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Influence of the synthesis route on $MgAl_2O_4$ spinel properties

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$MgAl_2O_4$ spinels were synthesized either from an oxide mixture (MgO and Al_2O_3) or a sulfate mixture ($MgSO_4{\cdot}7H_2O$ and $NH_4Al(SO_4)_2{\cdot}12H_2O$) at temperatures of 1000 to 1600 °C for heating times ranging from 2 to 14 hours. The crystallinity of as-synthesized samples was determined by X-ray diffraction. In similar heating conditions, samples synthesized from sulfates give higher crystallite sizes than samples synthesized from oxides. Furthermore, the sulfate route allows us to obtain pure spinels in softer conditions than the oxide route. The cation distribution was studied by ^{27}Al MAS NMR spectroscopy. An inversion parameter (x) characterizing the Al^{3+} ratio in tetrahedral and octahedral sites of the structure was determined. It was shown that this parameter is highly dependent on the nature of the reactants. The dielectric permittivity of non-stoichiometric materials was measured using a Fabry–Pérot resonator.

Introduction

The spinel structure consists of a face-centered cubic arrangement of oxygen ions. A unit cell contains 32 O^{2-} ions, 64 tetrahedral and 32 octahedral sites which are occupied by A^{2+} (A = Mg, Fe, Ca, Zn, *etc.*) and B^{3+} (B = Al, Fe, *etc.*) cations.[1,2] The distribution of cations between both sites varies between two limiting cases. In the "normal" spinel, one half of the octahedral interstices are occupied by the B^{3+} cations whereas A^{2+} cations are located in one-eighth of the tetrahedral sites. The general formula of the "normal" spinel is $(A)[B]_2O_4$ where the parentheses ( ) and [ ] represent tetrahedral and octahedral positions respectively. In the "inverse" spinel, tetrahedral sites are occupied by half of the B^{3+} whereas the other half and A^{2+} are located in the octahedral sites (formula: $(B)[AB]O_4$). Structures with intermediate cation distributions exist between these two limiting cases. The formula of these structures is then: $(A_{1-x}B_x)[B_{2-x}A_x]O_4$, where x is the "inversion parameter" ($0 \leqslant x \leqslant 1$).

The physical and chemical properties of spinels not only depend on the nature of A and B but also depend on the distribution of these cations in the different crystallographic sites. Investigations have already been carried out in order to determine the location of Mg^{2+} and Al^{3+} cations in the spinel $MgAl_2O_4$.[3,4] Indeed, natural and synthetic products were studied by ^{27}Al Magic Angle Spinning NMR.

This paper deals with the synthesis of $MgAl_2O_4$ spinels by two different routes. As-synthesized samples were characterized by X-ray Diffraction, Scanning Electron Microscopy, ^{27}Al MAS NMR spectroscopy and the dielectric properties of the materials were measured using a Fabry–Pérot resonator.

Synthesis

$MgAl_2O_4$ samples were synthesized either from oxides (MgO and $Al_2O_3{\cdot}2H_2O$) or sulfates ($MgSO_4{\cdot}7H_2O$ and $NH_4Al(SO_4)_2{\cdot}12H_2O$). All the reagents were provided by Baïkowski Chimie. The first step was to weigh the reagents respecting their stoichiometric amounts and to grind them in a mortar in order to obtain a homogeneous mixture. The mixed reagents were then heated in an oven at temperatures ranging from 1200 °C to 1600 °C (in air in a thermogravimetric analyzer oven, heating rate: 10 °C min^{-1}) for 2 to 14 hours and the decomposition process was followed. Before undergoing the same thermal treatment, the sulfate mixtures were first heated at 1000 °C (heating rate: 30 °C min^{-1}) for 10 hours in a muffle furnace in order to avoid the corrosion of the stainless steel parts of the apparatus by SO_x vapors. Samples were then cooled to room temperature (cooling rate: 4 °C min^{-1}) before being characterized.

