

Spectroscopic study of ordering in non- stoichiometric magnesium aluminate spinel

- Revision 1

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Abstract

FTIR and RAMAN spectroscopic methods were used to study the ordering of non-stoichiometric nano-magnesium aluminate spinels ($\text{MgO}_n\text{Al}_2\text{O}_3$, $0.4 < n < 12$) synthesized using a combustion synthesis method. It was established that the degree of structural disorder (i.e. the inversion parameter, i) can be quantified using the intensities of the γ_1 and γ_3 IR modes or 670 and 723 cm^{-1} Raman shifts. The results indicated that the as-synthesized materials were heavily disordered and obey earlier conclusions that the defect chemistry of non-stoichiometric spinels is dominated by clusters formed from anti-site defects. Analysis of the temperature dependency of cation distribution in the Mg- and Al-rich samples showed that the spinel phase moved toward equilibrium upon increases in temperature. Where decomposition occurred, the disordered level decreased at temperatures up to 1000°C. Above this temperature, the order level dropped far below the expected equilibrium value and the γ_3 mode (a mode that is characterized for ordered structures, such as a natural spinel) that appears. These findings, together with Raman results of partly decomposed Al-rich samples, support the hypothesis that a MgAl_2O_4 - γ - $\text{Al}_{8/3}\square_{1/3}\text{O}_4$ solid solution comprises of series of complex micro-phases with considerable short-range order.

Keywords: FTIR, Inversion parameter, Magnesium aluminate spinel, Raman

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Introduction

Magnesium aluminate spinel is an interesting material from both the fundamental and the applied perspectives. In the MgO-Al₂O₃ system, only one stable intermediate phase, magnesium aluminate spinel (MgAl₂O₄), exists (Hallstedt 1992). At temperatures above 1300 K, the spinel phase can exhibit considerable non-stoichiometry. The high temperature spinel phase field is not symmetric in terms of stoichiometric ratio, accommodating a greater degree of Al₂O₃ excess than of MgO (Hallstedt 1992). This spinel solid solution can be viewed as one between MgAl₂O₄ and a defect spinel Al_{8/3}□_{1/3}O₄ related to γ -alumina.

The spinel structure with the general formula AB₂O₄ presents an almost-perfect cubic close-packed anion-oxygen arrangement in which the cations A and B reside on tetrahedral and octahedral interstices, respectively. The unit cell is obtained by doubling the approximately face-centered cubic oxygen sub-lattice along each of three directions. In the normal MgAl₂O₄ spinel structure, Mg²⁺ ions occupy eight tetrahedral or A sites (out of 64 in a unit cell), while Al³⁺ ions occupy 16 octahedral or B sites (out of 32 in a unit cell) (Bragg 1915; Nishikawa 1915). In stoichiometric spinel (i.e. MgAl₂O₄), the main intrinsic defects correspond to anti-site pairs where Mg²⁺ and Al³⁺ ions exchange sites. A measure of the degree of cation disorder is provided by the inversion parameter, *i*, defined as (Mg_{1-*i*}Al_{*i*})[Mg_{*i*}Al_{2-*i*}]O₄, where the curved brackets refer to the tetrahedral sites and the square brackets to the octahedral sites. In other words, *i* represents the fraction of tetrahedral sites occupied by trivalent cations. The inversion parameters are 0,

