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3 Ways to $MgAl_2O_4$ Spinel Powders Used as a Humidity Sensor

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Abstract

The preparation of spinel powder by various chemical techniques, such as co-precipitation, sol-gel and spray-drying, has been extensively studied. Recently, the oligomer-like precursor to $MgAl_2O_4$ spinel has been developed and successfully synthesized in one step directly from $Al(OH)_3$ and MgO with triethanolamine [TEA, $N(CH_2CH_2OH)_3$] in ethylene glycol solvent or from the reaction of alumatrane and magnesium methoxide. The precursors were converted to spinel by pyrolyzing at 1100°C for 2 h. in air. Characterization was carried out using NMR, XRD and SEM. As compared both simple and straightforward synthetic routes to the mixed oxide route, they offered more advantages, such as shorter processing times, higher homogeneity and higher product purity.

Keywords : Spinel, Humidity Sensor, Aluminium Hydroxide, Magnesium Hydroxide and Alumatrane

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Introduction

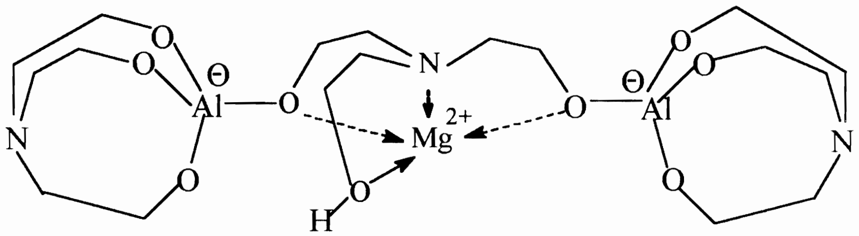
Ryshkewitch first recognized the important of spinel, $MgAl_2O_4$, which was later used as a refractory material in the ceramic industry owing to its low density (3.58 g/cm^3) and stability in harsh environment (Kingdom, *et al.* 1991; and Sharafat, *et al.* 1993). It has also been suggested for use as a fusion reactor power core insulating material due to its radiation stability (Waldner, *et al.* 1996). Alais described the preparation of spinel by electrofusion and casting. The spinel was characterized using high refractoriness and exceptional dielectric property (Gitzen, 1970). Navias also studied the preparation and some properties of spinel synthesized by the vapor transport of MgO from periclase in hydrogen atmosphere at 1500° to 1900°C (Gitzen, 1970). The spinel was successfully fabricated by standard ceramic processing methods, such as casting, extrusion or cold pressing, followed by sintering at temperature of 1650° to 1850°C (Kingdom, *et al.* 1991).

Humidity sensing has become ever more important, principally in controlled systems for industrial processes and human comfort (Kulwicki, 1991). In recent years, spinel, one of many mixed-metal oxides, has been used as sensing element for humidity devices due to its sensitivity, stability and other characteristics (Gusmano, *et al.* 1993; Seiyama, *et al.* 1983; and Laobuthee *et al.* 2000). Nevertheless, the ceramic materials possess a unique structure consisting of grains, grain boundaries, surfaces and pores which make them suitable for use as chemical sensors when they have a controlled microstructure (Shimizu, *et al.* 1985).

Many synthetic routes have been developed to a wide variety of inexpensive preceramic polymers directly from the corresponding metal oxides or hydroxides. One of them, called the "oxide one pot synthesis (OOPS)" process, is very simple and straightforward (Laine, *et al.* 1991). It provides several advantages, as compared to other chemical techniques, e.g. higher purity, homogeneity and low processing temperature (Laine, *et al.* 1991). Additionally, this process could provide new chemicals, polymers and ceramics, in one or two steps directly from mineral sources. Precursors containing any combination of aluminum, silica with or without group I or II metals are readily produced in ethylene glycol solvent (Laine, *et al.* 1991).

The preparation of a spinel oligomeric precursor is based on the OOPS process, as shown in the following reaction;

$$MgO + 2\ Al(OH)_3 + x\text{'s}\ EG + 3\ TEA \xrightarrow{200^{\circ}C/\ -H_2O}$$



The aim of this work was to develop spinel, $MgAl_2O_4$, produced by the OOPS process, the mixed oxide route and the reaction of alumatrane and MgO.

Experimental

Materials

Aluminun hydroxide hydrate [$Al(OH)_3.XH_2O$], magnesium powder [Mg, 99% purity] and magnesium oxide (MgO) were purchased from Aldrich Chemical Co. Inc (USA), Fluka Chemical (Switzerland) and Carlo Erba, respectively. They were used as received. Ethylene glycol (EG, $HOCH_2CH_2OH$) was purchased from Carlo Erba (Barcelona), and distilled prior to use.