Physico-chemical characterization

The X-ray diffraction (XRD) patterns were recorded on an INEL XRG 3000 diffractometer using $CuK_{\alpha 1}$ radiation ($\lambda = 154$ pm). The average crystal size of calcined samples (a/nm) was calculated from the X-ray line broadening using the Debye–Scherrer equation:[5] $a = \lambda/\varepsilon_{hkl}\cos\theta_{hkl}$, with ε_{hkl} being the band half-width (radian) of the *hkl* peak.

The morphology of the crystalline solids was characterized by scanning electron microscopy, using a Philips XL 30 microscope coupled to an EDS analyzer.

The ^{27}Al MAS NMR spectra were recorded on a Bruker DSX 400 spectrometer. An $Al_2(SO_4)_3$ aqueous solution was used as the reference. The recording conditions were as follows: frequency = 104 MHz, pulse width = 0.5 µs, recycle time = 2 s, spinning rate = 10 kHz, number of scans = 10.

Dielectric permittivities of powders were measured with a Fabry–Pérot resonator (working in the range 1–5 GHz), connected to a WILTRON 360 analyzer.

Results and discussion

Crystallization field and morphology

The most representative syntheses of $MgAl_2O_4$ samples are described in Tables 1 and 2. X-Ray diffraction patterns of samples prepared with oxides or sulfates are quite similar and characteristic of well crystallized $MgAl_2O_4$ samples. For example, Fig. 1 displays the XRD pattern of sample S5 (obtained by calcination of sulfates at 1600 °C for 14 hours) which is representative of all synthesized $MgAl_2O_4$ samples.

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Table 1 Average crystal size of $MgAl_2O_4$ samples synthesized at 1000 to 1600 °C for 14 hours (samples O1 to O3 and S1 to S5 were prepared with oxides and sulfates respectively)

Sample	O1[a]	O2	O3	S1	S2	S3	S4	S5
Temperature/°C	1200	1400	1600	1000	1100	1200	1400	1600
Average crystal size[5]/nm	26.3	29.9	37.7	23.8	28.6	30.1	40.6	44.0

[a] Presence of residual MgO and Al_2O_3.

Table 2 Average crystal size of $MgAl_2O_4$ samples synthesized at 1600 °C for 2 to 14 hours (samples O3 to O6 and S5 to S8 were prepared with oxides and sulfates respectively)

Sample	O4	O5	O6	O3	S6	S7	S8	S5
Time/h	2	4	8	14	2	4	8	14
Average crystal size[5]/nm	26.3	28.3	32.0	37.7	27.5	30.3	36.1	44.0

Only the pattern of sample O1 shows the presence of residual MgO and Al_2O_3, linked to the initial mixture of oxide powders. Contrary to the cobalt system where cation deficiency is observed,[6] it is probably not the case for the $MgAl_2O_4$ system under the used synthesis conditions. In addition, EDS analyses confirmed that no other residual element is present in the samples.

The crystal sizes of all samples were determined with the Debye–Scherrer equation. As measurements made for sample S5 using several *hkl* peaks ((440), (311) and (511)) led to similar particle sizes, only the (440) peak was used to determine the crystal size of all other samples.

The average crystal size of spinel samples prepared by the calcination of oxide or sulfate mixtures during 14 hours increases with temperature, from 26.3 nm to 37.7 nm for oxide mixtures and 23.8 nm to 44.0 nm for sulfate mixtures, for samples synthesized at 1000 to 1600 °C (Table 1). The evolution is the same for the samples synthesized at 1600 °C for increasing dwell times. Sizes vary from 26.3 nm to 37.7 nm and 27.5 nm to 44 nm for samples obtained by the calcination of oxides and sulfates respectively at 1600 °C for 2 to 14 hours (Table 2). Under similar synthesis conditions, samples synthesized from sulfates always present a higher crystal size than samples synthesized from oxides, which suggests a better crystallinity. Indeed, the crystal size of sample S5 (44 nm), obtained by calcination of sulfates at 1600 °C for 14 hours, is the highest observed.