2/3 and 1 for normal, statistically random and inverse spinels, respectively (Bragg 1915; Nishikawa 1915). It was previously established that the energy associated with the anti-site defects is an order of magnitude lower than for those related to other intrinsic defect processes and that the anti-site disorder dominated the defect chemistry of this system (Nishikawa 1915). As such, cation anti-site defects play a central role in the accommodation of non-stoichiometry. These charged defects are compensated for by other oppositely charged point defects but not the opposite cation of the anti-site pair, as this would not lead to changes in stoichiometry. In particular, spinel crystals with a Al_2O_3 excess are characterized by $\text{Al}_{\text{Mg}}^{\bullet}$ defects (Ball et al. 2008; Sickafus et al. 1996), which can be charge-compensated by $\text{O}_i^{\prime\prime}$, $\text{V}_{\text{Mg}}^{\prime\prime}$ or $\text{V}_{\text{Al}}^{\prime\prime\prime}$ defects. MgO-rich spinel crystals incorporate Mg'_{Al} defects (Hinklin and Laine 2007) that can be charge-compensated by $\text{V}_\text{O}^{\bullet}$, $\text{Mg}_i^{\bullet\bullet}$ or $\text{Al}_i^{\bullet\bullet\bullet}$. Jagodzinski and Saalfeld (1958) suggested that non-stoichiometry in an Al_2O_3 rich system is characterized by an increased concentration of cation vacancy. Murphy et al. (2010) studied the defect chemistry accommodating non-stoichiometry in the $\text{MgO}n\text{Al}_2\text{O}_3$ spinel system using empirical and quantum mechanical (density functional theory) atomistic simulation methods. The authors concluded that the defect chemistry of the non-stoichiometric spinel is dominated by defect clusters from anti-site defects and other point defects that preserve overall charge neutrality. While these results support the prediction of Jagodzinski and Saalfeld (1958), no clear preference for $\text{V}_{\text{Al}}^{\prime\prime\prime}$ over $\text{V}_{\text{Mg}}^{\prime\prime}$ was established. The MgO-rich system is characterized by an increased concentration of defect clusters involving either $\text{V}_\text{O}^{\bullet\bullet}$ or $\text{Mg}_i^{\bullet\bullet}$ defects and at higher deviations from stoichiometry, these represent charge neutral $\{\text{Mg}_i^{\bullet\bullet}:2\text{Mg}'_{\text{Al}}\}^\times$ and $\{\text{V}_\text{O}^{\bullet\bullet}:2\text{Mg}'_{\text{Al}}\}^\times$ defect clusters. It was suggested that the lower incorporation energy per

excess Al^{3+} ion, as compared to Mg^{2+} ions, explains why the spinel lattice accommodates a greater degree of Al_2O_3 than MgO excess (Hallstedt 1992).

The lattice vibrations in the $\text{MgO}n\text{Al}_2\text{O}_3$ spinel system have been well studied and reported in the literature (White and DeAngelis 1967; Preudhomme and Tarte 1971; O'horo et al. 1973; Gillot 1994; Fabian et al. 2001; Ptáček et al. 2011). From group theory, a perfectly ordered MgAl_2O_4 spinel should have four IR active modes, designated as γ_1 at 714 cm^{-1} , γ_2 at 555 cm^{-1} , γ_3 at 588 cm^{-1} and γ_4 at 303 cm^{-1} (White and DeAngelis 1967; O'horo et al. 1973). According to Preudhomme and Tarte (1971), modes γ_1 and γ_2 are assigning to vibrations of the trivalent cation (Al^{3+}) located in the octahedral sites and are practically independent of the bivalent cation (Mg^{2+}). The other two modes, γ_3 and γ_4 , are affected by the bivalent cation, with γ_4 being solely affected by the Mg-O vibration. γ_3 is more complex and is affected by both the octahedral and the tetrahedral vibrations. FTIR measurements of synthetic spinels showed that modes γ_1 and γ_2 shifted to lower wave numbers (688 and 522 cm^{-1} , respectively), while mode γ_4 remained essentially constant (Preudhomme and Tarte 1971). It should be noted that the γ_3 mode is absent in synthetic spinels, whereas in natural spinels, it is present (Fabian et al. 2001). Such behavior may be related to cation distribution within the spinel structure. Natural spinels are considered as presenting an almost perfect ordered structure, where the Mg^{2+} and Al^{3+} ions are located solely at the tetrahedral and octahedral sites, respectively, and the inversion parameter is close to zero. The formation of anti-site defects (inversion parameter > 0.1) and fading of the γ_3 mode are observed during the annealing of natural spinels. Therefore, it was suggested that the absences of γ_3 in synthetic spinels could be related to disorder appearance in the spinel structure (Fabian et al. 2001). Finally, two

additional resonance modes at about 825 cm^{-1} (γ_2) and 910 cm^{-1} (γ_6) became visible in partially inverse spinels (Fabian et al. 2001; Ptáček et al. 2011). These modes are related to Al^{3+} ions occupying tetrahedral voids and are independent of Mg-O vibrations.

Recently, it was established that a non-stoichiometric nano-magnesium aluminate spinel can be synthesized using the solution combustion method (Ianoş et al. 2008). In the present work, we describe a systematic FTIR spectroscopy study of the defective structure of stoichiometric and non-stoichiometric nano-magnesium aluminate spinels synthesized by this method.