Triethanolamine [TEA, $N(CH_2CH_2OH)_3$, 99.5% purity] was purchased from Merck Chemical Co. (Germany) and used as received. All reactions are moisture sensitive, therefore, all operations were carried out with careful exclusion of moisture and air.

Instrument

The precursor products obtained were characterized by FAB^+—MS (707 VG Autospec-ultima mass spectrometer, Manchester, England) employing a direct probe inlet and using the Cs gun to ionize sample. The peaks were calibrated using CsI as the reference. Samples were mixed with glycerol, used as a matrix. The mass range was set from m/z = 40 to 3000. Additionally, the precursor products obtained were characterized by ^1H- and ^{13}C-NMR (Bruker AM 400 NMR spectrometer at the Department of Chemical Science and Technology, University of Rome "Tor Vergata", Italy). The NMR spectrometer operating in the quadrature mode was used to obtain ^1H- and ^{13}C-NMR spectra. Typical ^1H-NMR spectra consisted of 64-128 transients of 8192 data points over a 8 KHz bandwidth using a 5.8 μs at 90° pulse. Typical ^{13}C-NMR spectra consisted of 12000 transients on a 35 KHz band width using a 10 μs at 90° pulse. Deuterated chloroform ($CDCl_3$) was used as a standard solvent.

The pyrolyzed samples were characterized by XRD (Philips PW 1830/00 No. DY 1241) at the range of 5-80°2θ and a scan speed of 1.5° 2θ/min in 0.02° 2θ increment. SEM (Leica-Cambridge mod. Steroscan 360, Cambridge, UK) was carried out to identify the microstructure of the powder samples. The powders were glued on aluminum stubs using a liquid carbon paste and coated with Au/Pd to avoid particle charging. Finally, the four point BET method using N_2 as adsorbate (Micromeritics Instrument Corporation, FlowSorb II model 2300) was used to determine the specific surface area of the samples. The gaseous mixture of nitrogen and helium using a gas mixer was allowed to flow through the system at a constant rate of 30 cc/min. Each powder sample was dried at 200°C and degassed for 1 h.

Procedure

a). Preparation of $MgAl_2O_4$ spinel by the "OOPS" Process

Aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as Al_2O_3), magnesium oxide (4.24 g, 100 mmol, 95% as MgO), three moles of triethanolamine (40 mL, 300 mmol) and 150 mL of EG solvent were put into a 250 mL two-necked round bottom flask. The mixture gave a milky solution. It was then heated under nitrogen at 200°C to distill off EG and by-product water that was produced during the reaction. The reaction was continuously distilled for approximately 7 h and then distilled further under vacuum (approximately 0.01 torr) at 100°C to remove excess EG for 6 h. The products obtained were characterized by FAB^+—MS, ^{1}H- and ^{13}C-NMR.

The precursor was pyrolyzed in an alumina boat in horizontal tube at 1100°C for 2 h to obtain spinel product. The product was ground with an alumina mortar/pestle and characterized by XRD, BET, and SEM.

b). Preparation of Spinel by Mixed Oxide Route

Aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as Al_2O_3) and magnesium oxide (4.24 g, 100 mmol, 95% as MgO) were weighed and mixed by ball-milling under ball media for 1 h. The mixture was transferred to the alumina crucible for calcining at 1100°C for 15 and 20 h. The powder samples obtained were characterized by XRD, BET, and SEM .

c). Preparation of Spinel from Alumatrane and $Mg(OMe)_2$

Firstly, aluminum hydroxide hydrate (16.26 g, 100 mmol, 62.7% as Al_2O_3 by TGA), triethanolamine (26.7 mL, 200 mmol) and 100 mL of EG solvent were put into a 250 mL two-necked round bottom flask. The mixture was stirred and heated under nitrogen at 200°C to distill off EG and by product water produced during the reaction. The reaction was continuously distilled for approximately 6 h. to obtain clear and yellow color product. The product was characterized using FAB^+—MS.

Magnesium powder (2.45 g, 100 mmol) was weighed and dissolved in 75 ml dried methanol. Turbid solution, $Mg(OMe)_2$, was obtained after the mixture was stirred for 3 h. Triethanolamine (13.4 mL, 100 mmol), prepared alumatrane, and 100 mL of ethylene glycol were then added into the mixture of $Mg(OMe)_2$. The mixture was heated and distilled continuously for 2 h. The resulting clear and yellow solution was then distilled further under vacuum (approximately 10^{-2} torr) at 100°C to remove excess EG for 6 h. Viscous, clear, and brown color product obtained was characterized by FAB^+—MS, ^1H-NMR and TGA.

The precursor was pyrolyzed in an alumina boat in horizontal tube at 1100°C for 2 h to obtain spinel product. The product was ground with an alumina mortar/pestle and characterized by XRD, BET and SEM.