The higher crystallinity of samples obtained by the sulfate route can be explained by the presence of a liquid aqueous phase between about 160 and 650 °C during the heating treatment. This liquid phase was evidenced by heating an opened crucible containing a sulfate mixture at about 800 °C in a muffle furnace. This liquid phase leads to a better homogeneity of the sulfate mixture, in comparison to the oxide mixture. This allows the acceleration of reactant diffusion and therefore favors crystallization.

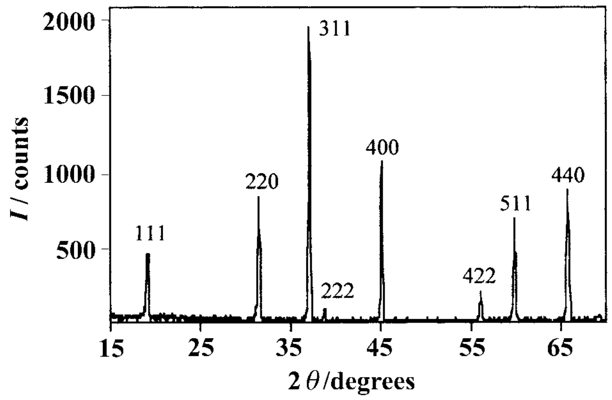

Fig. 1 X-Ray diffraction pattern of $MgAl_2O_4$ spinel synthesized from sulfates at 1600 °C for 14 hours (sample S5).

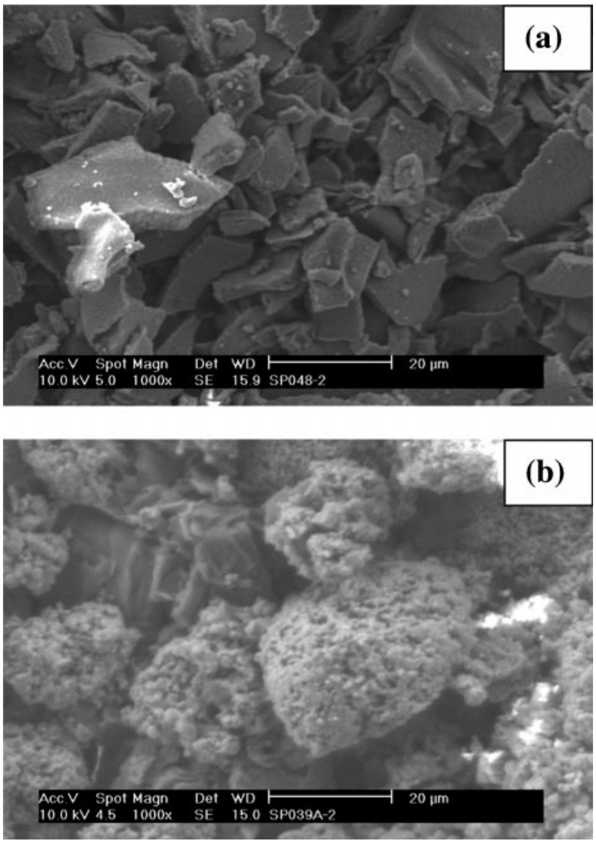

Fig. 2 Scanning electron micrographs of spinel samples S8 (a) and O6 (b).

Scanning electron micrographs of spinel samples S8 and O6 (prepared by calcination at 1600 °C for 8 hours) are presented in Fig. 2(a) and (b) respectively. Sample O6 consists of spherical aggregates of micrometer particles whereas sample S8 is composed of small platelets of sizes ranging from *ca.* 10 to 30 µm. Similar morphologies were observed for all other spinels synthesized with either oxides or sulfates. The platelet morphology can be explained by the presence of the liquid aqueous phase during the heating treatment.