Experimental procedure

$\text{MgO}_n\text{Al}_2\text{O}_3$ nanoparticles with $0.4 < n < 12$ were synthesized by the solution combustion method (Ianoş et al. 2008). Nitrate water solutions with different molar ratio (Table 1) were obtained by mixing $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in deionized water. To obtain a three-dimensional polymer network with high viscosity, ethylene glycol and citric acid were mixed at a molar ratio of 1 to 2 and added to the nitrate water solution. A homogeneous solution was obtained upon mixing by magnetic stirring. The mixed nitrate-citrate complex solution was evaporated at 150°C under agitation by magnetic stirring until a highly viscous foam-like colloid was formed. This colloid was heated to 900°C at a rate of $10^\circ\text{C}/\text{min}$ and a soaking time of 96 h to obtain the final material. The as-synthesized samples were annealed at temperatures of $900\text{--}1400^\circ\text{C}$ for 12 h and cooled to room temperature with the furnace. X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku RINT 2100 (Tokyo, Japan) diffractometer with $\text{Cu K}\alpha$ radiation. The operating parameters were 40 kV and 40 mA, with a 2θ step

size of 0.02° . Si (NIST SRM 640c) served as internal standard for cell parameter determination. The powders were studied by atomic absorption spectroscopy (AAS) and were shown to have compositions in good agreement with those expected (Table 1).

IR spectra were recorded at room temperature using a Bruker Model Equinox model 55/S FTIR spectrometer with a DTGS detector in the range spanning $400\text{-}4000\text{ cm}^{-1}$. A spectrum was taken as the average of 128 scans; spectral resolution was 4 cm^{-1} . Spectra were minimum/maximum-normalized after baseline correction by the rubber band method. Peak positions were determined by OPUS software using the second derivation method. Micro-Raman spectra of the samples were recorded at room temperature using a Jobin Yvon Horibra LABRAM-HR 800 spectrometer with Argon 514 nm excitation. The laser power on the sample was about 5 mW. Back-scattering geometry was used. The measurements were taken with a 600 g mm^{-1} grating and a confocal microscope with a $100\text{ }\mu\text{m}$ aperture.

Results

XRD measurements

Figure 1 shows the XRD patterns of as-synthesized and annealed at 1400°C powders. The broad peaks are indicative of the fine grain size ($\langle D \rangle \sim 10\text{-}15\text{ nm}$) of the samples (Fig. 1a), with the exception of the MgAl_2O_4 sample which displayed a grain size of about 60 nm. The peaks observed in the spectra reveal that for powders with $0.95 < n < 1.2$, only the spinel phase exists. For samples with $n < 0.95$, both MgO and $\text{MgO}n\text{Al}_2\text{O}_3$ spinel phases are present. The cell parameters and crystallite sizes of the as-synthesized samples are provided in Table 1. The annealed samples with $0.95 < n < 1.07$ remained as a solid solution (Fig. 1b) up to 1400°C , while in the case of samples with

$n > 1.07$, precipitation of α - Al_2O_3 started to appear at 1000°C , in accordance with Hallstedt (1992).

FTIR measurements

FTIR spectra of as-synthesized stoichiometric spinels are shown in Fig. 2. Four main modes (γ_2 , γ_1 , γ_5 and γ_6) at about 523, 692, 828 and 910 cm^{-1} were detected (Table 2). FTIR spectra of as-synthesized non-stoichiometric samples are shown in Fig. 3. It can be seen that for the Al_2O_3 excess samples ($n > 1$), the intensity of γ_5 and γ_6 increased and the position of γ_2 mode was shifted to lower wave numbers, relative to the same mode in the stoichiometric sample (Table 2). MgO excess samples displayed similar behavior but the increased intensities of γ_5 and γ_6 were less pronounced and the shift in the γ_2 mode was more pronounced. FTIR spectra of samples annealed at different temperatures with $0.95 < n < 1.07$ displayed similar features to those of the as-synthesized samples. Nevertheless, the intensities of γ_5 and γ_6 were seen to decrease with increasing temperatures and γ_2 shifted back to the stoichiometric value (around 523 cm^{-1}) (Fig. 4, Table 2). In accordance with the XRD results, the FTIR spectra of samples with $n > 1.07$ demonstrated the presence of only $\text{MgO}_n\text{Al}_2\text{O}_3$ solid solution up to 1000°C (Fig. 4). Above this temperature, peaks related to α -alumina also appeared, in addition to those reflecting spinel modes. Interestingly, a new IR mode, γ_3 at about 570 cm^{-1} was revealed (Fig. 5a). The picture became even clearer after removing the contribution of α -alumina from the annealed $\text{MgO}_{2.47}\text{Al}_2\text{O}_3$ sample (Fig. 5b). This mode was also seen upon decomposition of the spinel with $n = 11.45$ and a composition close to that of γ -alumina (Fig. 5c).