Results and Discussion

a). Preparation of $MgAl_2O_4$ spinel by the "OOPS" Process

The solid product obtained after the reaction was complete and the excess EG was removed by vacuum distillation was easily dissolved in alcohol, chloroform and dichloromethane. The characterization using FAB^+-MS showed the parent peak of the spinel precursor at m/z 518, see Figure 1, as indicated by Waldner et.al. (1996). The structure of the spinel precursor was a trimetallic species, consisting of one TEA group per metal center. It was assumed that Mg^{2+} was actually enfolded by the third TEA. This structure minimizes the charge separation and appears to be the most stable for the di-positive cation. Thus the electrostatic interaction is diminished.

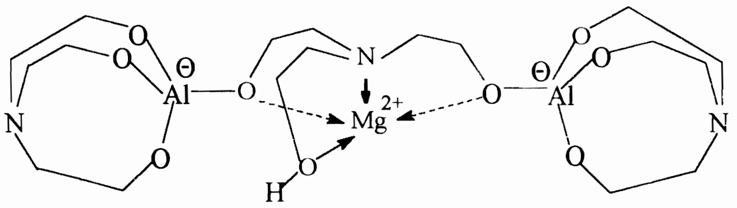


Figure 1 The structure of spinel precursor

^{1}H-NMR result of the spinel precursor, is presented in Table 1 and shows the peak positions for methylene groups adjacent to oxygen and nitrogen atoms, occurring at chemical shifts of 3.73 ppm (triplet) and 2.72 ppm (triplet), respectively. The integration ratio of CH_2-O:CH_2-N was 1:1. The peak positions for these methylene groups were not identical in chemical shifts, indicating that the methylene groups adjacent to oxygen and nitrogen atoms have different environments and are effected from each other. The result also indicated the presence of free TEA, which is difficult to remove due to its high boiling point.

Table 1 ^{1}H-NMR peak positions and assignments for spinel precursor

Chemical Shift (ppm)	Tentative Assignments
2.67 (t)	N(**CH_2**CH_2OH)$_3$, free TEA
3.65 (t)	N(CH_2**CH_2**OH)$_3$, free TEA
4.5 (br)	OH either from free of Mg^{2+} coordinated TEA or free TEA
2.72 (t)	CH_2 adjacent to N alumatrane
3.73 (t)	CH_2 adjacent to N alumatrane

^{13}C-NMR of the precursor Table 2 shows the peak positions corresponding to the carbon positions in the spinel precursor and in free TEA. The presence of TEA can be confirmed by the TGA result which shows the decrease in the powder yield, as well.

Table 2 ^{13} C-NMR peak positions and assignments for spinel precursor

Chemical Shift (ppm)	Tentative Assignments
52.7	N(**CH_2**CH_2OH)$_3$, free TEA
52.8	N(**CH_2**CH_2O)Al
56.7	bridging, N(**CH_2**CH_2O)
56.3	N(CH_2**CH_2**O)Al
59.5	bridging, N(CH_2**CH_2**O)
63.6	N(CH_2**CH_2**OH)$_3$, free TEA

The experimental powder yield, 29.4%, is lower than that of the calculated yield, 32.8%, as shown in Figure 2. There are three regions of mass loss in the TGA thermogram. The first mass loss corresponded to organic ligand decomposition in the range of 220° to 340°C. The second mass loss was oxidative decomposition of carbon residue (char) at 340° to 600°C. The final mass loss between 600° and 900°C was belong to the decomposition of trace of $MgCO_3$ which was formed during organic ligand decomposition (Waldner, et al. 1996; and Sadtler Research Laboratories, 1965).

The spinel obtained after pyrolysis of the precursor at 1100°C for 2 h was a white powder. Since the precursor is highly viscous, this viscosity limits escape of the decomposition products, namely, CO, CO_2, H_2O, and volatile hydrocarbon products, produced during precursor decomposition. Thus, a gas-filled and foam-like structure which is retained as a porous structure forms during pyrolysis.

