorder is observed in synthesized samples.

The MgAlON compounds have also the spinel structure. However, during the synthesis process, the introduction of aluminium nitride leads to modifications of the original spinel cell: firstly, the nitrogen element brings a covalent character to the structure which modifies its crystallochemical properties, secondly, the oxygen/nitrogen substitution has also a large impact on cationic and anionic sublattices. We will try to identify and explain the consequences of the anionic substitution by making use of spectroscopic techniques.

## III. Experimental conditions

### III.1. Powders preparation

Three mixed powders, denoted A<sub>0</sub>, B<sub>0</sub>, C<sub>0</sub> with different molecular percentages of starting materials, were prepared as follows (Table 1): a mixture of AlN, MgO and Al<sub>2</sub>O<sub>3</sub> was placed in an azeotropic solvent (slurry contains 60 wt.% of powders) with phosphoric ester and polyvinylpyrrolidone PVP as dispersant agents (respectively 1.1 and 0.9 wt.%). Table 2 gives information about the starting powders, especially impurities. The de-agglomeration was achieved by an ultrasonic treatment of 2 min and the homogenisation of the slurry was then realized on roller bearings during 24 h. The two following steps were a soft drying of the slurry at 80 °C and sieving at 200 μm. Lastly, the preparation of samples was followed by a thermal treatment in a graphite furnace at 1450 °C for 9 h under nitrogen (grade U) static atmosphere (atmospheric pressure). The materials obtained after this treatment are called A, B and C. The concentrations of metal impurities measured in these products are reported in Table 3.

In order to allow the comparison with the other products, the industrial powder S30Cr also underwent a thermal treatment. Temperature and duration of this thermal treatment were similar to those used to synthesize MgAlON compounds (1450 °C–9 h) but four different atmospheres were used: two neutral ones (pure argon and nitrogen) and two reducing ones (pure hydrogen and an argon–hydrogen (10%) mixture). All the gases used were of U grade (<5 ppm O<sub>2</sub> and H<sub>2</sub>O).

### III.2. Thermoluminescence (TL)

A small amount of powder (roughly 3 mg) was deposited on an aluminium cupel by the technique of acetone sedimentation in order to obtain a thin homogeneous layer of powder. Irradiation was performed at room temperature with a UV low pressure mercury lamp working at λ=254 nm (4.89 eV), the excitation duration was 90 s. TL measurements were achieved at a heating rate of 1 °C/s from room temperature up to 500 °C.

Two photomultipliers were used to monitor the TL signal (2018B with S13 photocathode between 200 and 600 nm and XP1017 with S20R photocathode between 300 and 850 nm). Ten minutes were required between the end of irradiation and the TL readout beginning in order to eliminate any phosphorescence signal.

### III.3. TL spectral analysis (OMA)

The TL spectral analysis was performed for powders irradiated during 10 min with a deuterium UV lamp (with a spectral range from 200 to 400 nm). During the heating of the solid, which was realized at a heating rate of 0.5 °C/s, an optical fibre bundle located just above the sample collected the emitted signal and sent it to a spectrophotometer containing CCD sensors. This technique also called “optical multichannel analyser” (OMA), is a powerful tool which allows to obtain the emission spectra at any temperature.

### III.4. Fluorescence

Emission and excitation spectra were obtained, at room temperature, with a 450-W Xenon arc lamp.

### III.5. Fourier-transform infrared spectroscopy (FTIR)

Infrared spectra were recorded at room temperature on a Digilab FTS185 spectrophotometer in the domain 400–4000 cm<sup>-1</sup>. 1 mg of powder was mixed with potassium bromide KBr and then pressed into pellet. The dispersion of KBr is required in order to optimize the resolution of broad peaks.

## IV. Results and discussion

### IV.1. Formulation and XRD measurements

In order to determine their chemical compositions, the four compounds A, B, C, and S30Cr were characterized by Inductively Coupled Plasma/Atomic Emission spectroscopy analysis (ICP–AES) and by X-ray fluorescence. As a result, expanded formulae, lattice parameter measured at room temperature ( $a_{\text{exp}}$ ) and grain size of the four studied compounds are reported in Table 4. The grain size was measured by Scanning Electron Microscopy (SEM) analysis.

The values of the  $a_{\text{exp}}$  parameter are measured ( $\pm 0.0003$  nm) and compared to the  $a_{\text{calc}}$  values obtained from the equation developed in the text (Section IV).