Raman measurements

A typical micro-Raman spectrum for an as-synthesized $\text{MgO}1.07\text{Al}_2\text{O}_3$ sample is presented in Fig. 6. The peaks near 670 cm^{-1} and 723 cm^{-1} are associated with Al^{3+} ions found in AlO_6 octahedral and AlO_4 tetrahedral sites, respectively (Rousseau et al. 1981). It was noted that the Raman spectra of all as-synthesized samples displayed similar peaks. Nevertheless, the intensities of the peaks (670 cm^{-1} and 723 cm^{-1}) changed upon deviation from spinel stoichiometry (Fig. 7, Table 3). Interestingly, $\text{MgO}1.75\text{Al}_2\text{O}_3$ samples after annealing at 1400°C displayed two types of Raman spectra. Some collected spectra consisted only of Raman modes related to $\text{MgO}n\text{Al}_2\text{O}_3$ solid solution, while others also displayed modes related to $\alpha\text{-Al}_2\text{O}_3$ (Fig. 8, Table 3). These results may originate from the poor averaging of the micro-Raman method, while the FTIR method used here offers better averaging of the sample volume. Nevertheless, the Raman shift and intensities observed for annealed $\text{MgO}1.75\text{Al}_2\text{O}_3$ were found to differ. The reasons for this are discussed below, in the section entitled “*Temperature-dependence of cation distribution*”.

Discussion

Phase stability in the $\text{MgO}n\text{Al}_2\text{O}_3$ system

Shou–Yong et al. (2000) suggested an additive relation for determining the cell parameter of $\text{MgO}n\text{Al}_2\text{O}_3$ solid solution from the cell parameter of MgAl_2O_4 and $\gamma\text{-Al}_2\text{O}_3$:

$$a_{\text{MgO} \cdot n\text{Al}_2\text{O}_3} = \frac{a_{\text{MgAl}_2\text{O}_4} + 0.75(n-1)a_{\gamma\text{-Al}_2\text{O}_3}}{1 + 0.75(n-1)} \quad 1$$

A calculated curve using $a_{\text{MgAl}_2\text{O}_4} = 8.0833\text{ \AA}$ and $a_{\gamma\text{-Al}_2\text{O}_3} = 7.9050\text{ \AA}$, together with the lattice parameter, as determined by the XRD, as function of n (i.e. total alumina content)

is plotted in Fig. 9. The lattice parameter of $\text{MgO}n\text{Al}_2\text{O}_3$ solid solution with $n=1$ (i.e. the stoichiometric spinel, MgAl_2O_4) is 8.0833 Å. As the amount of alumina in the solid solution increases to $n>1$, the lattice constant decreases and approaches the lattice parameter of a pure γ -alumina, 7.9050 Å. This observation is consistent with other works in this field (Navrotsky et al. 1986; Yoo et al. 1991; Shou-Yong et al. 2000) (Fig. 9). For MgO-rich solid solution spinels, the lattice parameter increases to $n\sim 0.95$. At $n<0.95$, no more solid solution exists. Instead, spinel and MgO co-exist, and the lattice parameter of the $\text{MgO}n\text{Al}_2\text{O}_3$ solid solution is close to that of stoichiometric spinels. Nevertheless, there are some works that showed considerably higher solubility of MgO in $\text{MgO}n\text{Al}_2\text{O}_3$ spinels (Alper et al. 1962; Sarjeant and Roy 1967; Yoo et al. 1991). Sarjeant and Rustum (1967) showed that upon conducting splat-quenching of melts, the $\text{MgO}n\text{Al}_2\text{O}_3$ system can accommodate up to 32 at% ($n\sim 0.6$) excess magnesia. Alper et al. (1962), using induction heating of pressed pellet specimens at 1975°C for 2 h followed by water quenching at room temperature, measured levels up to 11 at% ($n\sim 0.82$) excess magnesia. Yoo et al. (1991), relying on a co-perception method, achieved 16 at% ($n\sim 0.76$) magnesia enrichment before decomposition into two phases. The apparent discrepancies between the previous works and the present study may be attributed to the different sample preparation methods employed. Yet, the agreement between the theoretical curve and the experimental data confirms that as-synthesized nano- $\text{MgO}n\text{Al}_2\text{O}_3$ samples with $0.95<n<12$ are an extended solid solution of MgAl_2O_4 and γ -alumina. As mentioned above, cation disorder plays a central role in the accommodation of non-stoichiometry. While order/disorder phenomena in crystalline materials are usually studied using the XRD method, the $\text{MgO}n\text{Al}_2\text{O}_3$ system is not amenable to this method because the X-ray

scattering factors of Mg^{2+} and Al^{3+} ions are too similar to reveal site-occupancy distinctions (Sheldon et al. 1999). Thus, spectroscopic methods related to lattice vibrations may be used as a complementary method to study cation distribution and defective structures in the magnesium aluminate spinel.

