

“MgAlON” spinel structure: A new crystallographic model of solid solution as suggested by ^{27}Al solid state NMR

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Abstract

^{27}Al high-resolution magic-angle spinning (MAS) nuclear magnetic resonance (NMR) experiments revealed that “MgAlON” spinel solid solutions have three different aluminium local structural environments. Two of them are characteristic of the MgAl_2O_4 spinel reference structure and involve of aluminium atoms in four- and six-fold oxygen co-ordinations. The presence of the third site is correlated firstly with oxygen/nitrogen substitution on the anionic lattice and secondly with the presence of magnesium in the spinel structure. This specific environment corresponds to a tetragonal site where the aluminium is surrounded by nitrogen atoms exclusively. Consequently, a model of solid solution is proposed for aluminium magnesium oxynitride and the chemical formulation of “MgAlON” samples is deduced.
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1. Introduction

A spinel solid solution derived from MgAl_2O_4 is studied: the magnesium aluminium oxynitride denoted “MgAlON”. This phase was first observed by Jack¹ at 1800 °C in the Mg–Si–Al–O–N system, more recently Sun et al. and Willems extended the knowledge of the system Mg–Al–O–N.^{2,3} Furthermore, the “MgAlON” formation mechanism was investigated by several authors^{4–6} but no specific investigation concerning point defects or local structural and chemical environment has been undertaken about this phase. As a result we suggest, in the present study, a first comprehensive description of the “MgAlON” spinel phase. In particular a schematic crystallographic model of this solid solution with regard to nitrogen content is proposed. This model is the consequence of observations made with the help of ^{27}Al MAS NMR experiments but also results from discussion of a previous study dealing with point defects in the “MgAlON” spinel phase.⁷

In order to understand better, how the local structure of aluminium atoms is arranged in this oxynitride phase, a preliminary study is performed on the reference spinel oxide

MgAl_2O_4 for which the different aluminium co-ordination states are widely referenced.⁸ Appropriate other compounds (considered as structural models) are also characterised by ^{27}Al MAS NMR experiments such as annealed MgAl_2O_4 powders, corundum, γ -AlON and the raw materials, mainly AlN and γ -alumina, which lead after synthesis to the “MgAlON” spinel phase.

The spinel structure is well-known for showing cation mixing between octahedral and tetrahedral sites. MgAl_2O_4 , as many other spinel compounds, exhibits a complex disordering phenomenon characterised by the degree of inversion (or the inversion parameter) i . As a consequence the general chemical formula becomes $[\text{Mg}_{1-i}\text{Al}_i]_{\text{T}}[\text{Mg}_i\text{Al}_{2-i}]_{\text{O}}\text{O}_4$ where $[\dots]_{\text{T}}$ and $[\dots]_{\text{O}}$ represent the tetrahedral T and octahedral O sites, respectively. i is the inversion parameter which specifies the fraction of Al in (T) site; for $i = 0$ the spinel compound is called normal whereas it is called inverse spinel for $i = 1$.

2. Experimental procedure

2.1. Powders preparation

The “MgAlON” powders were prepared by solid reaction between Al_2O_3 , AlN and MgO mixed powders in

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Table 1
Studied compositions

Compound	Formulation	<i>a</i> (measured) (nm)	<i>a</i> (calculated) (nm)
A	Mg _{0.726} Al _{2.222} O _{3.883} N _{0.117}	0.8044	0.8083
B	Mg _{0.538} Al _{2.419} O _{3.667} N _{0.333}	0.8026	0.8031
C	Mg _{0.374} Al _{2.551} O _{3.598} N _{0.402}	0.7993	0.8008

nitrogen atmosphere at 1450 °C during 9 h.⁷ Indeed three single-phase “MgAlON” compositions denoted A, B, C with different nitrogen contents (1.1, 3.2 and 4.1 wt.%, respectively) were synthesised. Their chemical formulations, resulting from ICP-AES analyses, are shown in Table 1, with the lattice parameter measured and calculated according to Granon et al.⁵ This chemical formulation of “MgAlON” is the starting point for the structural investigation of the studied compounds. The final chemical formulation given the ion repartition in the unit cell will be precisely determined and explained thanks to ²⁷Al MAS NMR results.