The measured lattice parameters  $a_{\text{exp}}$  were in good agreement with the calculated lattice parameters  $a_{\text{calc}}$  given by the formula proposed by Granon *et al.* [4]:

$$a_{\text{calc}}(\text{nm}) = 0.79 + 0.0375[\text{MgO}] + 0.0150[\text{AlN}]$$

where the [MgO] and [AlN] concentrations are in mol%.

### IV.2. TL results

Figure 1 shows the TL curves obtained for S30Cr powder before and after annealing under different atmospheres. One can notice that the unannealed sample and the annealed one under reducing conditions exhibit no TL signal (Figure 1).

Two intense glow peaks are clearly observed on material obtained after annealing under neutral and oxidizing atmospheres at about 100 and 300 °C. These peaks have been previously observed on different synthesized MgAl<sub>2</sub>O<sub>4</sub> samples [5, 6, 7 and 8]. TL peaks are provoked by detrapping of charge carriers. The TL peak at about 100 °C has been related to electron release from the [AlMg<sup>v</sup>] trap [7 and 8], whereas the other is due to hole release from the [MgAl<sup>v</sup>] trap [7 and 8]. The existence of these two sites is in agreement with the cationic disorder characteristic of the spinel structure [15].

TL spectral analyses of MgAl<sub>2</sub>O<sub>4</sub> materials were performed at a heating rate of 0.5 °C/s. The most intense signal was obtained for sample annealed under nitrogen flow (Figure 2). Two main emission bands were clearly observed at 520 and 700 nm. They appeared at 70 and 230 °C, as indicated in Figure 2. The difference between the temperature of TL peaks (100 and 300 °C) and the temperatures obtained by spectral analysis (70 and 230 °C) is due to the

difference between the heating rates (respectively 1 and 0.5 °C/s). TL spectral emission is related to the recombination of detrapped charge carriers. The emission band centered at 520 nm (2.38 eV) is attributed to divalent manganese ions substituted for magnesium ions in tetrahedral sites [9 and 11]. The second emission is more complex. It is located at about 700 nm (1.77 eV) and presents also an emission line at 690 nm. Such an emission is characteristic of trivalent chromium ions substituted for aluminium cations in octahedral sites [5 and 6]. These results are consistent with ICP–AES analysis which shows the presence of Mn and Cr impurities (Table 3).

The nuclear magnetic resonance measurements (NMR) of  $^{27}\text{Al}$  confirm the presence of an antisite disorder between Mg and Al on initial  $\text{MgAl}_2\text{O}_4$  powder [21]. Thus,  $[\text{Mg}_{\text{Al}}^{\cdot}]$  and  $[\text{Al}_{\text{Mg}}^{\vee}]$  defects exist in this initial powder and probably act as hole and electron traps, respectively. The TL emission can thus be the result of radiative recombination of detrapped charges with impurities such as  $\text{Mn}^{2+}$  and  $\text{Cr}^{3+}$  ions. One can notice that Tijero and Ibarra [9] have shown that the degree of disorder in  $\text{MgAl}_2\text{O}_4$  can be measured from  $\text{Cr}^{3+}$  and  $\text{Mn}^{2+}$  luminescence characteristics. The absence of TL signal for the initial powder is probably due to the small size of grains for this unannealed sample. For  $\text{MgAl}_2\text{O}_4$  powders annealed under reducing atmosphere, it can be assumed that, consecutively to the reducing thermal treatments, manganese and chromium ions, which normally act as radiative recombination centers, or any other chemical impurity, are stabilized in valence states which do not allow any radiative recombination, explaining thus the absence of TL peak. Because it contains a small amount of oxygen ( $[\text{O}_2] < 5$  ppm), the “neutral” gas can have the same effect as oxidizing atmosphere.

TL experimentations have also been carried out on the oxynitrides A, B and C (Figure 3 and Figure 4). These  $\text{MgAlON}$  compounds exhibit a complex TL peak at about 100 °C (for a heating rate of 1 °C/s) which shifts to higher temperature when the nitrogen content increases (from A to C composition). For the sample A (low nitrogen content), the TL peak is relatively well resolved and its position coincides with the first TL peak observed on the  $\text{MgAl}_2\text{O}_4$  sample. By analogy with the features of  $\text{MgAl}_2\text{O}_4$ , we assume that the 100 °C TL peak observed in  $\text{MgAlON}$  could be due to the  $\text{Al}_{\text{Mg}}^{\vee}$  electron traps. The shift of the TL peak can be interpreted as the appearance of a new peak at about 150 °C associated to the enhancement of nitrogen content in the  $\text{MgAlON}$  lattice. The negative charge of anionic site  $\text{N}_{\text{O}}^{\cdot}$  could be responsible for the creation of  $\text{N}_{\text{O}}^{\cdot}$  hole traps in  $\text{MgAlON}$  solid solution.