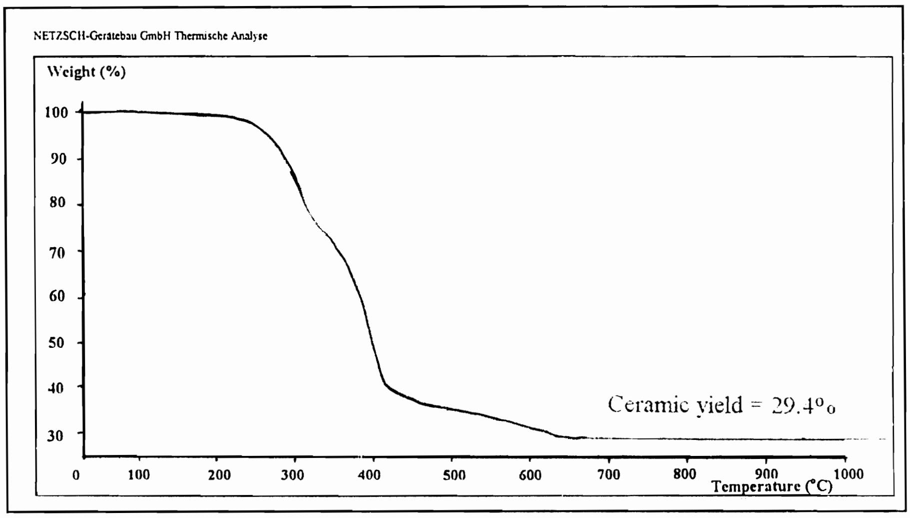


Figure 2 TGA Thermogram of the precursor obtained from the OOPS process

X-ray diffraction analysis was conducted on spinel samples heated to 1100°C for 2 h under air Figure 3. All the peak positions were identified by comparing with JCPDS file No. 21-1152. The major peaks for spinel were the 311 hkl reflection (d = 0.244 nm, I = 100%) and 400 hkl reflection (d = 0.202 nm, I = 56%). The method of Pasquier (Pasquier, *et al.* 1991) was used to follow the phase evolution as a function of pyrolysis temperature by comparing the relative intensity ratio of the 400 and 311 peaks. The ratio value of 0.6 was found for a commercial high purity spinel, whereas that of the product obtained after pyrolysis was 0.56, as the material transforms to pure spinel (Waldner, *et al.* 1996).

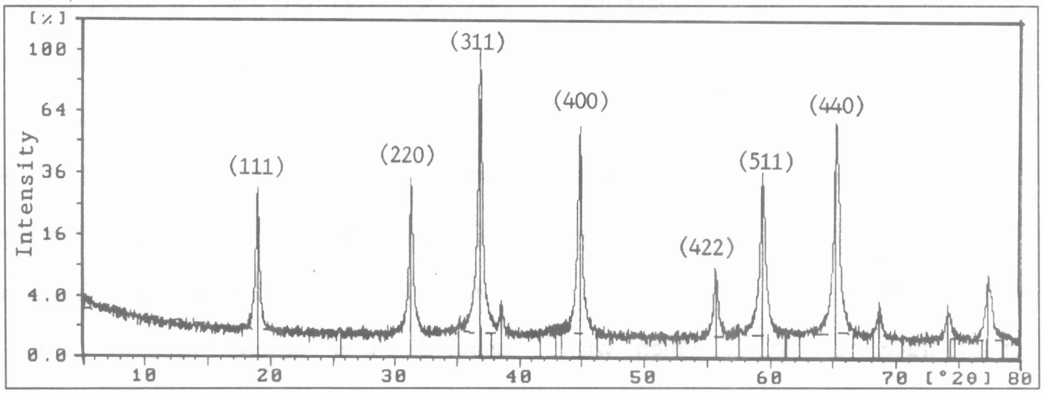


Figure 3 XRD pattern of spinel powder obtained after pyrolysis of the precursor at 1100°C for 2 h in air.

The specific surface area of the 1100°C spinel powder was measured by BET analysis to be 11.2 m^2/g. The particle sizes were determined by SEM Figure 4 favorably compatible with the average particle diameters derived from the BET surface area and the XRD data. The equivalent spherical diameter predicted from the surface area was 150 nm. The powder was irregularly shaped with more perfect particle and blocky particles possibly due to excessive necking between particles occurred during pyrolyzing the precursor. This occurrence led to the larger particle size and less surface area. The sizes range from submicron to greater than 50 μm.

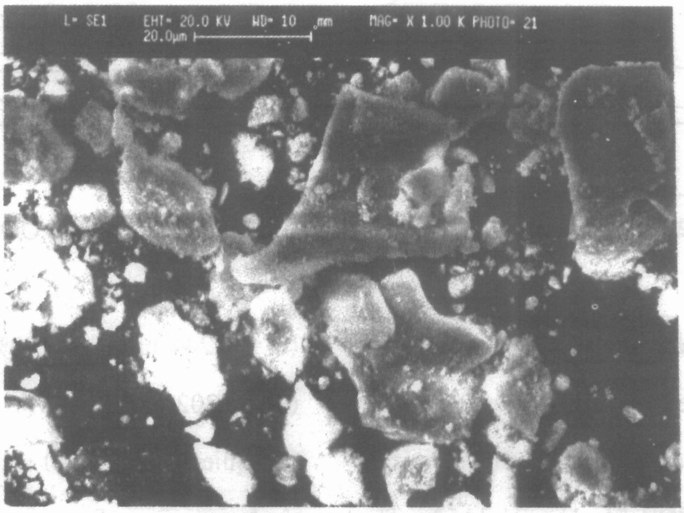


Figure 4 SEM of spinel powder obtained after pyrolysis of the precursor at 1100°C for 2 h in air.