An aluminium oxynitride spinel compound, denoted γ -AlON, was synthesised under nitrogen static atmosphere by mixing α -Al₂O₃ (66 wt.%) and AlN (33 wt.%) at high temperature. After synthesis, a washing stage in boiling ammoniac (10 N) was conducted in order to eliminate non reacted AlN aggregates. X-ray diffraction pattern confirmed the efficiency of this stage (disappearance of the AlN peaks) which does not affect the chemical structure of the host aluminium oxynitride structure (no lattice parameter variation). Finally, an γ -AlON single phase powder was obtained. After chemical analyses, a 6.5 wt.% nitrogen content value was determined. This spinel compound presents both O and T sites and deviates from γ -Al₂O₃ as a result of the oxygen/nitrogen substitution on the anionic lattice. Therefore, this particular compound has a synthesis route close to the “MgAlON” one, however, its specific crystallographic and thermodynamical properties allow higher nitrogen content incorporation on the anionic lattice. Moreover, whereas Mg and Al cations share both O and T sites in the “MgAlON” structure, in the γ -AlON phase these sites are occupied by Al cations only.

2.2. NMR measurements

High-resolution solid state ²⁷Al MAS NMR experiments were conducted at room temperature with a MSL300 Bruker spectrometer equipped with a wide bore 7 T magnet. At this field ²⁷Al resonance ($I = 5/2$) occurs at 78.2 MHz. Magic-angle spinning (MAS) experiments were realised with a commercial double bearing 4 mm MAS probe allowing a 15 kHz maximum spinning rate. The radio frequency magnetic field strength was 37 kHz. A solid echo pulse sequence $\tau_p - \tau - 2\tau_p$ was used to overcome dead time distortion in the spectra. In order to minimise distortion of the spectra, the first pulse duration τ_p was set to 1.8 μ s which is much smaller than $\tau_{\pi/2}$, to ensure a linear irradiation

regime.⁹ To synchronise data acquisition and sample rotation, the spinning rate was $\nu_r = 14,286$ Hz and then τ was chosen equal to a rotor period (i.e. 70 μ s). A 20 s recycling delay makes it possible to avoid long relaxation time effects. Four thousand sampling points were recorded for a spectrum width of 1.7 MHz. For each spectrum 320 scans were accumulated.

Since ²⁷Al is a quadrupolar nucleus, its MAS NMR spectrum is mainly influenced by the quadrupolar interaction. But in MAS experiments, to a first order, the quadrupolar interaction averages to zero by sample spinning.

The recorded spectra (called CT spectra) will present a numerical value for the chemical shift δ (in ppm) for the central line, with $\delta = (\nu - \nu_0)/\nu_0 \times 10^6$, where ν_0 is the resonance frequency of ²⁷Al in a nitric acid reference; δ depends on the co-ordination number of the Al ions and on the nature of its ligands and contribute to the line position.

3. Results

3.1. [Al]_T and [Al]_O identification in oxides

CT spectra of α - and γ -Al₂O₃ whose crystallographic structures are well-known are shown in Fig. 1a and b, respectively. The corundum phase is an hexagonal structure with exclusively octahedral environments $\langle \text{AlO}_6 \rangle$ for Al atoms in axial symmetry. The CT NMR spectrum contains a single peak located at 8 ppm. This result is in agreement with previous results^{9–11} which associate this line position with an isotropic chemical shift $\delta_{\text{iso}} = 16$ ppm, a quadrupolar frequency $\nu_Q = 357$ kHz and an asymmetry parameter $\eta_Q = 0$. Then the characteristic line positions related to $\langle \text{AlO}_6 \rangle$ environments may be expected to be close to 0 ppm, typically from -20 to 20 ppm according to the strength of the quadrupolar and chemical shift interactions.¹¹ The γ -Al₂O₃ spinel phase spectra show a distribution of Al atoms over two sites: the narrow line at 5 ppm corresponds to octahedral $\langle \text{AlO}_6 \rangle$ sites and the broad one situated at 50 ppm has to be related to tetrahedral $\langle \text{AlO}_4 \rangle$ sites. The $\langle \text{AlO}_4 \rangle$ characteristic CT line positions may be expected at higher values on the chemical shift scale typically 40–80 ppm.¹¹ By spectrum deconvolution, the relative proportions of $\langle \text{AlO}_6 \rangle$ and $\langle \text{AlO}_4 \rangle$ contributions are found to be about 80 and 20%, respectively.

The main conclusion of this first investigation is that in any case the resolution of the MAS NMR spectra in “MgAlON” samples should be sufficient to distinguish these two sites without any ambiguity.