The TL of A, B and C oxynitride compounds present mainly one large emission band which shifts from 692 to 740 nm with nitrogen content increasing (Figure 4). An emission line at 690 nm is observed only for the A compound. The disappearance of the line at 690 nm and the shifting of the emission band towards high wavelengths could be interpreted as a progressive decrease of the crystalline field around the  $\text{Cr}^{3+}$  site but, unfortunately, this trend is not confirmed by the fluorescence study.

### IV.3. Fluorescence results

The excitation spectrum of the 700 nm emission of  $\text{MgAl}_2\text{O}_4$  presents two maxima at 395 and 547 nm. This result is in agreement with the observations of Tijero and Ibarra [9] and coincides with the positions of excitation bands observed for  $\text{Al}_2\text{O}_3/\text{Cr}^{3+}$  [22]. These excitation bands at 395 and 547 nm are attributed to the  $^4\text{A}_2 \rightarrow ^4\text{T}_1$  and  $^4\text{A}_2 \rightarrow ^4\text{T}_2$  transitions of  $\text{Cr}^{3+}$  ion, respectively. In accordance with these results, the emission spectra of  $\text{Cr}^{3+}$  of these different samples were recorded at room temperature under excitation at 395 nm (Figure 5). Despite the weakness of the signal, two lines at 690 and 695 nm were observed in the emission spectrum of unannealed  $\text{MgAl}_2\text{O}_4$  sample (S30Cr). These lines are labelled 1 and 2, respectively (Figure 5). The meaning of labels 1 and 2 will be justified in the last part of this paper. After annealing at 1450 °C for 9 h under nitrogen flowing atmosphere, the emission spectrum of the reference compound S30Cr was strongly enhanced (Figure 5). One relatively intense line at 690 nm and a group of weaker lines on each side (677–700–709–719 nm) were observed; they are labelled 1. This behaviour is very similar to the one observed by Lapraz *et al.* [22] on single crystals of  $\text{Cr}^{3+}$  doped alumina. A very weak shoulder was also detected at about 695 nm (label 2).

In Figure 6, we have reported the emission spectra of A, B and C oxynitride compounds observed under 395 nm excitation. Some differences appear between the MgAlON solid solution spectrum and the MgAl<sub>2</sub>O<sub>4</sub> one. The emission line 2 (695 nm) is enhanced and dominates in the spectra of A, B and C materials. This emission line increases from A to C compounds, whereas line 1 remains unchanged in intensity. As a result, it appears reasonable to ascribe the increase of line 2 intensity to the increase of the nitrogen content.

A new energy level concept of Cr<sup>3+</sup> in MgAlON solid solution can be proposed:

- ❖ line 1 (690 nm and others) and line 2 (695 nm) are related to the presence of Cr<sup>3+</sup> ions substituted for Al in octahedral coordination; they correspond to <sup>2</sup>E→<sup>4</sup>A<sub>2</sub> transitions of Cr<sup>3+</sup> in two distinct environments [23]. The position of line 1 (690 nm) is not affected by the presence of nitrogen corresponding to transitions in pure CrO<sub>6</sub> site.
- ❖ the intensity of line 2 (695 nm) is perturbed by the oxygen/nitrogen substitution in Al [ON]<sub>6</sub> in deformed octahedral site. This assumption is ascertained by the fact that Cr<sup>3+</sup> ions are very sensitive to the crystalline field and that the O↔N substitution causes a severe anionic distortion of the oxynitride lattice because the ionic radius of nitrogen is about 20% larger than the one of oxygen ion. As a result, the crystal field strength of Cr<sup>3+</sup> site is perturbed by the oxygen/nitrogen substitution and the wavelength of the <sup>2</sup>E→<sup>4</sup>A<sub>2</sub> transition is increased.