b). Preparation of Spinel by Mixed Oxide Route

The mixed oxide route occurs at the surfaces of solids where they touch each other due to lattice imperfections or the defects (Kingery, *et al.* 1975; West, 1989; and Koller, 1994). One of the factors that influences the rate of reaction between solids is their surface areas. The mixing of both reactants by ball-milling was used before sintering the mixed powder to obtain the maximized surface areas, as well as to bring fresh surfaces into contact, and hence a better reaction rate.

The XRD pattern of the product obtained on reacting $Al(OH)_3$ and MgO at 1100°C for 15 h in air, is shown in Figure 5. Again all peak positions are identified by comparing with standard JCPDS files No.21-1152 for spinel and No.04-0829 for MgO. One of major peaks of MgO ($2\theta = 43$, $d = 0.211$ nm, $I = 36.5$ %) gave high intensity as compared to the major peak of spinel ($hkl = 311$, $d = 0.244$ nm, $I = 100\%$), indicating that the reaction between $Al(OH)_3$ and MgO was incomplete due to the presence of unreacted MgO and presumable $Al(OH)_3$. Furthermore, this occurrence probably results from a change in the ratio between $Al(OH)_3$ and MgO, or the incorrect stoichiometries resulting from mechanical loss of sample during sample preparation or solid-solid state reaction. The relative intensity ratio of the 400 and 311 peaks was 0.735, as the product had not transformed to pure spinel.

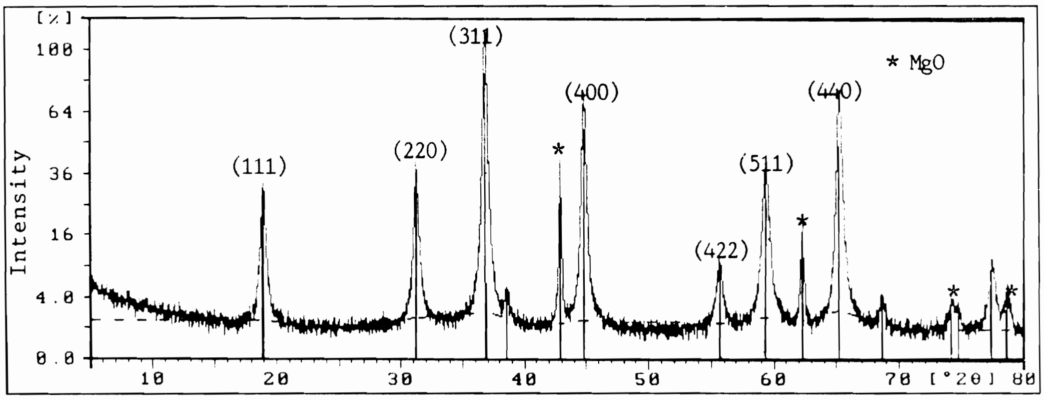


Figure 5 XRD pattern of spinel powder prepared by mixed oxide route at 1100°C for 15 h in air.

The BET surface area of the product obtained was 28 m^2/g and the average particle diameters calculated from BET surface area was 60 nm. The results indicated that the product obtained had high surface area due to the presence of large amount of the reactant, MgO, and/or it did not transform to pure spinel as suggested by the relative intensity ratio of the 311 and 400 peaks.

Generally, the solid-solid state reactions need more than 15 h heating to completion the reactions and obtain the highest conversion to product because the rate of spinel formation is a function of heating time (Kingery, *et al.* 1975; and West, 1989). To confirm this assumption, the other spinel was therefore prepared by calcining in air at the same calcined temperature of 1100°C for longer time, 20 h. The pyrolyzed product was investigated by XRD, BET and SEM.

From the XRD pattern of the product obtained on reacting $Al(OH)_3$ and MgO at 1100°C for 20 h in air, Figure 6, one of the major peaks of MgO ($2\theta = 43$, d = 0.211 nm, I = 19.6 %) showed moderate intensity as compared to the major peak of spinel (hkl = 311, d = 0.244 nm, I = 100%), again indicating the incomplete reaction. However, the results showed that the XRD intensity of the MgO peak decreases with increasing reaction time.