3.2. [Al]_T and [Al]_O identification in MgAl₂O₄

The CT lines in the ²⁷Al MAS NMR spectra for the untreated and heat treated MgAl₂O₄ samples are shown in Fig. 2 (for further comparison, the MgAl₂O₄ powders were

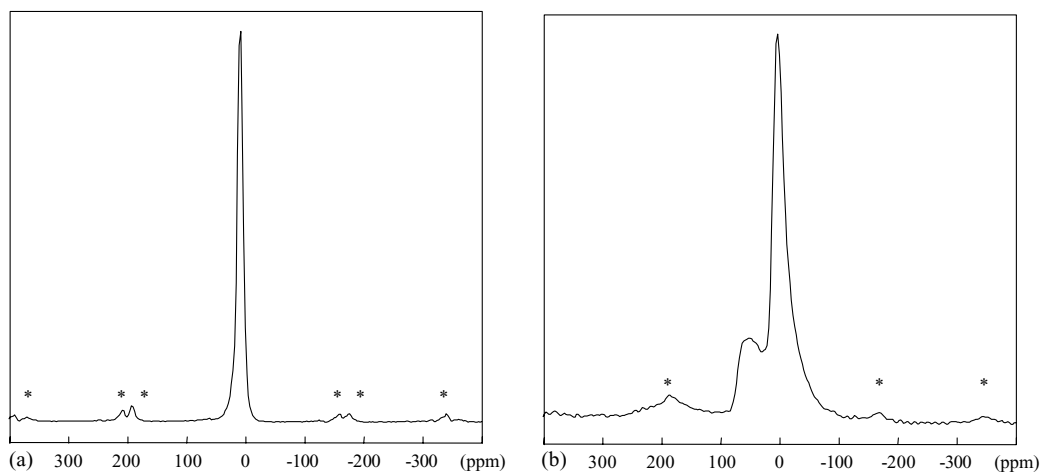


Fig. 1. High resolution ^{27}Al CT MAS NMR spectra of two alumina samples: (a) $\alpha\text{-Al}_2\text{O}_3$; (b) $\gamma\text{-Al}_2\text{O}_3$. The lines labelled as * are spinning side bands of satellite transitions.

annealed at 1450°C during 9 h, like that the “MgAlON” powders). The two spectra show the same trend: a prominent line in the range -20 to 10 ppm corresponding to AlO_6 octahedra and a less intense line in the range 50 – 80 ppm which is characteristic of Al atoms in a tetrahedral environment. The characteristic quadrupolar second order contribution line shapes are broadened due to the statistical distribution of Mg and Al atoms on O and T sites. These spectra are consistent with those observed by previous authors for MgAl_2O_4 .^{11–13}

The intensity of the $[\text{Al}]_{\text{T}}$ peak obviously decreases with the heat treatment. Proportions of the different aluminium sites are obtained by performing a numerical integration of the experimental lines. Aluminium proportions in the O and T sites for synthetic MgAl_2O_4 are summarised in Table 2. This suggests that cation disorder in the MgAl_2O_4 spinel is partially reduced after annealing. One can remark that the natural MgAl_2O_4 spinel is normal but becomes inverse by heating.¹⁴

Table 2

Al atoms repartition rates in MgAl_2O_4 samples

MgAl_2O_4 sample	$[\text{Al}]_{\text{O}}$	δ (ppm)	$[\text{Al}]_{\text{T}}$	δ (ppm)	i (%)
As-received	78	13.7	22	68.5	44
Annealed	88	13.4	12	72.1	24

3.3. Identification of $\langle\text{AlN}_4\rangle$ sites

In order to better understand the role of the nitrogen content on the Al atom occupation rates in the “MgAlON” structure, two compounds AlN and $\gamma\text{-AlON}$ containing nitrogen were analysed in the same way. The wurtzite AlN spectrum shown on Fig. 3a reveals a single peak located at 111 – 113 ppm. This is in agreement with the well-known $P6_3mc$ space group wurtzite structure which involves the $\langle\text{AlN}_4\rangle$ environment exclusively. The ^{27}Al MAS NMR spectrum of the $\gamma\text{-AlON}$ sample is shown in Fig. 3b. After numerical integration 99% of the Al atoms are found to occupy