#### IV.4. FTIR results

The IR spectrum of MgAl<sub>2</sub>O<sub>4</sub> (Figure 7) revealed two intense broad absorption bands near 700 and 520 cm<sup>-1</sup>. These two bands have been attributed to the stretching vibration of AlO<sub>6</sub> octahedra and MgO<sub>4</sub> tetrahedra, respectively [24]. IR spectra of A, B and C compounds are shown in Figure 8. We note the presence of two broad bands corresponding to the vibration mode mentioned above. The MgO<sub>4</sub> stretching vibration observed with the A, B and C compounds appear at energies slightly higher (about 40 cm<sup>-1</sup>) than in MgAl<sub>2</sub>O<sub>4</sub>. On the other hand, in spite of the appearance of a small shoulder at about 920 cm<sup>-1</sup>, no significant difference occurs between the AlO<sub>6</sub> stretching vibrations. The FTIR spectra of AlON-γ and Al<sub>2</sub>O<sub>3</sub>-γ (Figure 9) confirm that this shoulder is likely correlated to nitrogen presence.

#### V. Conclusion

The study of thermoluminescence and fluorescence characteristics of the spinel compounds of general formula Mg<sub>x</sub>Al<sub>y</sub>O<sub>4-z</sub>N<sub>z</sub> gives prominence to the role of thermoluminescence activator played by Mn<sup>2+</sup> and Cr<sup>3+</sup> ions respectively substituted for Mg (tetrahedral site) and for Al (octahedral site).

The compound MgAl<sub>2</sub>O<sub>4</sub> (z=0) exhibits two TL peaks at about 100 and 300 °C. The first one is related to electrons release from [Al<sub>Mg</sub><sup>0</sup>] traps, whereas the other TL peak is due to holes release from [Mg<sub>Al</sub><sup>+</sup>].

The presence of nitrogen (compounds with z>0) is clearly observed by the disturbance produced in the emission spectrum of Cr<sup>3+</sup> ions. This disturbance is interpreted as a consequence of the deformation of the octahedral site by the replacement of oxygen by some nitrogen in the Cr<sub>Al</sub> site environment.

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## Figures

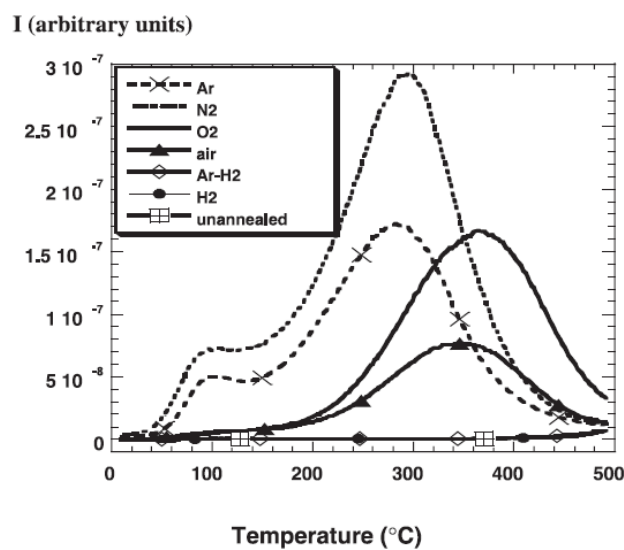


Figure 1: TL curves obtained after UV irradiation at room temperature and readout at  $1^{\circ}\text{C/s}$  on  $\text{MgAl}_2\text{O}_4$  samples: unannealed or annealed under six different atmospheres.