Cation distribution

The obtained FTIR spectra of the as-synthesized nano- $MgOnAl_2O_3$ spinels (Fig. 2) are in agreement with previous results on $MgOnAl_2O_3$ spinel single crystals (Fabian et al. 2001). According to Fig. 2, the as-synthesized samples displayed a high degree of structural disorder, as indicated from modes γ_3 and γ_5 that became stronger with departure from stoichiometry and the absence of mode γ_1 . The degree of structural disorder, reflecting occupation of tetrahedral sites by Al^{3+} ions (i.e. the inversion parameter, i), can be quantified by quantifying the intensities of the γ_3 and γ_5 modes using the following relation:

$$i = \frac{I_{\gamma_5}}{I_{\gamma_1} + I_{\gamma_5}} \quad 2$$

The inversion parameters calculated by this formula are presented in Table 4. The inversion parameters of the as-synthesized $MgOnAl_2O_3$ solid solution spinels ($0.95 < n < 2.47$) as a function of alumina mole fraction are plotted in Fig 10. Even though the as-synthesized $MgAl_2O_4$ spinel has the lower i value (0.27), it still considerably disordered, as compared to the natural spinel (Fabian et al. 2001). The strong deviation of the i value from all other measured might be related to differences in grain size. The $MgAl_2O_4$ sample had grain sizes of about 60 nm in comparison to sizes of about 12 nm seen in the rest of the samples. The level of inversion strongly affected by the grain size

of the powders. This point is elaborated below (“*Temperature-dependence of cation distribution*”). The inversion parameter is determined by the number of tetrahedral sites occupied by the Al^{3+} ions. Therefore, this value should increase when the Al/Mg-ratio increases and decrease when this ratio decreases. However, the present results show that i is high even for the MgO excess spinels, as compared to stoichiometric spinels (Table 4). These results support earlier conclusions (Murphy et al. 2010) that the defect chemistry of non-stoichiometric spinels is dominated by clusters formed from anti-site defects.

The shift of the γ_2 mode in the non-stoichiometric samples to lower wave numbers, relative to such values in the stoichiometry spinel, is also of note (Table 4). As mentioned above, the γ_1 and γ_2 modes are only associated with cations located in the octahedral sites and are not affected by cations in the tetrahedral sites (Preudhomme and Tarte 1971). In addition, the absence of mode γ_3 , expected to be around 588 cm^{-1} , in as-synthesized spinels is due to diverse cation distribution. Specifically, considerable amounts of bivalent cations are located in octahedral sites. Thus, we suggest that the shift in mode γ_2 is due to the presences of Mg^{2+} ions in the octahedral sites.

Temperature-dependence of cation distribution

According to the XRD and FTIR results, only samples with $0.95 < n < 1.07$ consist solely of a solid solution up to $1400 \text{ }^\circ\text{C}$. Temperature-dependence of the inversion parameter is portrayed in Fig. 11. From these data, it can be seen that the degree of inversion of MgAl_2O_4 decreased from about 0.27 as-synthesized to 0.22 upon annealing at 1400°C . In other words, the annealed spinel became more ordered. The non-stoichiometric samples displayed different behavior. The degree of inversion of a Mg-rich sample

(MgO0.95Al₂O₃) decreased from about 0.39 as-synthesized to 0.28 upon annealing at 1300°C and then increased to 0.31 upon annealing at 1400 °C. The Al-rich sample (MgO1.07Al₂O₃) displayed similar tendencies, with a minimum inversion being measured after annealing at 1200 °C, followed by increases in the degree of inversion as annealing temperatures rose to 1300 °C. Above this temperature, no further disorder was observed in this sample.