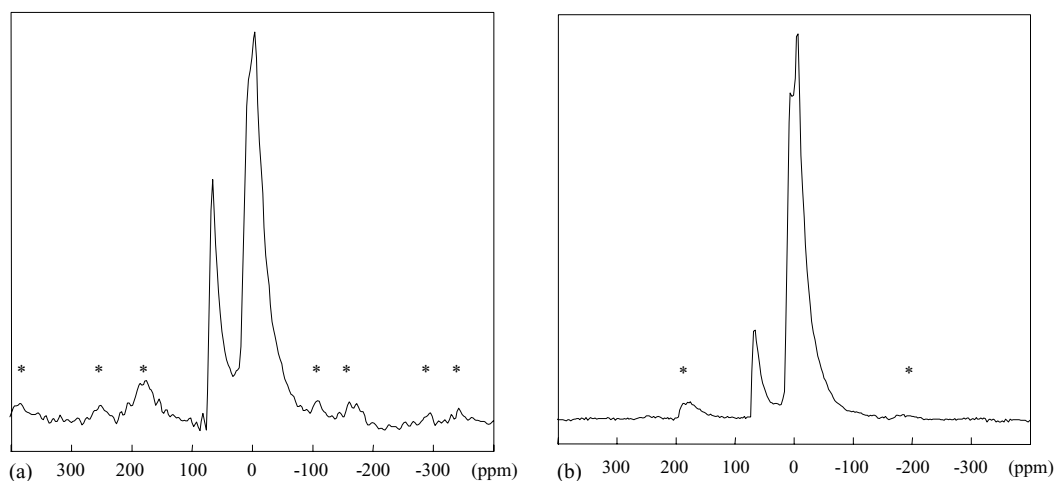


Fig. 2. High resolution ^{27}Al CT MAS NMR spectra of synthetic MgAl_2O_4 spinel: (a) as-received; (b) heat treated at $1450^\circ\text{C}/9\text{h}/\text{N}_2$. The lines labelled as * are spinning side bands of satellite transitions.

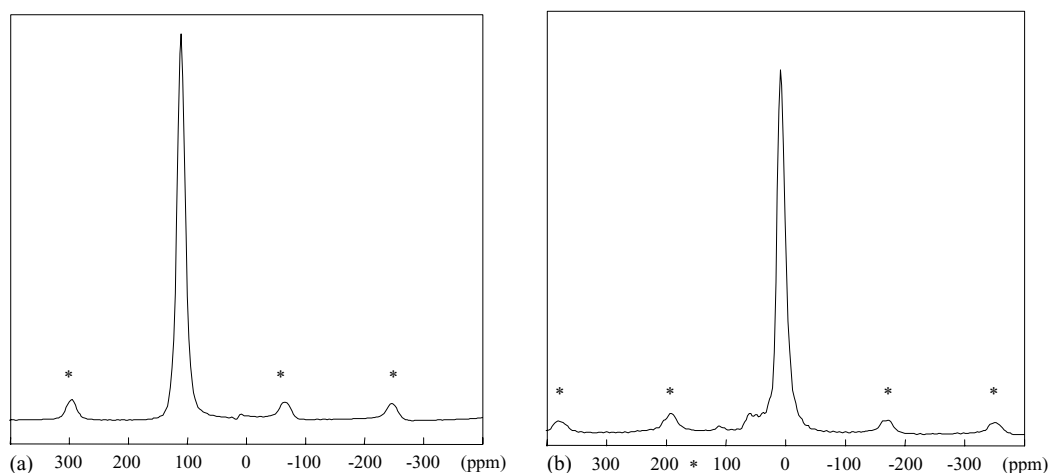


Fig. 3. High resolution ^{27}Al MAS NMR spectra of two alumina samples: (a) AlN; (b) γ -AlON. The lines labelled as * are spinning side bands of satellite transitions.

O and T sites (94 and 5%, respectively), nevertheless the slight peak at 111 ppm is significant and indicates that 1% of the Al atoms are consequently in four-fold nitrogen tetrahedral co-ordination. Then $\langle\text{AlN}_4\rangle$ environments have to be connected with CT lines located around 110 ppm which is much higher on the chemical shift scale than the $\langle\text{AlO}_4\rangle$ and $\langle\text{AlO}_6\rangle$ lines. Furthermore, it may be noted that the $\langle\text{AlN}_4\rangle$ environment percentage is rather low even in such a rich-nitrogen content sample.