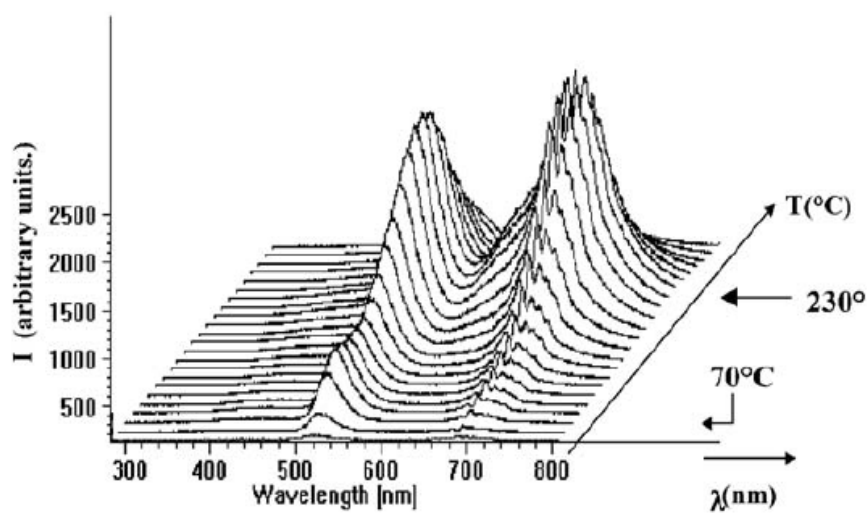


Figure 2: TL spectral analysis of  $\text{MgAl}_2\text{O}_4$  sample annealed under nitrogen flowing atmosphere (heating rate of  $0.5^{\circ}\text{C/s}$ ).



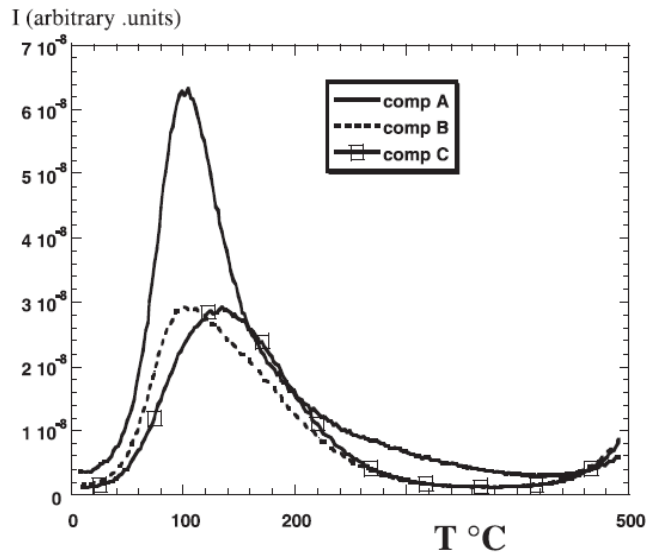


Figure 3: TL curves presented by the MgAlON samples A, B and C after UV irradiation at room temperature and heating rate of 1 °C/s. (These samples are synthesised at 1450 °C–9 h under nitrogen static atmosphere.)

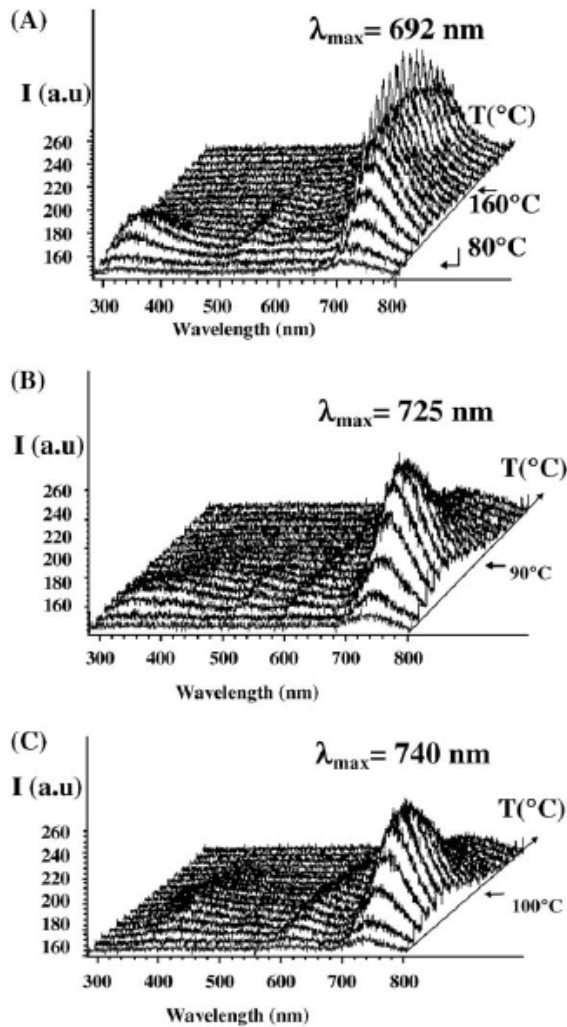


Figure 4: Spectral repartition of the three MgAlON compounds synthesised under nitrogen static atmosphere: A, B, C recorded at 0.5 °C/s (au: arbitrary units).

