

Nanocrystalline Spinel from Freeze-Dried Nitrates: Synthesis, Energetics of Product Formation, and Cation Distribution

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The formation of MgAl_2O_4 from a freeze-dried nitrate precursor was studied by thermogravimetric analysis, differential thermal analysis, powder X-ray diffraction, transmission electron microscopy, ^{27}Al magic angle spinning NMR, and high-temperature solution calorimetry. A single phase, slightly alumina-rich spinel of composition $\text{Mg}_{0.957}\text{Al}_{2.028}\text{O}_4$ was obtained from the precursor by calcination at temperatures ≥ 1073 K. Transmission electron microscopy revealed that material calcined at 1073 K was nanocrystalline, with grain sizes on the order of 20 nm. ^{27}Al NMR revealed that this material had an unusually high degree of cation disorder, with an order parameter of 0.59 at room temperature. This degree of disorder, which has previously only been achieved in MgAl_2O_4 via neutron bombardment, provides strong thermodynamic evidence that the freeze-dried precursor contained a highly disordered and probably close to random mixture of cations. Significant levels of five-coordinated Al^{3+} were detected in amorphous samples calcined at 973 K. Increasing calcination temperatures resulted in a decrease in the percentage of tetrahedral Al^{3+} and a simultaneous increase in the average particle size of the material. Drop solution calorimetry in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 975 K revealed an enthalpy difference of 39.9 ± 7.4 kJ mol⁻¹ between the disordered nanophase MgAl_2O_4 synthesized at 1073 K and the well-crystallized material synthesized at 1773 K. Particle size, cation distribution, and adsorbed H_2O affect the energetics, with the surface energy term dominant.

Introduction

The solid-state reaction between MgO and Al_2O_3 yielding spinel, MgAl_2O_4 , is relatively well studied, and reports of the reaction mechanism,¹ kinetics,^{2,3} and thermodynamics^{4,5} are abundant in the literature. This makes MgAl_2O_4 an attractive material for evaluating the utility of a nonconventional solid-state synthesis, and indeed MgAl_2O_4 has been synthesized by numerous solution-based methods, such as spray-drying,⁶ freeze-drying (the cryochemical method),⁷ and sol-gel meth-

ods.⁸ These solution methods have the common goal of producing a precursor in which Al^{3+} and Mg^{2+} ions are intimately mixed, ideally on the atomic scale. This enhanced homogeneity greatly reduces the diffusion distance necessary for product formation and enables synthesis of traditionally high-temperature phases under comparatively mild reaction conditions. Because lower temperatures can often be used in such syntheses, limited sintering and grain growth occur and the production of nanocrystalline materials⁹ is possible in some systems. Although these methods are often suc-

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cessful in their goal of synthesizing high-quality materials under milder reaction conditions, the results are often wholly attributed to this shortening of diffusion paths (i.e., kinetic factors). With few exceptions,¹⁰ the energetics of the processes are ignored, and the differences in structure and energetics between nanocrystalline and coarse-grained samples have seldom been detailed.

MgAl₂O₄ is the parent compound of the spinel structure, which ideally consists of a cubic closest packing of O²⁻ ions with Al³⁺ ions occupying one-half of the octahedral interstices and Mg²⁺ ions occupying one-eighth of the tetrahedral interstices. However, deviations in the cation distribution in MgAl₂O₄ are common, especially at high temperatures. The cation distribution can be expressed as (Mg_{1-x}Al_x)[Mg_xAl_{2-x}]O₄, where x is an order parameter, and parentheses denote tetrahedral sites, square brackets octahedral. Then $x = 0$ corresponds to a "normal" spinel, $x = 2/3$ corresponds to a statistically random distribution, and $x = 1$ corresponds to an "inverse" spinel. Synthetic MgAl₂O₄ is generally 10–30% disordered (i.e., $x = 0.1$ – 0.3) when quenched from temperatures above ~ 1273 K.^{11–13} Natural MgAl₂O₄ specimens, which have slowly cooled over geologic time periods, have order parameters near zero.¹⁴ MgAl₂O₄ with a nearly inverse cation distribution has recently been obtained via neutron bombardment of single crystals.¹⁵ Here we describe the cryochemical preparation of MgAl₂O₄ with a nearly random cation distribution. The crystallization of MgAl₂O₄ from freeze-dried nitrates was studied through powder X-ray diffraction and simultaneous thermogravimetric and differential thermal analysis. The variation in cation distribution with increasing calcination temperature was studied by ²⁷Al magic angle spinning NMR, and the particle size and morphology of the materials was studied by transmission electron microscopy. High-temperature oxide melt solution calorimetry was used to study the evolution of the total energy of the material with heat treatment and to elucidate the energetic pathway to product formation.