The temperature-dependence of cation ordering in synthetic and natural MgAl₂O₄ spinels has been considerably investigated over the years, with different thermodynamic and kinetic models being proposed (Brun and Hafner 1962; Schmocker and Waldner 1976; Navrotsky et al. 1986; Wood, et al. 1986; Redfern et al. 1999). O'Neill and Navrotsky (1983) suggested the thermodynamic model $\left[\alpha + 2\beta i + RT \ln \left(\frac{i^2}{(1-i)(2-i)} \right) = 0 \right]$ for describing the temperature-dependence of cation distribution in a spinel. The inversion parameter as a function of the annealing temperature, together with predictions of the O'Neill and Navrotsky model for MgAl₂O₄ and slightly non-stoichiometric MgAl_{2.01}O₄ spinels using the parameters of Redfern et al. (1999) ($\alpha = 32.8 \pm 0.9$, $\beta = 4.7 \pm 2.0$ kJ/mole and $\alpha = 25.7 \pm 1.4$, $\beta = 11.4 \pm 2.8$ kJ/mole, respectively), are presented in Fig.11. In the present study, we were unable to directly fit the obtained data to any of the thermodynamic models, as the samples were naturally cooled and not quenched. Nevertheless, it can be seen that the as-synthesized samples differ from thermodynamic equilibrium solid solution spinels yet present behavior similar to that of quenched materials that are heated slowly to high temperatures (Harrison and Purnis 1996; Redfern et al. 1999). Thus, the as-synthesized samples obtained using the solution combustion method were found to be not in thermodynamic equilibrium, with the deficiency or

excess of Mg in the structure increasing the degree of inversion, as was previously predicted (Murphy et al. 2010).

The as-synthesized $\text{MgOnAl}_2\text{O}_3$ spinels with $n > 1.07$ decomposed into two phases, $\text{MgOnAl}_2\text{O}_3$ solid solution and $\alpha\text{-Al}_2\text{O}_3$, above 1000 °C. It was observed that the inversion parameter of $\text{MgO}2.47\text{Al}_2\text{O}_3$ decreased toward equilibrium at temperatures up to 1000 °C. Above this temperature, the inversion parameter dropped far below the expected equilibrium value and γ_3 mode appeared (Fig. 5 and Fig. 11).

These findings, which to the best of our knowledge have never been reported before, shed light on the structure of $\text{MgOnAl}_2\text{O}_3$ solid solution and the $\alpha\text{-Al}_2\text{O}_3$ precipitation mechanism. Based on their thermodynamic data, Navrotsky et al. (1986) suggested that the $\text{MgOnAl}_2\text{O}_3$ solid solution is not a "simple" $\text{MgAl}_2\text{O}_4\text{-}\gamma\text{-Al}_2\text{O}_3$ solid solution but rather constitutes a series of complex micro-phases with considerable short-range order. Gobbi et al. (1984) suggested that the Mg ions are preferentially located in octahedral sites in Al-rich spinels. Jagodzinski and Saalfeld (1958) proposed that Al-rich spinels are characterized by an increased concentration of cation vacancies, an idea that was supported by theoretical calculations (Murphy et al. 2010). The decrease in the inversion value of the as-synthesized disorder at temperatures up to 1000 °C (Fig. 11) indicates that the materials start to relax toward equilibrium by returning Al^{3+} ions to octahedral sites. The unchanged position of mode γ_2 (Table 2), which is assumed to be partly related to the occupation of octahedral sites by Mg^{2+} ions, suggests that the Mg ions are less mobile at this point and remain in the octahedral sites. Above 1000 °C, more Al^{3+} ions move back to the equilibrium octahedral sites and Mg ions, which are more mobile at higher temperatures, simultaneously move back to equilibrium tetrahedral sites.

As a result of these processes, the amount of anti-site defects and concentration of cation vacancies decreases and some microphases grow as more ordered $\text{MgO}_n\text{Al}_2\text{O}_3$ spinels, while others which are now mainly composed of Al (γ - Al_2O_3) start to precipitate as α - Al_2O_3 . This mechanism is supported by the strong drop in the inversion parameter and the presence of the γ_3 mode, indicative of an ordered structure where most of the Al and Mg ions are in their equilibrium sites.

The Raman results support the FTIR analysis. The inversion parameters for the as-synthesized samples and those annealed at 1400 °C were calculated with Eq. 1 using Raman modes 670 and 723 cm^{-1} related to AlO_4 and AlO_6 , respectively, and plotted in Fig. 12. The difference in inversion parameter values, as compared to the FTIR analysis, may originate from the poor averaging of the micro-Raman method (see section “*Raman measurements*”, above). The two types of spectra obtained from the annealed $\text{MgO}_{1.15}\text{Al}_2\text{O}_3$ sample give different inversion parameters and confirm that particles that do not fully decompose present higher degrees of disorder ($i=0.17$), as compared to particles that fully decompose ($i=0.12$).