3.4. “MgAlON” compounds

MgAlON solid solutions have a crystallographic structure which deviates from that of the original spinel crystal MgAl_2O_4 by nitrogen/oxygen substitution on the anionic lattice. The $Fd\bar{3}m$ space group is preserved on average but specific points defects directly due to the nitrogen presence were found.⁷

The ^{27}Al MAS NMR spectra for the three “MgAlON” compounds as synthesised are shown in Fig. 4. As expected two intense peaks characteristic of MgAl_2O_4 samples are clearly observed; this indicates that a large amount of Al atoms are located in the four-fold and six-fold oxygen co-ordinations labelled $\langle\text{AlO}_4\rangle$ and $\langle\text{AlO}_6\rangle$. On the one hand, the chemical shifts of ^{27}Al nuclei in O and T sites do not seem to be strongly affected by the nitrogen presence in the “MgAlON” structure. However, a peak asymmetry which is characteristic of quadrupolar line shapes in disordered systems^{9,15} becomes visible. This might be due to an enhanced distortion of the octahedral and tetrahedral environments by the nitrogen/oxygen substitution. This has also been suggested to explain the shift of the excitation band observed for $\text{AlO}_6/\text{Cr}^{3+}$ in “MgAlON”.⁷ On the other hand, the spectra of the “MgAlON” samples reveal the presence of a third peak located in the range of 105–115 ppm. This line position is in the range of that measured in the AlN

Table 3

Al atoms repartition rates in “MgAlON” samples

MgAlON samples	[Al] _O	[Al] _T	Other site (%)	δ (ppm)
A	86	13	1	112.7
B	84	12.5	3.5	108.6
C	84	9.5	6.5	108.6

and AlON samples. Therefore, a clear connection between the unidentified site in the “MgAlON” structure and that of the $\langle\text{AlN}_4\rangle$ environment can be put forward: the aluminium ions can have a local environment constituted of nitrogen anions as nearest neighbours in “MgAlON” single phase compounds. The related line could be fitted with a Gaussian line shape and its intensity was found to increase with the nitrogen content in the structure. The aluminium atom proportions attributed to the third sites are summarised in Table 3. It appears that the introduction of nitrogen stabilises the quantity of occupied octahedral sites. As a result, the tetrahedral occupation rate decreases, whereas the intensity of the third peak increases with nitrogen content. A slight change in the line position of this peak is also observed.

The $\langle\text{AlN}_4\rangle$ proportion in the low-nitrogen content “MgAlON” compounds is surprisingly larger than (or at least equal to) the one observed in γ -AlON which is a rich nitrogen sample. This suggests that the $\langle\text{AlN}_4\rangle$ environment is specific to the “MgAlON” structure.

4. Discussion

4.1. Enhancement of $\langle\text{AlN}_4\rangle$ sites in “MgAlON”

The amount of $\langle\text{AlN}_4\rangle$ sites in “MgAlON” is greater than in γ -AlON. This result can be justified if the “MgAlON” synthesis route is clarified. During the heat treatment a large