Experimental Section

A. Freeze-Dried Precursor Preparation. The reagents used were Al(NO₃)₃·9H₂O and MgO ($\geq 99.9\%$ metal basis, Johnson Matthey). The Al(NO₃)₃·9H₂O was analyzed thermogravimetrically to determine its water content. A nitrate solution was prepared by dissolving 0.1000 mol of MgO and 0.2000 mol of Al(NO₃)₃·9H₂O in 2000 mL of distilled and

deionized H₂O acidified with 13.0 mL of 16.8 M HNO₃. Upon complete dissolution of the reagents, the solution was vacuum-filtered to reduce the concentration of dissolved gases. The resulting solution was then atomized through an ultrasonic spray nozzle (Sonotek) and rapidly frozen by allowing the aerosol to fall into rapidly stirred liquid nitrogen. The frozen solution was placed in a commercial freeze-drying apparatus and dried at a primary sublimation temperature of 243 K and a background pressure (at the condenser) of 45 mTorr. After several days sublimation was complete and the temperature of the sample was raised to 298 K at a rate of 5 K h⁻¹ yielding the *freeze-dried precursor*. Further details of the procedure are provided elsewhere.¹⁶

A portion of the original solution was not frozen but was evaporated to dryness by heating in open air to 353 K. The residual solid material was subjected to several of the experiments outlined below as a comparison, and to evaluate the effectiveness of the freeze-drying procedure with respect to phase purity and overall quality of products. This sample is referred to below as the *mechanical mixture*, to distinguish it from freeze-dried precursors which, ideally, have cations mixed on the atomic scale.

B. Thermal Processing. The freeze-dried Mg(NO₃)₂:2Al(NO₃)₃: n H₂O mixture contained significant amounts of H₂O, and the as-prepared material would dissolve in its waters of hydration upon thermal processing. This "melting" is a source of phase separation and destroys the intimate mixing of cations achieved through the freeze-drying procedure. Phase separation can be avoided if the waters of hydration are carefully removed below the solidus of the precursor. This was achieved by slowly (10 K h⁻¹) heating the precursor under vacuum (~ 1 Torr) to 338 K, holding at this temperature for 15 h, and then slowly heating to 383 K and holding at this temperature for 20 h. The resulting *dehydrated precursor* showed no visible signs of melting during calcination. Identical dehydration procedures were used for the mechanical mixture.

The dehydrated precursor was calcined in Pt crucibles by plunging into a box furnace (Lindberg model #51848) at temperatures ranging from 873 to 1373 K for 1 h. The samples were then quenched to room temperature by quick removal from the furnace. Additional samples were calcined at 1473, 1573, 1673, or 1773 K in a high-temperature furnace (Deltech DT31) by plunging the dehydrated precursor in Pt crucibles to 1073 K, heating at 50 K min⁻¹ to the desired temperature, holding at the desired temperature for 1 h, and cooling at 50 K min⁻¹ to 1273 K. They were then quenched from 1273 K to room temperature by quick removal from the furnace.

C. Precursor and Sample Characterization. The freeze-dried and dehydrated precursors were studied by powder X-ray diffraction (XRD) with a Scintag PAD V diffractometer using Cu K α radiation. Samples were mounted from an acetone slurry onto quartz zero-background plates. Data were collected from spinning samples while continuously scanning 2 θ at 1 °2 θ min⁻¹. Calcined MgAl₂O₄ samples were studied by XRD using identical equipment and procedures. Full widths at half-maximum were calculated using Pearson VII profiles by a curve-fitting program in the Scintag software. Dehydrated precursors were also studied by simultaneous thermogravimetric and differential thermal analysis (TGA/DTA) using a Netzsch STA 409. TGA experiments were run at a heating rate of 10 K min⁻¹ from 298 to 1773 K under flowing Ar or He.