Indeed, this platelet morphology is typical for samples prepared from intimate mixtures and was already observed for $MgAl_2O_4$ samples prepared by the calcination of an aqueous gel.[7]

Characterization

^{27}Al MAS NMR. The cation disorder of spinels synthesized at 1600 °C either from sulfates or oxides was studied by ^{27}Al MAS NMR spectroscopy. The spectra obtained are shown in Fig. 3. All spectra display a small peak around 70 ppm and a broad doublet peak around 0 ppm. These two signals are attributed to tetracoordinated (Al^{IV}) and octacoordinated (Al^{VI}) aluminium respectively.[4] The observation of two peaks around 0 ppm suggests an environment change of the Al^{VI}, probably due to the migration of Mg^{2+} from tetrahedral to octahedral sites. Indeed, the presence of octacoordinated Mg^{2+} locally modifies the environment of a part of the Al^{VI}.

Fig. 4(a) and (b) respectively display the evolution of the relative intensities of Al^{IV} and Al^{VI} peaks as a function of the heating time at 1600 °C. It can be deduced from these figures that the synthesis procedure has an influence on the distribution of Al^{3+} between both sites. Indeed, whatever the heating time, spinels synthesized from sulfates present about twice the

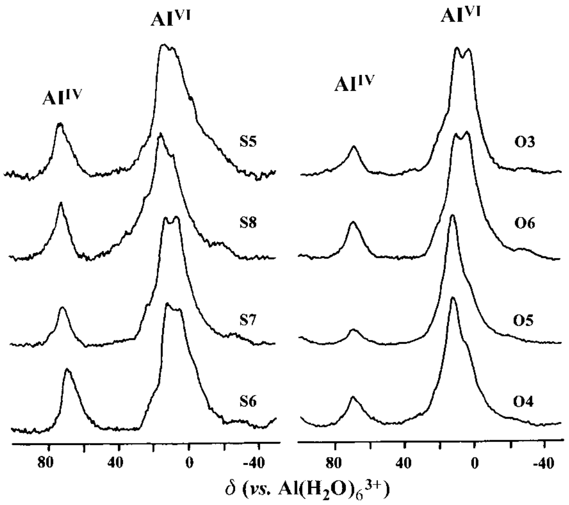

Fig. 3 ^{27}Al MAS NMR spectra of $MgAl_2O_4$ spinels synthesized at 1600 °C for 2 to 14 hours.

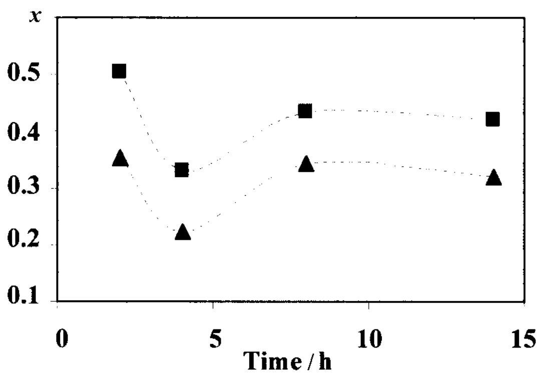

Fig. 5 Inversion parameter for $MgAl_2O_4$ samples synthesized at 1600 °C for 2 to 14 hours from oxide (▲) or sulfate (■) mixtures.

amount of aluminium in tetrahedral sites than spinels synthesized from oxides. The liquid phase observed during the heat treatment of sulfates could explain these observations. By leading to a good homogeneity of the mixture and a rapid diffusion of cations, this intermediate liquid allows a higher migration of Al^{3+} in tetrahedral sites.