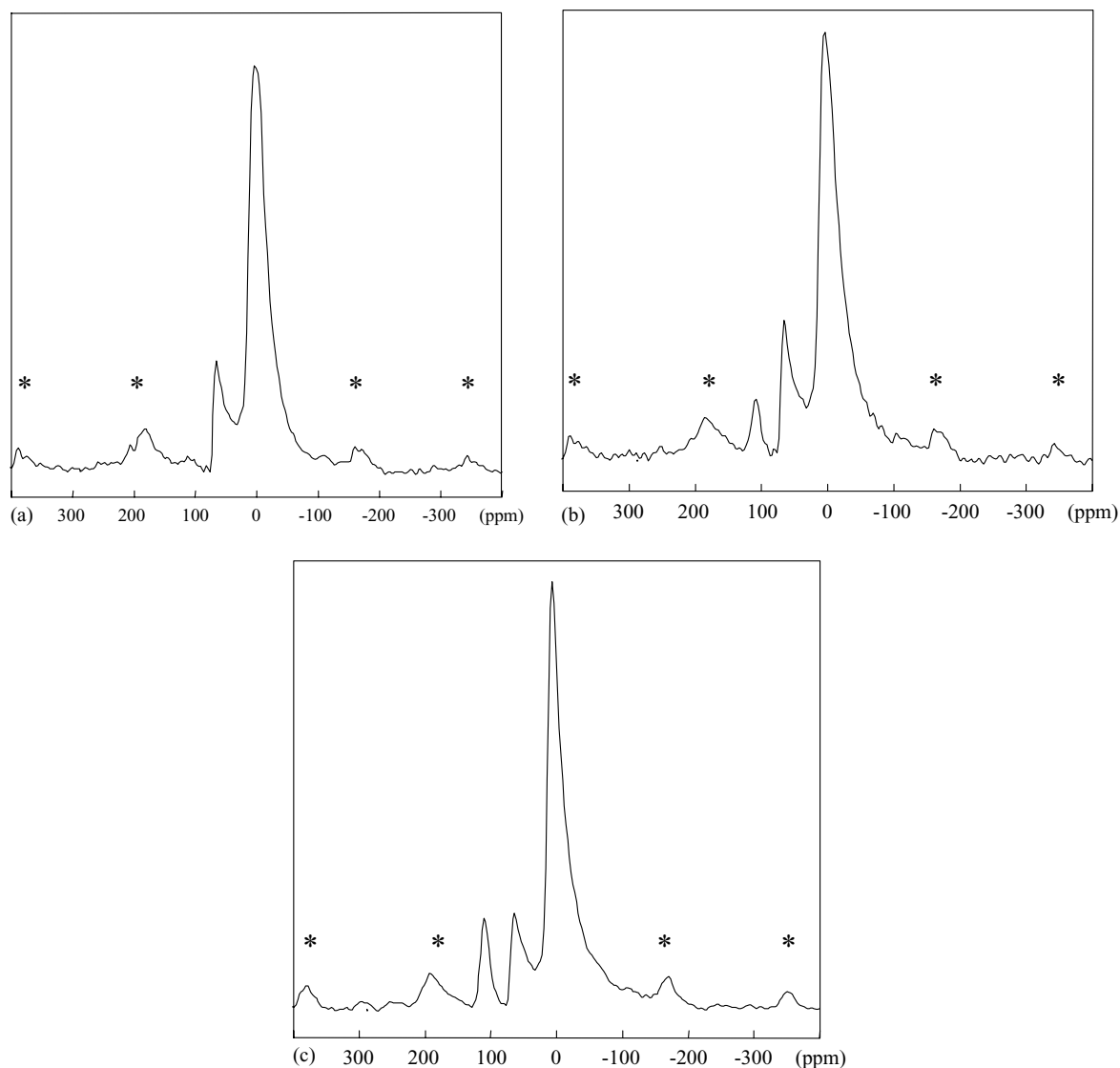


Fig. 4. High resolution ^{27}Al CT MAS NMR spectra of “MgAlON” samples: (a) A composition; (b) B composition; (c) C composition. The lines labelled as * are spinning side bands of satellite transitions.

reactivity between AlN and MgO, leading to the formation of MgAl_2O_4 and Mg_3N_2 volatile species⁵ has been put forward. In order to minimise this parasite reaction, a stabilising powder bed made of AlN and MgO (50:50 wt.%) must be placed around the crucible in which the raw materials react. Nevertheless, nearest neighbour coexistence of Mg and N atoms in “MgAlON” solid solution seems to be hardly plausible. As a consequence, the concept of a minimum distance between magnesium and nitrogen is established to avoid gaseous Mg_3N_2 formation. Since nitrogen promotes four-fold co-ordination, $\langle\text{AlN}_4\rangle$ environments become realistic. Nitrogen atoms are not homogeneously distributed in this solid solution, but are on the contrary locally grouped as cluster zones. Finally, according to the NMR measurements and synthesis route considerations we can confidently assert that the $\langle\text{AlN}_4\rangle$ environment is specific to “MgAlON” solid solutions.







4.2. New chemical formulation of “MgAlON”

According to chemical analyses (Table 1) and NMR results (Tables 2 and 3), a new chemical formulation of “MgAlON” samples is proposed in Table 4, based on the

Table 4
New chemical formulation of studied composition (according to Kröger writing)