²⁷Al magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy was performed using a home-built spectrometer based on a Nicolet 1280 data system. MAS was performed at 9–10 kHz at an H_0 magnetic field of 11.7 T (500 MHz 1H frequency) using a Doty Scientific probe. Pulse lengths were 1 ms, 1/6 of the solid 90° pulse length, to minimize possible differential signal loss and consequent spectral effects of a likely range of ²⁷Al quadrupole coupling constants in the samples. The amount of Al detected in a particular coordina-

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tion was determined via integration of the central spectral peaks. Because the Al[6] peak is broadened to negative chemical shift values due to unaveraged second-order quadrupole effects, the small Al[4] sideband sits on the tail of the Al[6] peak. This, along with the nonsymmetrical peak shape, made curve fitting difficult, and the peak areas obtained are accurate to only about $\pm 5\%$. However, the relative values, which were used to determine order parameters, are considerably more accurate (about $\pm 2\%$).

Bright field transmission electron microscopy (TEM) images were obtained using a Philips CM30 TEM. Powders were collected from an acetone suspension using a holey carbon grid. This grid was then air-dried and examined immediately.

D. Calorimetry. High-temperature drop solution calorimetry was performed in a Tian-Calvet twin microcalorimeter, which has been described in detail by Navrotsky,¹⁷ operating at ~ 975 K with $2\text{PbO}\cdot\text{B}_2\text{O}_3$ as the solvent. Samples were pressed into pellets of 10–20 mg, weighed on a semimicrobalance to ± 0.01 mg, and dropped from room temperature into the hot zone of the calorimeter. The measured heat effect is a combination of the heat content and heat of solution of the MgAl_2O_4 . The heat effect was calibrated with the heat content of Pt by dropping small (~ 250 mg) pieces of Pt wire from room temperature into the calorimeter. Due to the small particle size and high surface area, samples calcined below 1373 K readily adsorbed atmospheric H_2O . The removal of this adsorbed H_2O upon sample dissolution in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ also contributed to the measured heat effect. As it was very difficult to maintain a constant H_2O content in relatively anhydrous samples during pelletizing and handling prior to calorimetry, they were left exposed for several days to the precisely controlled atmosphere of the calorimetry laboratory (295 ± 1 K and $55 \pm 2\%$ relative humidity). The resulting steady-state water content was then determined by TGA/DTA (Netzsch STA 409) or by heating weighed pellets of the material to 1373 K for 12–20 h in Pt boats and attributing the weight loss of the sample to H_2O . To confirm that all weight loss could be attributed to H_2O , evolved gas analysis (EGA) was performed in conjunction with the TGA/DTA experiments with a Balzers MS500 Thermocube mass spectrometer, sampling the exit gas of the TGA/DTA system. To correct the solution calorimetric data for the heat effect due to removal of adsorbed H_2O , transposed temperature drop calorimetry, wherein the sample is dropped from room temperature into the calorimeter without solvent present, was performed on two of the hydrated nanophase MgAl_2O_4 samples. All calorimetric experiments were performed under flowing Ar (90 mL/min) to expel evolved $\text{H}_2\text{O}(\text{g})$ from the calorimeter and to avoid baseline shifts. The calorimetric procedures for dealing with hydrated phases have been previously established.¹⁸

Results and Discussion

A. Sample Characterization. The freeze-dried precursor was a white, highly voluminous and hygroscopic powder. The XRD pattern of the material (Figure 1) consisted largely of amorphous scattering with the only identifiable peaks being indexed to $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$. The largely amorphous XRD pattern from the precursor is evidence for a lack of long range order in the material. This is consistent with the achievement of an atomic level mixing of ions through the freeze-drying procedure. The detection of crystalline $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ may be the result of water adsorption and crystallization during sample mounting and data collection. This idea is supported by the detection of $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ peaks in the XRD pattern of the