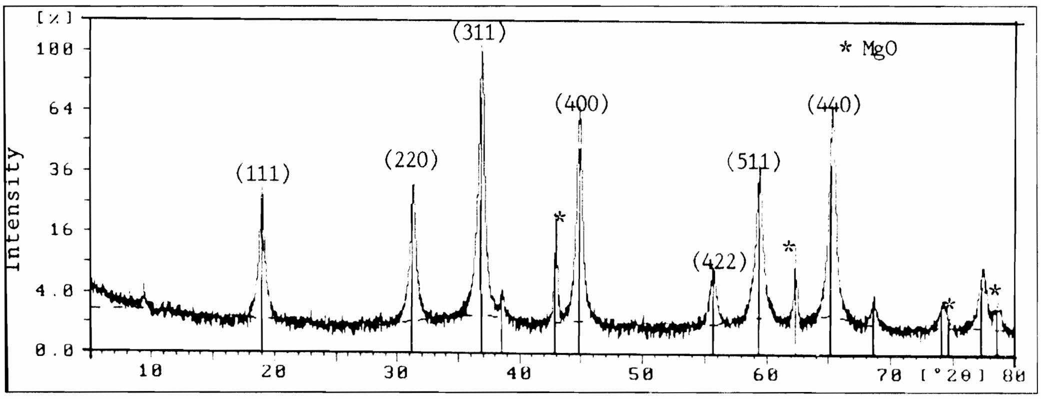


Figure 6 XRD pattern of spinel powder prepared by mixed oxide route at 1100°C for 20 h in air.

Furthermore, the relative intensity ratio of the 400 and 311 peaks, is 0.622, as the product transforms to pure spinel. The BET surface area obtained, 14 m^2/g, was lower than the 15 h product. The average particle diameters of both products calculated from the BET surface area were 120 nm and 340 nm, respectively. The XRD, BET, and SEM Figure 7 and 8 results indicated that the particle size of the product heated for 20 h was larger than that of the one heated for 15 h.

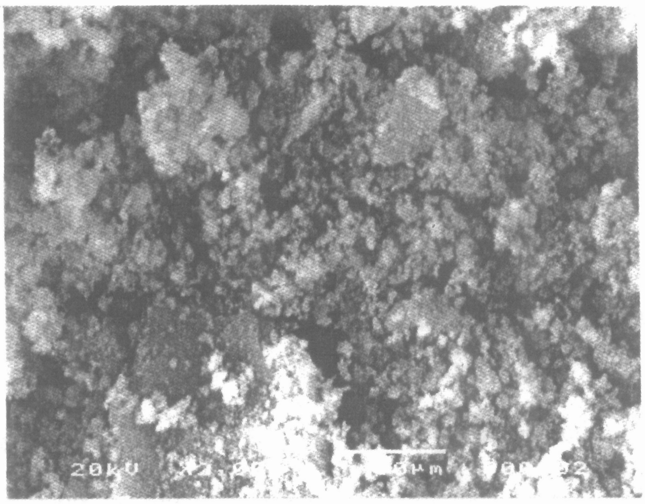


Figure 7 SEM of spinel product obtained by mixed oxide route at 1100°C for 15 h in air.

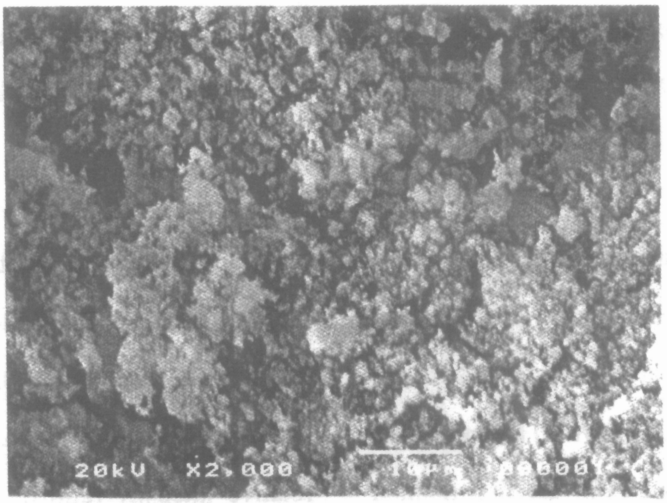


Figure 8 SEM of spinel product obtained by mixed oxide route at 1100°C for 20 h in air.

c). Preparation of Spinel from Alumatrane and Mg(OMe)$_2$

An alternate synthesis of spinel precursor was to improve the precursor yield by first synthesizing Mg(OMe)$_2$ (Kansal, *et al.* 1995; and Ozaki, 1988) and alumatrane to be used as reactants. Synthesis of alumatrane resulted in dimeric species Figure 9 as the base peak in the mass spectral analysis.