Implications

The level of the structural disorder (i.e. the inversion parameter, i) in a spinel system is of great importance for understanding phase stability and behavior. In this study, we used FTIR/Raman spectroscopic methods to assess levels of structural order in nano-magnesium aluminate spinels spanning a large range of homogeneity. The presence of IR mode γ_3 in decomposed Al-rich spinels was detected for the first time. According to Fabian et al. (2001), this mode is characteristic of an ordered structure (e.g., natural

spinel) where almost no Mg cations are located in octahedral sites. Moreover, the inversion parameter drops far below the expected equilibrium value in such cases (O'Neill and Navrotsky 1983; Redfern et al. 1999). Based on these results and the Raman findings, we were able to confirm the hypothesis of Navrotsky et al. (1986) predicting that the $\text{MgO}n\text{Al}_2\text{O}_3$ solid solution is comprised of a series of complex micro-phases with considerable short-range order.

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Tables:

Table 1. Analytical data and lattice parameters of as-synthesized and annealed samples.

<i>n</i>		0.41	0.65	0.95	0.98	1.00	1.07	1.15	2.47	11.45	
Analysis (per 4 oxygen)	Mg	1.81	1.36	1.04	1.02	1.00	0.95	0.90	0.48	0.11	
	Al	1.46	1.76	1.97	1.99	2.00	2.03	2.07	2.35	2.59	
<i>a</i> , Å	Mg _{0n} Al ₂ O ₃	900 °C	8.0799(48)	8.0803(4)	8.0891(19)	8.0873(7)	8.0833(10)	8.0785(17)	8.0651(57)	7.9897(39)	7.9252(55)
		1200 °C	-----	-----	-----	-----	-----	-----	-----	8.0762(2)	-----
		1300 °C	-----	-----	8.0834(2)	8.0827(1)	-----	-----	-----	-----	-----
		1400 °C	8.0831(1)	8.0819(1)	8.0834(2)	8.0835(1)	8.0831(2)	8.0658(1)	8.0611(1)	8.05857(1)	8.0774(2)
	MgO	4.2139(4)	4.2130(6)	-----	-----	-----	-----	-----	-----	-----	-----
	Al ₂ O ₃	-----	-----	-----	-----	-----	-----	-----	4.7619(2)	4.7620(2)	4.7618(1)

Table 2. Positions and intensities (in parentheses) of FTIR modes in as-synthesized (900 °C) and annealed (1000-1400 °C) samples.

IR mode	Annealing <i>n</i>	0.41	0.65	0.95	0.98	1.00	1.07	1.15	2.47
γ ₆	900 °C	-----	908.5 (0.23)	909.8 (0.49)	911.1 (0.46)	910.3 (0.13)	911.7 (0.42)	911.6 (0.66)	917.7 (1.63)
	1000 °C	-----	-----	910.2 (0.42)	-----	911.8 (0.13)	913.3(0.28)	-----	923.1(1.02)
γ ₅	900 °C	836.1 (0.55)	824.8 (0.80)	826.0 (1.14)	831.7 (0.99)	827.9 (0.69)	827.0 (1.07)	826.5 (1.11)	830.8 (1.56)
	1000 °C	-----	-----	832.0 (1.03)	-----	828.3 (0.63)	820.6 (0.90)	-----	812.0(1.13)
	1200 °C	-----	-----	827.1 (0.82)	-----	-----	829.5(0.77)	-----	827.1(0.54)
	1300 °C	-----	-----	829.8 (0.76)	-----	-----	828.9 (0.93)	-----	-----
γ ₁	1400 °C	826.1 (0.36)	826.2 (0.54)	826.3 (0.69)	828.0 (0.76)	824.9 (0.55)	825.3 (0.80)	822.5 (0.60)	826.4 (0.35)
	900 °C	690.1 (1.34)	692.0 (1.63)	689.0 (1.82)	688.3 (1.74)	692.0 (1.87)	691.3 (1.84)	688.7 (2.00)	691.5 (1.90)
	1000 °C	-----	-----	681.8 (2.00)	-----	692.9 (1.72)	686.0 (1.73)	-----	681.4(1.93)
	1200 °C	-----	-----	694.4 (2.00)	-----	-----	687.5 (1.96)	-----	686.7(1.975)
	1300 °C	-----	-----	687.4 (2.00)	-----	-----	686.6 (1.99)	-----	-----
γ ₂	1400 °C	697.9 (1.69)	689.7 (2.00)	693.8 (2.00)	694.5 (2.00)	693.0 (1.93)	689.7 (2.00)	685.3 (2.00)	683.2 (2.00)
	900 °C	505.6 (2.00)	509.9 (2.00)	502.5 (2.00)	503.1 (2.00)	522.9 (2.00)	508.7 (2.00)	510.9 (1.95)	517.7 (2.00)