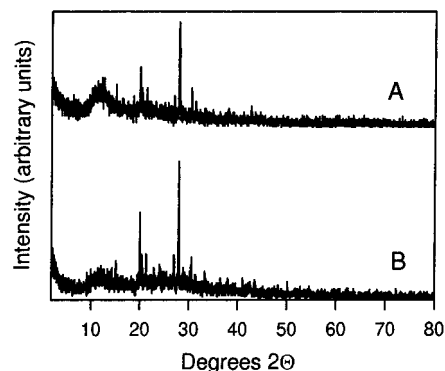
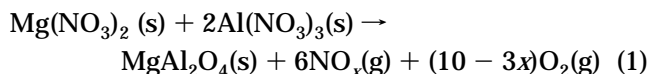


Figure 1. XRD patterns from (A) the freeze-dried precursor and (B) the dehydrated precursor. All identifiable peaks were indexed to $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$.

dehydrated precursor (Figure 1), which should not have contained any highly hydrated nitrates after the vacuum heat treatment.

Elemental analysis of the dehydrated precursor via ICP revealed a 1.000 Mg to 2.115 Al ratio in the material. Al_2O_3 and MgAl_2O_4 form a broad range of solid solutions,¹⁹ and the slight ($\sim 5\%$) excess Al_2O_3 does not phase separate but after calcination yields an alumina-rich spinel, $\text{Mg}_{0.959}\text{Al}_{2.028}\text{O}_4$. Assuming all of the Mg occupies tetrahedral sites, a more crystallographically accurate description of the material would be $(\text{Mg}_{0.959}\text{Al}_{0.027}\square_{0.014})[\text{Al}]_2\text{O}_4$, with \square denoting vacancies. This slightly alumina-rich stoichiometry was probably a result of adsorbed H_2O on the MgO used in preparation of the original solution. Although the exact composition of our samples is slightly different, the products will still be referred to below as MgAl_2O_4 , unless the stoichiometry has an obvious bearing on the result discussed.

The thermal decomposition of the dehydrated precursor was studied by simultaneous TGA/DTA. TGA revealed that the nitrate decomposition of the dehydrated precursor was essentially complete by 800 K (Figure 2A). The weight change of the dehydrated precursor from 298 to 1673 K was -69.4% . This value is slightly less than the theoretical weight change for the reaction



of -75.2% , which is not surprising, as the decomposition of $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ occurs through hydroxynitrate intermediates rather than anhydrous nitrates. (Various nitrogen oxide byproducts are possible, i.e., $\text{NO}_x = \text{NO}, \text{NO}_2$, etc.) The nitrate decomposition of the dehydrated precursor is also evident through DTA as a large endothermic peak at ~ 450 K and a second smaller endotherm at ~ 750 K. An exothermic peak was also detected at ~ 1073 K. This latter temperature corresponds to the lowest calcination temperature at which crystalline MgAl_2O_4 was detected by XRD (see below), and the exotherm is probably due to this amorphous to crystalline transition.

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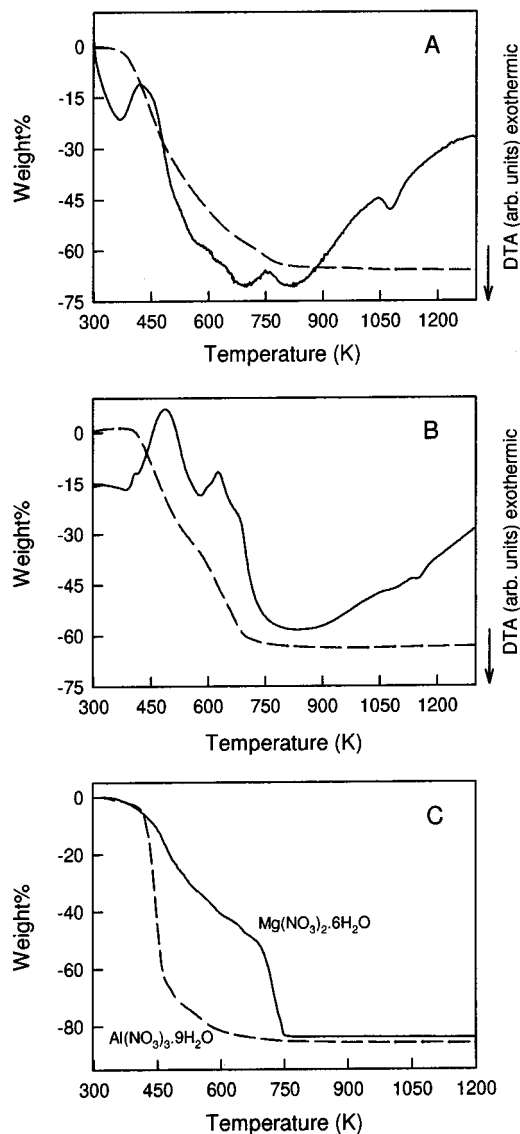