A	$[\text{0.689Mg}_{\text{Mg}}\text{0.289Al}_{\text{Mg}}\text{0.022Al}_{\text{Mg}}]_{\text{T}}\{1.911\text{Al}_{\text{Al}}\text{0.037Mg}'_{\text{Al}}\text{0.052V}'''_{\text{Al}}\}_{\text{O}}\text{3.883O}_\text{O}\text{0.117N}'_{\text{O}}$
B	$[\text{0.538Mg}_{\text{Mg}}\text{0.302Al}_{\text{Mg}}\text{0.085Al}_{\text{Mg}}\text{0.075V}'_{\text{Mg}}]_{\text{T}}\{2\text{Al}_{\text{Al}}\text{0.032Al}'_i\}_{\text{O}}\text{3.667O}_\text{O}\text{0.333N}'_{\text{O}}$
C	$[\text{0.348Mg}_{\text{Mg}}\text{0.246Al}_{\text{Mg}}\text{0.167Al}_{\text{Mg}}\text{0.240V}'_{\text{Mg}}]_{\text{T}}\{2\text{Al}_{\text{Al}}\text{0.162Al}'_i\}_{\text{O}}\text{3.582O}_\text{O}\text{0.418N}'_{\text{O}}$
MgAl_2O_4	$[\text{0.55Mg}_{\text{Mg}}\text{0.45Al}_{\text{Mg}}]_{\text{T}}\{1.58\text{Al}_{\text{Al}}\text{0.42Mg}'_{\text{Al}}\text{0.01V}'''_{\text{Al}}\}_{\text{O}}\text{4O}_\text{O}$

Table 5
Symbolic representation of ionic species in “MgAlON” samples

					
O ²⁻ anion	N ³⁻ anion	Mg ²⁺ cation	Al ³⁺ cation	Al ³⁺ interstitial	Al ³⁺ vacancy

following rules:

- The spinel structure ($Fd3m$) $A^{II}B^{III}O_4$ is preserved such that A and B atoms occupy 1/8 tetrahedral T sites and 1/2 octahedral O sites, respectively.
- All anionic sites are occupied by oxygen or nitrogen ($O_{4-x}N_x$).
- Electric charge neutrality must be satisfied (each species being considered to have its ionic charge).

Thus, the presence of vacancies has to be taken into account:

- cationic vacancies (V_{Al}''') in O site for A and $MgAl_2O_4$ samples;
- cationic vacancies (V_{Mg}'') in T site for B and C samples;
- aluminium interstitials ($Al_i^{••}$) for B and C samples.

In the “MgAlON” unit cell, according to NMR results, the Al ions in the $\langle T \rangle$, noted Al_{Mg} site, can be in a $\langle O_{4-x}N_x \rangle$ (with $x = \{0-3\}$) surrounding or in the $\langle N_4 \rangle$ one given, respectively, the 70 and 110 ppm peaks in NMR. The rate of $\langle Al_{Mg}N_4 \rangle$ in the crystal structure is given from the intensity of the 110 ppm peak in the CT spectra (0.022, 0.085, 0.167 for the A, B, C samples, respectively).

So, $\langle AlN_4 \rangle$ clusters generate a local excess of negative charge which should be compensated by aluminium interstitials (Table 4). With an increasing nitrogen content, the magnesium atoms are more and more localised in T four-fold oxygen co-ordination and their presence in O sites is unlikely, as described in oxynitride glasses and crystallised $MgSiN_2$.¹⁶ As a result, the existence of the trapping centre Mg'_{Al} (a Mg^{2+} cation occupying a O site) is reduced. This hypothesis is supported by the small amount of Mg'_{Al} determined for the A sample and the absence of these centres in the B and C ones (cf. Table 4).

Moreover, a previous thermoluminescent study has put forward the fact that point defects are closely dependent on the nitrogen content of “MgAlON” synthesised powders.⁷ Two main results were shown:

- A progressive evolution of a high temperature TL peak is observed: a small shoulder at 250 °C for A slightly disappears for the B to C samples; this peak was attributed to a Mg'_{Al} hole trapping centre whose evolution is consistent with previously described chemical formulations.
- Optical multi-channel analysis revealed a broad minor emission around 320 nm exclusively for the A sample.

This was previously observed by Springis¹⁷ who attributed these emission to anionic vacancies centres (denoted F centres) which associated Mg'_{Al} hole traps to form F_{Mg} centres ($V^{\bullet\bullet} + Mg'_{Al}$) and which emit at 305 nm.

The hole trapping centres Mg'_{Al} only observed for the A sample support the existence of F_{Mg} emitting centres. B and C samples have no emission relative to F_{Mg} centres which is consistent with the absence of the Mg'_{Al} entity within their chemical formulation. We assume that these results relative to point defects in “MgAlON” powders are well-correlated with the new chemical formulation resulting from the NMR experiments.