	1000 °C	-----	-----	505.5 (1.96)	-----	520.3 (2.00)	503.0(2.00)	-----	517.5(2.00)
	1200 °C	-----	-----	526.6 (1.95)	-----	-----	505.5(2.00)	-----	522.5(1.07)
	1300 °C	-----	-----	521.1 (2.00)	-----	-----	510.8 (2.00)	-----	-----
	1400 °C	522.2 (2.00)	523.1 (1.77)	520.7 (1.93)	524.9 (1.89)	524.5 (2.00)	524.9 (1.88)	533.0 (1.67)	508.6 (1.24)
γ_3	1200 °C	-----	-----	-----	-----	-----	-----	-----	567.0(1.765)
	1400 °C	-----	-----	-----	-----	-----	-----	-----	586.3 (1.56)

Table 3. Positions and intensities (in parentheses) of the Raman modes 723 cm^{-1} and 670 cm^{-1} in some as-synthesized (900 °C) and annealed at 1400 °C spinels.

<i>n</i>	As-synthesized		Annealed at 1400 °C	
0.41	670.7 (0.43)	726.3 (0.14)	-----	-----
0.95	670.0 (0.48)	723.5 (0.23)	669.9 (0.57)	722.3 (0.25)
0.98	666.6 (0.47)	724.4 (0.22)	666.7 (0.57)	724.4 (0.26)
1.00	669.6 (0.47)	725.1 (0.16)	669.3 (0.50)	726.0 (0.16)
1.07	670.6 (0.46)	725.6 (0.17)	669.8 (0.43)	724.3 (0.08)
1.15	671.3 (0.38)	725.1 (0.11)	671.1 (0.32)*	723.3 (0.04)*
			673.0 (0.44)**	726.6 (0.09)**
2.47	no resolution		672.2 (0.23)	722.0 (0.03)

*With decomposition

**Without decomposition

Table 4. Inversion parameters and shifts of γ_2 mode of all as-synthesized (900 °C) and annealed at different temperatures spinels.

<i>n</i>	0.41	0.65	0.95	0.98	1.00	1.07	1.15	2.47
As-synthesized	0.29	0.33	0.39	0.36	0.27	0.37	0.36	0.45
Annealed at 1000 °C		---	0.33		0.27	0.34		0.37
Annealed at 1200 °C		---	0.29		---	0.28		0.21
Annealed at 1300 °C			0.29			0.32		
Annealed at 1400 °C	0.26	0.22	0.31	0.28	0.22	0.32	---	0.15
Shift of γ_2 mode from								
stoichiometric position	17.3	13.0	20.4	19.9	0.0	14.2	12.0	5.2
as-synthesized to annealed at 1400 °C position	16.6	13.2	18.2	21.9	1.6	16.2	22.1	---

Figures caption:

Fig. 1 - XRD patterns of as-synthesized (a) and annealed at 1400°C (b) samples. The reflections related to the MgO phase are indicated by *, while reflections related to the α -Al₂O₃ phase are indicated by @.

Fig. 2 - FTIR spectra of the as-synthesized stoichiometry spinel. The active IR modes are assigned in the spectra.

Fig. 3 - FTIR spectra of as-synthesized samples.

Fig. 4 - FTIR spectra of as-synthesized and annealed MgO1.07Al₂O₃ samples.

Fig. 5 - FTIR spectra of a) MgO2.47Al₂O₃ annealed at 1400 °C and α -Al₂O₃; b) by removing α -alumina spectra from the annealed MgO2.47Al₂O₃ sample, the presence of the γ_3 mode is clearly seen; c) MgO11.45Al₂O₃ annealed at 1400°C and α -Al₂O₃. The presence of the γ_3 and γ_1 modes is clearly evident.

Fig. 6 - Micro-Raman spectrum of an as-synthesized MgO1.07Al₂O₃ spinel.

Fig. 7 - Raman spectra of some as-synthesized spinels in the 600-850 cm⁻¹ range.

Fig. 8 - Raman spectra of spinels ($n=1.15$) with or without decomposition and of α -alumina.

Fig. 9 - Cell parameter of as-synthesized spinels compared with experimental data from other sources and calculated according to the curve generated using Eq. 1.

Fig. 10 - Inversion parameter (i) of as-synthesized spinels as a function of stoichiometry (n).

Fig. 11 - Dependence of the inversion parameter on annealing temperature as obtained from FTIR measurements, in comparison to values obtained with the O'Neill and Navrotsky (1983) thermodynamic model using the parameters of Redfern et al. (1999)

Fig. 12 - Inversion parameter as a function of stoichiometry (n) for as-synthesized and annealed at 1400 °C samples calculated using Raman 670 cm^{-1} and 723 cm^{-1} modes.