Figure 2. TGA (dashed line) and DTA (solid line) curves for (A) the dehydrated freeze-dried precursor, (B) the dehydrated mechanical mixture, and (C) individual $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (solid line) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (dashed line).

Some insight into the mixing of cations achieved through the freeze-drying process can be gained by comparison of the TGA/DTA data of the material with those obtained from the mechanical mixture. TGA of the dehydrated precursor (Figure 2A) gave a smooth, continuous curve, with little or no sign that two separate decomposition reactions may be occurring. The TGA curve from the mechanical mixture, however, clearly shows a shoulder beginning at ~ 573 K, and two discrete endotherms are seen by DTA below 673 K (Figure 2B). Comparison with TGA/DTA of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (as obtained from Johnson Matthey) suggests that the shoulder is due to decomposition of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the lower temperature decomposition is primarily that of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Figure 2C). The decomposition of the freeze-dried material is clearly different from that of the mechanical mixture, resembling that of a single phase. The decrease in intensity and shift to higher temperature of the ~ 1073 K exotherm of the mechanical mixture is evidence that MgAl_2O_4 can be obtained at lower processing temper-

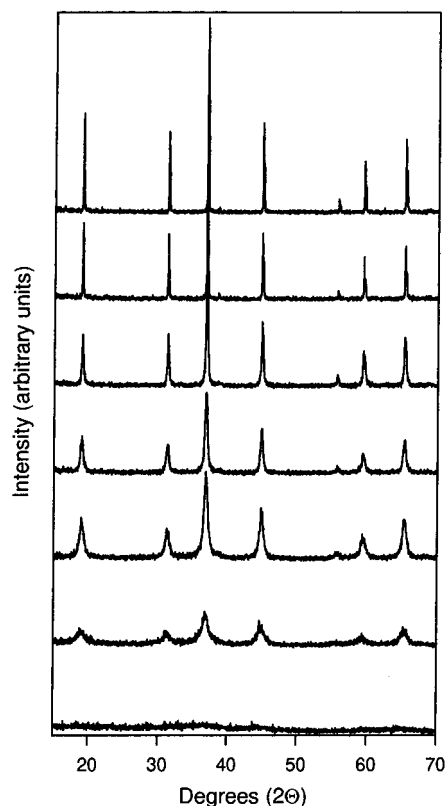


Figure 3. XRD patterns of MgAl_2O_4 samples obtained from calcination of the dehydrated precursor for 1 h at (from bottom) 973, 1073, 1173, 1273, 1373, 1573, and 1773 K. All peaks were indexed to MgAl_2O_4 .

atures through the use of freeze-dried nitrate precursors.