An inversion parameter x can be calculated from ^{27}Al MAS NMR spectra[4] in order to quantify cation disorder. For a spinel with the formula $(Mg_{1-x}Al_x)[Al_{2-x}Mg_x]O_4$, the ratio of octahedral to tetrahedral aluminium corresponds to $Al^{VI}/Al^{IV}=(2-x)/x$, which leads to $x=2/[1+(Al^{VI}/Al^{IV})]$. Fig. 5 displays calculated inversion parameters for spinels synthesized by the two different routes at 1600 °C for various times. Whatever the heating time, x is always higher for samples synthesized from sulfates than those obtained with oxides. For example, after 14 hours of heating at 1600 °C, x is equal to 0.32 and 0.22 for spinels synthesized from sulfates and oxides respectively (samples S5 and O3). This confirms that the sulfate synthesis route allows a higher occupation of tetrahedral sites by A^{3+} than the oxide route. Furthermore, the calculated x values are similar to the values previously determined by other authors. Millard *et al.*, for example, calculated x for $MgAl_2O_4$ samples synthesized from oxides at temperatures varying from 700 to 1000 °C and found x values ranging from 0.22 to 0.28.[4]

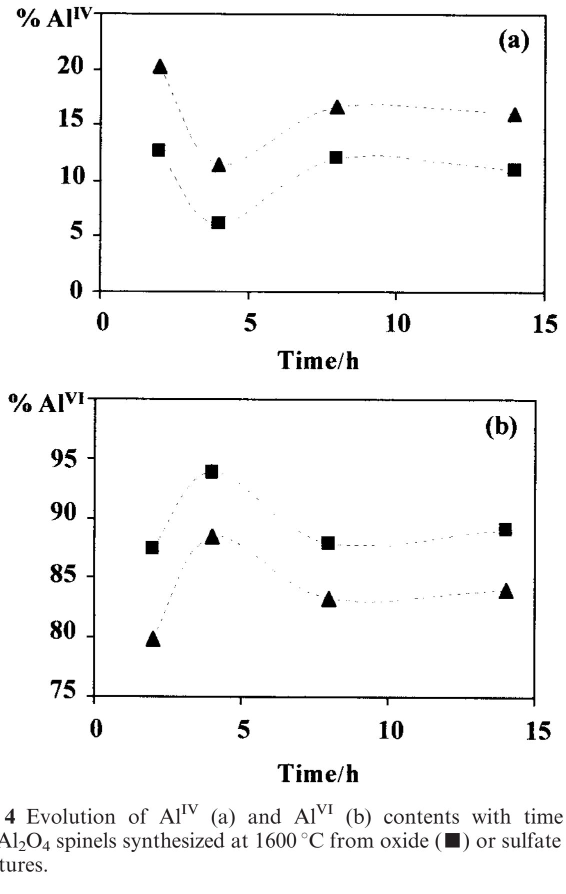

Fig. 4 Evolution of Al^{IV} (a) and Al^{VI} (b) contents with time for $MgAl_2O_4$ spinels synthesized at 1600 °C from oxide (■) or sulfate (▲) mixtures.

Electrical properties. Dielectric permittivities of non-stoichiometric spinels prepared by the calcination of sulfates at 1600 °C for 14 hours were measured. The calcined samples studied had the following compositions: xMgO·Al_2O_3 ($x=0$, 1, 1.1 and 1.2) and MgO·$y$$Al_2O_3$ ($y=1.05$, 1.1 and 1.2). After calcination, samples were manually ground before being sifted with a 60 µm sieve, in order to obtain homogeneous grain sizes. Then, 1.3 g of the ground powder were placed in the measurement cell, which is composed of a brass cylinder (length 70 mm, diameter 10 mm) with a brass wire in the center (Fig. 6). The powder is maintained in the cell by two hollow Teflon cylinders. The measured permittivity values (ε_A) are corrected in order to take into account the porosity of the materials:[8] $\varepsilon_A=\varepsilon_M\cdot\kappa_M+\varepsilon_{air}\cdot\kappa_{air}$, with κ_M and κ_{air} being the volume ratios of the spinel and the air in the measurement cell and ε_M being the corrected permittivity. As $\varepsilon_{air}=1$, the corrected permittivity of the material is: $\varepsilon_M=(\varepsilon_A-\kappa_{air})/\kappa_M$. Fig. 7 shows the corrected permittivities as a function of composition.