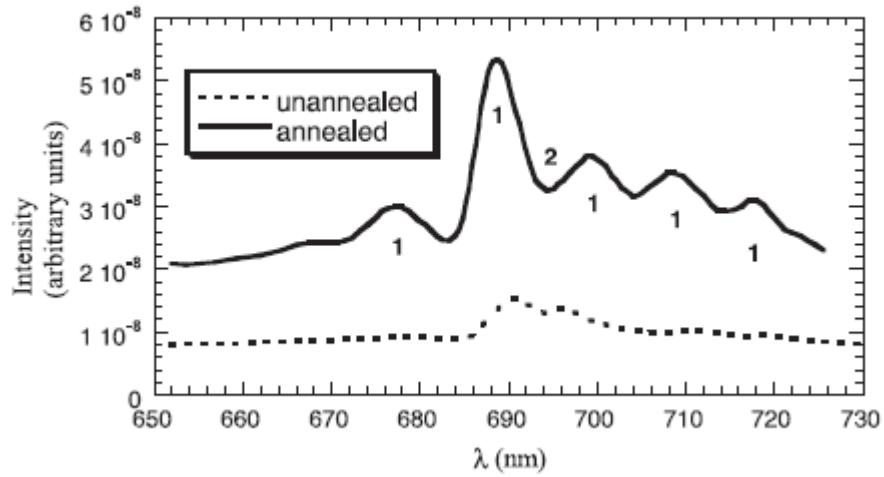


Figure 5: Emission spectra of  $MgAl_2O_4$  obtained at room temperature ( $\lambda_{exc}=395$  nm) before and after neutral annealing.

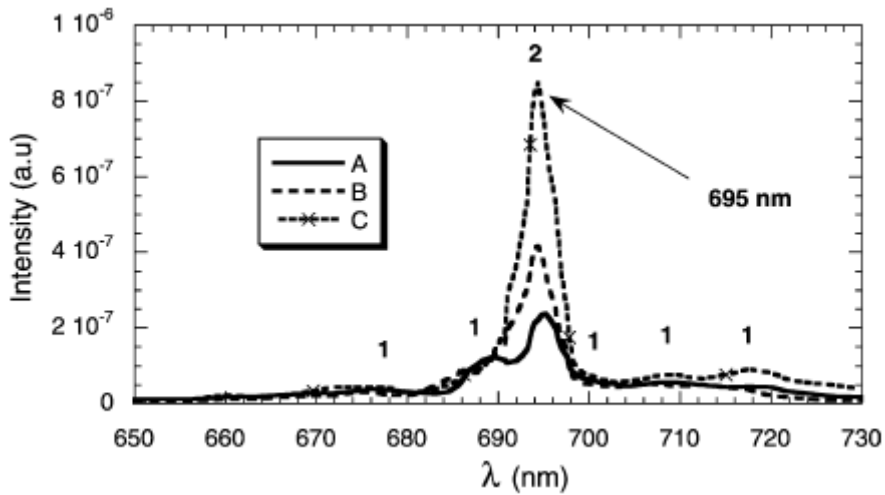


Figure 6: Emission spectra of the  $MgAlON$  compounds obtained at room temperature and irradiated at 395 nm (au: arbitrary units).

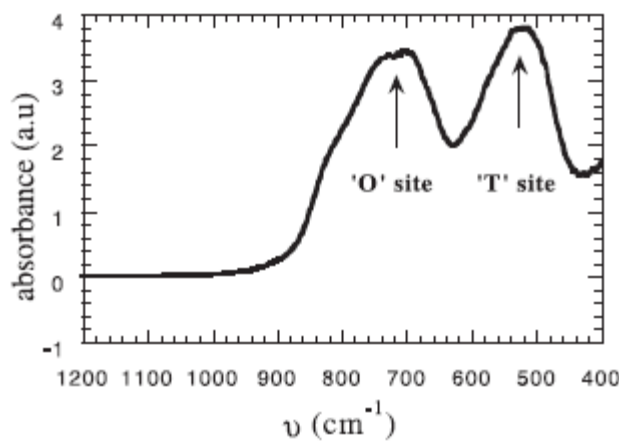


Figure 7: FTIR spectra of  $MgAl_2O_4$  (au: arbitrary units).