The XRD patterns of samples obtained by calcining the dehydrated precursor for 1 h at 973–1773 K vary significantly (see Figure 3). Material calcined below 1073 K was amorphous to X-ray diffraction. The XRD patterns of all samples calcined for 1 h at ≥ 1073 K showed single-phase MgAl_2O_4 . No impurity peaks were detected. Significant peak broadening due to small particle size was evident in samples calcined at ≤ 1373 K. A smooth and regular decrease of the full width at half-maximum (fwhm) of the 311 peak (most intense reflection in randomly oriented MgAl_2O_4) was evident with increasing calcination temperature (Table 1). The “excess broadening” (and therefore fwhm) of a diffraction line is inversely proportional to the particle size of the material by the Scherrer formula.²⁰ The regular decrease in fwhm indicates a regular increase in particle size with increasing calcination temperature, and suggests that the particle size of the MgAl_2O_4 may be selected by appropriate thermal processing. Similar behavior has been found in nanocrystalline BaTiO_3 prepared from freeze-dried nitrates.²¹ Although samples were calcined for 1 h, this length of time was not necessary for crystallization of MgAl_2O_4 at temperatures ≥ 1073 K. Calcination times of 10 min (shortest time period investigated) gave material with XRD patterns nearly identical to those of samples calcined for 1 h at

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Table 1. Results of Sample Characterization and Drop Solution Calorimetry Experiments

calcination temperature (K)	fwhm of 311 peak (deg 2 θ)	estimated surface area (m ² g ⁻¹)	order parameter x	measured ΔH_{ds} (kJ mol ⁻¹ MgAl ₂ O ₄ · n H ₂ O) ^a	wt % H ₂ O	n (mole fraction H ₂ O)	ΔH_{ds} (kJ mol ⁻¹ MgAl ₂ O ₄) ^d
873	b			273.31 \pm 2.10 (6)	20.10 ^c	1.98	72.5 \pm 19.9 ^c
973	b		1.0256	240.5 \pm 2.85 (8)	16.91	1.60	78.2 \pm 16.3
1073	1.098	140	0.5880	198.50 \pm 1.30 (13)	8.39	0.722	125.3 \pm 7.3
1173	0.644	78	0.3776	163.21 \pm 1.44 (7)	2.92	0.237	139.2 \pm 2.8
1273	0.402	45	0.3496	155.45 \pm 0.56 (3)	1.06	0.084	146.9 \pm 1.0
1373	0.260	25	0.3084	161.63 \pm 1.01 (13)	0.79	0.063	155.2 \pm 1.2
1473	0.117	5.7		159.91 \pm 0.88 (4)	0.00	0.00	159.9 \pm 0.9
1573	0.093	2.5	0.2412	164.19 \pm 1.08 (12)	0.00	0.00	164.2 \pm 1.1
1673	0.085	1.4		162.43 \pm 0.78 (6)	0.00	0.00	162.4 \pm 0.8
1773	0.075	0		165.17 \pm 0.97 (7)	0.00	0.00	165.2 \pm 1.0

^a Reported uncertainties are two standard deviations of the mean. Numbers in parentheses is the number of experiments performed.

^b These samples were amorphous to XRD. ^c Sample also contained adsorbed NO_x. ^d Heat effects were corrected for H₂O removal using 101.4 \pm 10.0 kJ mol⁻¹ H₂O.

the same temperature. This is a dramatic increase in reaction rate over that achieved through conventional ceramic processing. For example, a kinetic study by Beretka and Brown² has shown that reaction of a mechanical mixture of 1–3 μ m particles of MgO (periclase) and Al₂O₃ (corundum) does not reach completion after 90 h at 1573 K.

To study the morphology and particle size of the material, transmission electron microscopy was performed on a sample calcined for 1 h at 1073. Figure 4A shows a low-magnification bright field image of a single MgAl₂O₄ agglomerate. The material has an interesting fiberlike morphology, which might have resulted from rapidly escaping gases during nitrate decomposition. Higher magnification images (Figure 4B) show that this agglomerate is nanocrystalline, comprised of crystallites with linear dimensions in the range 10–20 nm. No amorphous material was detected by TEM.