In conclusion, a schematic crystallographic model of a solid solution which takes into account the NMR results and a chemical formulation for each studied compounds are proposed. All the species concerned in the chemical formulation (cations, anions, vacancies) are symbolised with a specific symbol (Table 5). Each reported size is proportional to the ionic radius related to the concerned entity.

The Fig. 5 shows the arrangement of the atoms in a low-nitrogen “MgAlON” sample (A compound case). Among the different elementary cells, thick ones illustrate the specific modification due to the nitrogen incorporation in this structure: a cationic disorder arrangement (Al and Mg atoms, respectively, in T and O sites), the presence of an aluminium vacancy and a random distribution of nitrogen atoms are shown.

For higher nitrogen contents (Fig. 6), the “MgAlON” solid solution evolves towards segregated $\langle AlN_4 \rangle$ clusters; excess of negative charges is locally compensated by Al interstitials. As mentioned by the chemical formu-

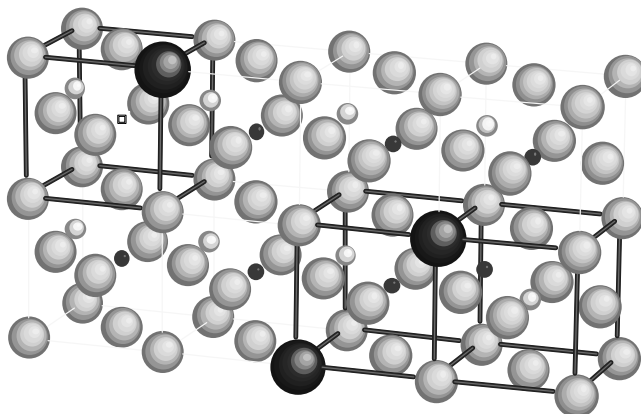


Fig. 5. Solid solution model for low nitrogen content in MgAlON.

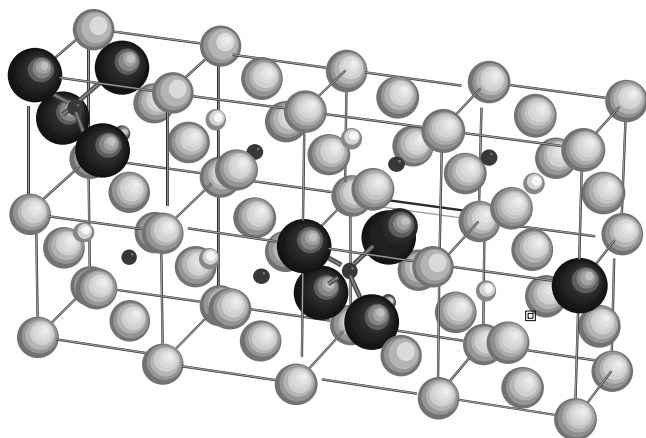


Fig. 6. Solid solution model for high nitrogen content in MgAlON.

lation of the C compound (Table 4), no Mg'_{Al} entity is observed.

5. Conclusion

A new crystallographic model of a “MgAlON” solid solution has been proposed taking into account ^{27}Al MAS NMR experiments. We have shown that an increasing nitrogen concentration is a factor promoting the appearance and growth of a specific site. This environment is related to an aluminium atom in four-fold nitrogen co-ordination. We suggest that the localisation of nitrogen into this structure is not random but can be directly linked to the incompatibility of nitrogen and magnesium as local neighbour since the formation of volatile Mg_3N_2 is observed during the synthesis. Consequently, these two elements require a minimum separation from each other and the concept of AlN_4 clusters is then proposed that implies cationic interstitials for electroneutrality reasons. This crystallographic model of “MgAlON” spinel solid solution validates a previous study dealing with spectroscopic experiments where point defects have been clearly identified.

The well-known mechanism of cation exchange between O and T sites in spinel compounds has been also investigated by ^{27}Al MAS NMR spectroscopy in the “MgAlON” solid solution: point defects such as Al'_{Mg} and Mg'_{Al} must be taken into account. This resulting degree of inversion has been estimated firstly to be less than that of a synthesised $MgAl_2O_4$ reference and secondly to be independent of the increasing nitrogen content which emphasises Al in O sites. This trend is confirmed by the disappearance of the Mg'_{Al} entities with increasing nitrogen content.

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