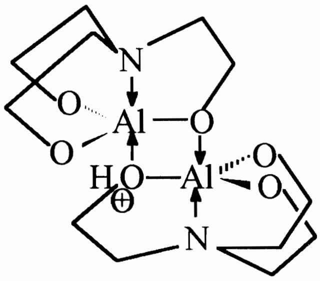


Figure 9 Dimeric alumatrane (m/z = 347, 100% intensity).

A reaction of the magnesium powder and dried methanol resulted in magnesium methoxide. After going through the alcoholysis reaction with ethylene glycol (Mehrotra, 1988), the Mg $(OCH_2CH_2OH)_2$ complex was obtained as a white gel. The white gel was heated with the mixture of TEA and alumatrane at 200°C for 2 h. The reaction was complete and resulted in a clear, orange colored solution.

The TGA of spinel the precursor was in agreement with that obtained in the first method. However, the powder yield obtained (28.9 wt.%) was lower than the theory (32.8 wt.%) and not much different from that obtained from the first method (29.4 wt.%). This is due to excess TEA added to ensure that the reaction goes completion, and thus it caused a difficulty of TEA removal from spinel precursor product.

To confirm the chemical composition of double alkoxide product, FAB^+-MS and H^1-NMR were used. The parent peak was observed in the mass fragmentation spectral at m/z = 518 (100% intensity) and the NMR showed two chemical shifts for methylene groups adjacent to nitrogen and oxygen atoms, occurring at 2.75 (triplet) and 3.74 (triplet), respectively.

The precursor was then calcined to obtain spinel which was characterized using XRD. The major peaks of XRD patterns Figure 10 were the 311 hkl reflection (d = 0.244 nm, I = 100%) and 400 hkl reflection (d = 0.202 nm, I = 56%). The relative intensity ratio of the 400 and 300 peaks, was 0.56 showing that the product has transformed to the pure spinel.

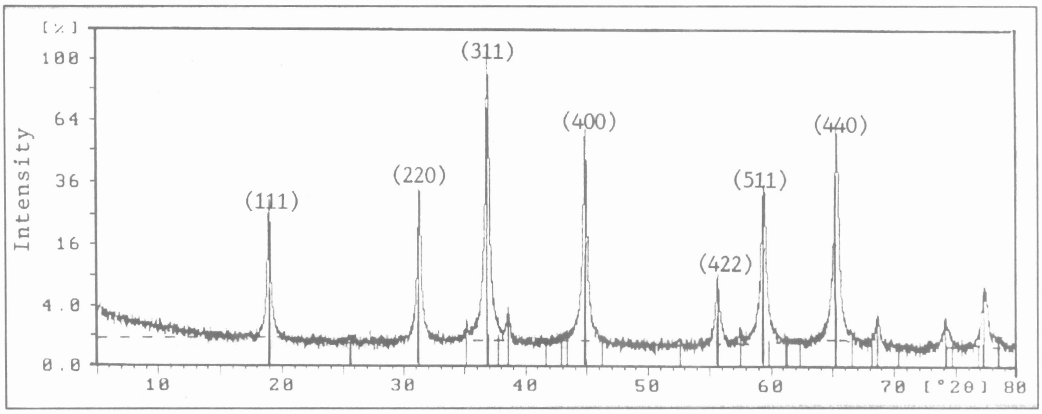


Figure 10 XRD pattern of spinel powder prepared by calcining precursor obtained from the reaction of alumatrane and $Mg(OMe)_2$ at 1100°C for 2 h in air.

The product was then characterized its microstructure by BET analysis. Its specific surface area was 7 m^2/g. The average spherical diameter predicted from the surface area was 240 nm. SEM measurement confirmed the microstructure of powder obtained after being calcined, as shown in Figure 11. The powder was in blocks with more perfect particle size, and was irregularly shaped due to the strong necking of unit particles. Thus, the size of powder was larger than 50 μm.

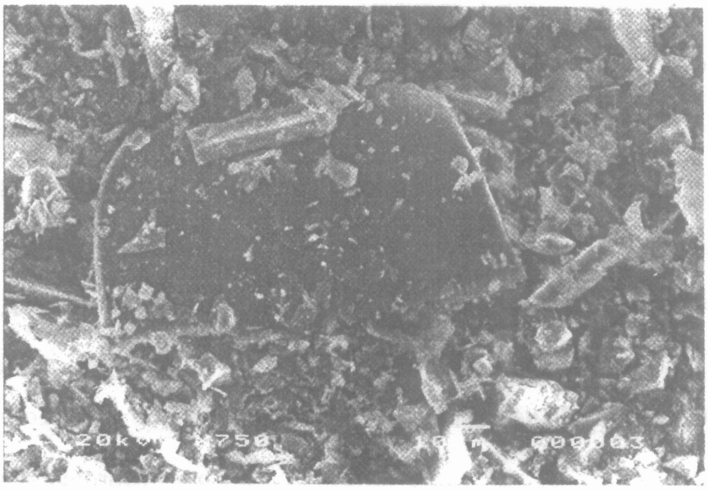


Figure 11 SEM of spinel powder prepared by calcining precursor obtained from the reaction of alumatrane and $Mg(OMe)_2$ at 1100°C for 2 h in air.