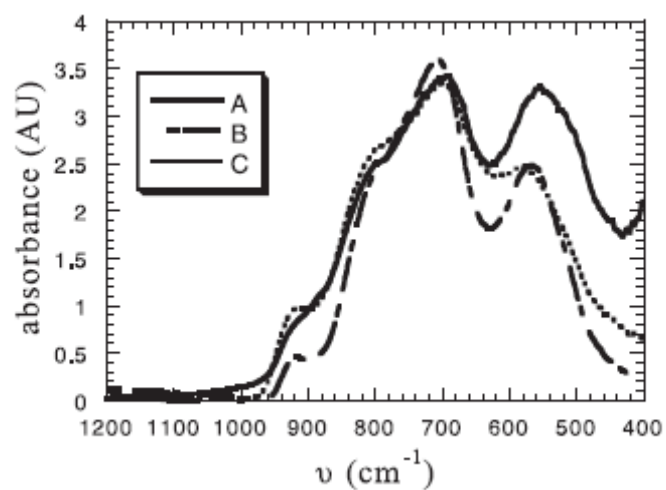


Figure 8: FTIR spectra of A, B, C (au: arbitrary units).

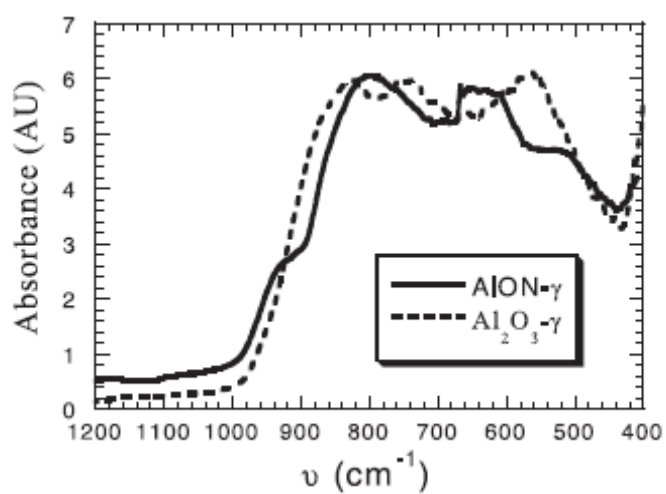


Figure 9: FTIR spectra of AlON- $\gamma$  and Al<sub>2</sub>O<sub>3</sub>- $\gamma$  (au: arbitrary units).

## Tables

Table 1: Starting compositions  $A_0$ ,  $B_0$ , and  $C_0$  before heat treatment

Powders	$Al_2O_3$ (mol%)	$AlN$ (mol %)	$MgO$ (mol %)
$A_0$	57	4	39
$B_0$	57	13	30
$C_0$	57	22	21

Table 2: Characteristics of starting powders

	$AlN$	$Al_2O_3$	$MgO$	$Mg Al_2O_4$
Name	Grade B	Cr6	$M_{30}Cr$	$S_{30}Cr$
Manufacturer	Starck	Baikowski	Baikowski	Baikowski
Specific surface ( $m^2/g$ )	3.2	6.2	25.6	32.5
Mean size ( $\mu m$ ) (Sedigraph)	1.3	0.55	0.30	0.21
Impurities				
N	34%			
O	1.6%			
C	0.07%			
Fe	0.005%	7 ppm		7 ppm
Na		8 ppm		6 ppm
K		15 ppm		23 ppm
Si		34 ppm		12 ppm
Ca		4 ppm		<1 ppm

Table 3: Main impurities detected in the studied samples

	Cr (ppm)	Mn (ppm)	Fe (ppm)	Ti (ppm)
A	43	<10	29	<10
B	42	<10	30	<10
C	42	<10	34	<10
$S_{30}Cr$	38	<10	19	<10

Table 4: Chemical formulations, lattice parameters  $a_o$  and grain sizes of studied compositions A, B, C and S30Cr

Composition	Formulation	$a_{oexp}$ (nm)	$a_{ocal}$ (nm)	Grain Size (nm)
S30Cr	Mg0.969Al2.021O4	0.8089	0.8084	220
A	Mg0.726Al2.222O3.883No.117	0.8044	0.8053	400
B	Mg0.538Al2.419O3.667No.333	0.8026	0.8031	400
C	Mg0.374Al2.551O3.598No.402	0.7993	0.8008	400

The values of the  $a_{oexp}$  parameter are measured (Fo.0003 nm) and compared to the  $a_{ocalc}$  values obtained from the equation developed in the text (Section 4).