The highest ε value is obtained for Al_2O_3 ($\varepsilon_{Al_2O_3}=7.8$) and the lowest for the stoichiometric spinel ($\varepsilon_{MgAl_2O_4}=5.5$). The permittivity of MgO is equal to 7.2. The addition of an excess of MgO or Al_2O_3 to the stoichiometric spinel leads to an increase of the permittivity. Similar evolution was already observed by Nazare *et al.* for samples prepared from oxides.[8] However, our determined ε_M values are always below the

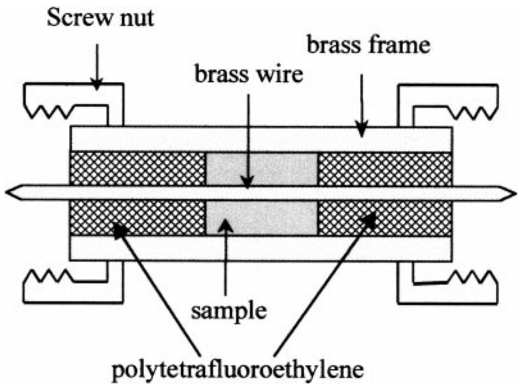

Fig. 6 Scheme of the permittivity measurement cell.

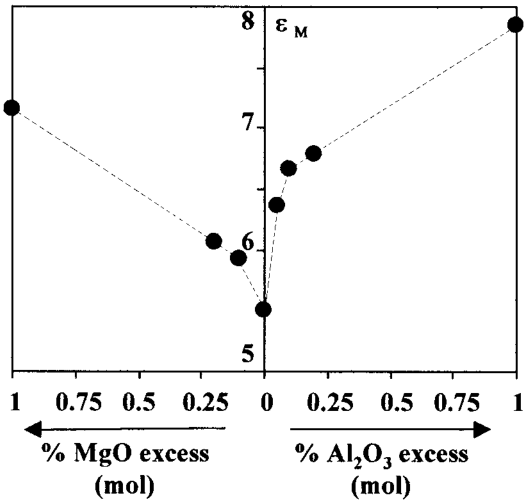

Fig. 7 Dielectric permittivities (ε_M) of non-stoichiometric spinels.

values determined by these authors, *i.e.* 9.8 for MgO, 8.3 for $MgAl_2O_4$ and 10.1 for Al_2O_3. This could be explained by the correction applied for porosity.

Conclusion

We have shown that structural differences exist for $MgAl_2O_4$ spinel samples synthesized at 1000 to 1600 °C for various dwell times (2 to 14 hours) by two different synthesis routes: the calcination of an oxide or a sulfate mixture.

X-Ray diffraction spectra show that in similar synthesis conditions, samples obtained from sulfates present a higher crystallinity than samples obtained from oxides.

^{27}Al MAS NMR spectroscopy was used to quantify cation disorder. Both synthesis routes lead to an incorporation of Al^{3+} in tetrahedral sites. However, a higher incorporation was always observed for samples synthesized from sulfates, which leads to a higher inversion parameter x.

Dielectric permittivities of the spinels measured with a Fabry–Pérot resonator are in agreement with those determined by other authors for similar materials.

All the structural differences observed between both sets of samples could be explained by a better homogeneity of the sulfate mixture compared to the oxide one, due to the presence of a liquid phase between about 160 and 650 °C. The sulfate synthesis route allows us to obtain materials free of residual reactants in softer conditions than the oxide route.

Owing to the interesting electric properties of synthesized spinels and also the well known hardness of these oxides, these latter could find applications as polishing powders for a large range of materials (metallographic samples, optical components, *etc.*).

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