Conclusions

The $MgAl_2O_4$ spinel powder produced from very inexpensive and relatively abundant starting materials was successfully obtained via the one oxide pot synthesis (OOPS) process, directly by mixed oxide route, and by the reaction of alumatrane and magnesium methoxide, [$Mg(OMe)_2$]. The OOPS process was only one step synthesis while the reaction of alumatrane and magnesium methoxide was three step synthesis. The powder yield of the precursor obtained from the OOPS process was very close to that obtained from the reaction of alumatrane and $Mg(OMe)_2$, but lower than the theoretical yield. However, both methods took much shorter time, 2 h, to convert to spinel, as compared with the mixed oxide route, which took more than 15 h at the same pyrolysis temperature of 1100°C. Additionally, the mixed oxide route gave more impurities due to non-uniformed reactants ratio and/or incomplete reaction.

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References

Gitzen, W. H. 1970. *Alumina as a ceramic material.* Ohio. The American Ceramic Society : 141.

Gusmano, G., Montotesperelli, G., Nunziante, P. and Traversa, E. 1993. Study of the conduction mechanism of $MgAl_2O_4$ at different environmental humidities. *Electrochimica Acta.* **38** : 2617-2621.

Kansal, P. and Laine, R.M. 1995. Group II Tris (glycolato)silicates as precursors to silicate glasses and ceramics. *J. Am. Ceram. Soc.* **78** : 529-538.

Kingdon, A.I., Davis, R.F. and Thackery, M.M. 1991. Introduction to glasses and ceramics. *ASM International.* **4** : 765.

Kingery, W.D., Bowenn, H.K. and Uhlmann, D.R. 1975. *Introduction to Ceramics.* 2nd edition, New York. John Wiley & Sons.

Koller, A. 1994. *Structure and Properties of Ceramics.* Amsterdam, Elsevier.

Kulwicki, B.M. 1991. Humidity sensors. *J. Am. Cerm. Soc.* **74** : 697-708.

Laine, R.M., Blohowiak, K.Y., Robinson, T.R., Hoppe, M.L., Nardi, P., Kampf, J. and Uhm, J. 1991. Synthesis of novel, pentacoordinate silicon complexes from SiO_2. *Nature.* **353** : 642-644.

Laobuthee, A., Wongkasemjit, S., Traversa, E. and Laine, R.M. 2000. $MgAl_2O_4$ Spinel powders from oxide one pot synthesis (OOPS) process for ceramic humidity sensors. *J. Eur. Cer. Soc.* **20** : 185-191.

Mehrotra, R.C. 1988. Synthesis and reactions of metal alkoxides. *J. of Non-crystalline Solid.* **100** : 1-15.

Ozaki, Y. 1988. Preparation and application of fine powder from the metal alkoxide. In : *Advanced Ceramic*. Oxford University Press : 165-183.

Pasquier, J.F., Komarneni, S. and Roy, R. 1991. Synthesis of $MgAl_2O_4$ spinel : Seeding effects on formation temperature. *J. Mat. Sci.*. **26** : 3797.

Sadtler Research Laboratories. 1965. *Sadtler High Resolution Spectra of Inorganics and Related Compounds*. Philadelphia.

Seiyama, T., Yamazoe, N. and Arai, H. 1983. Ceramic humidity sensors. *Sensors and Actuators.* **4** : 85.

Sharafat, S., Ghoniem, N.M., Cooke, P.I.H., Martin, R.C., Najamabadi, F., Schultz, K.R. and Wong, C.P.C. 1993. Materials analysis of the TITAN-I reversed-field-pinch fusion power core. *Fusion Engineering and Design.* **23** : 99.

Shimizu, Y., Arai, H. and Seiyama, T. 1985. Theoritical studies on the impedance humidity characeristic of ceramic humidity sensors. *Sensors and Actuators.* **7** : 11-22.

Waldner, K.F., Laine, R.M., Dhumrongvaraporn, S., Tayaniphan, S. and Narayanan, R. 1996. Synthesis of a double alkoxide precursor to spinel ($MgAl_2O_4$) directly from $Al(OH)_3$, MgO and triethanolamine and its pyrolytic transformation to spinel. *Chem. Mater.* **8** : 2850-2873.

West, A.R. 1989. *Solid State Chemistry and Its Applications*. New York, John Wiley & Sons.

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