The variation in cation distribution in the MgAl₂O₄ with increasing calcination temperature was studied by ²⁷Al magic angle spinning NMR (Table 1). O'Reilly²² examined the solid-state ²⁷Al NMR of α -Al₂O₃ and γ -Al₂O₃ and found that the NMR signal intensity from a constant number of Al nuclei decreased with increasing specific surface area. He concluded that the first two molecular layers of the Al₂O₃ do not contribute to the NMR signal, and attributed this to a large electric field gradient on these surface Al atoms. More recently, Huggins and Ellis²³ have examined this phenomenon. Although agreeing that the surface Al do not contribute to the NMR signal, they attributed the loss of intensity to dynamic events on the surface involving adsorbed OH and H₂O groups. In either case, our NMR data should likewise mainly reflect the bulk cation distribution. The amorphous material obtained via calcination at 973 K contained approximately 10% of the Al³⁺ in 5-fold coordination and a higher percentage of tetrahedral aluminum than octahedral aluminum. Pentacoordinated Al³⁺ has been previously detected in nanocrystalline γ -Al₂O₃, which suggests that the amorphous material is very similar to a transitional alumina.²⁴ The percentage of octahedrally coordinated Al³⁺ increased fairly regularly with increasing calcination temperature (see Table 1). The order parameter of the sample

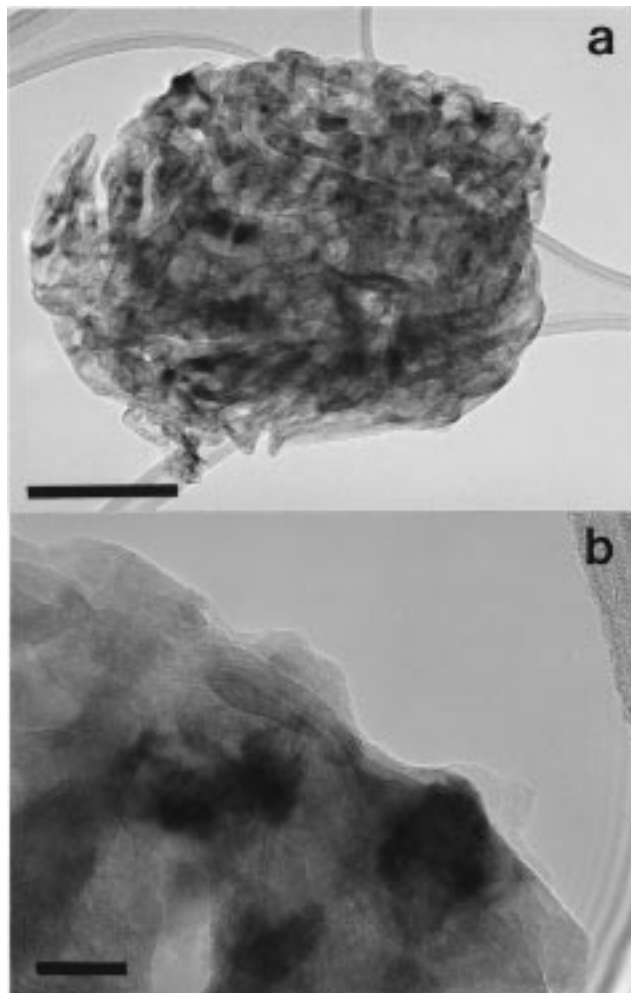


Figure 4. (A) A bright field TEM image (scale bar = 200 nm) of an agglomerate of MgAl₂O₄ synthesized at 1073 K and (B) a higher magnification image (scale bar = 20 nm) of a region of the same particle.

calcined at 1073 K, 0.59, is near the value (0.667) for a completely random distribution. The large percentage of Al³⁺ in tetrahedral sites cannot be attributed to the off-stoichiometry of our samples. The excess alumina (actual composition was Mg_{0.959}Al_{2.027}O₄) can only be responsible for an additional 4% of Al in tetrahedral sites or an increase in x of 0.04. This sample still has an order parameter >0.50 even when considering the Mg deficiency. This is the highest degree of inversion ever observed at room temperature in MgAl₂O₄ without the use of neutron bombardment.¹⁵

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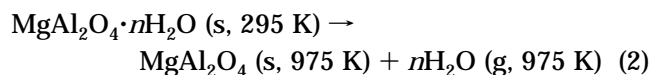
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The high degree of cation disorder in this sample suggests that the freeze-drying procedure produces a precursor with a random mixture of cations. The equilibrium degree of disorder parameter for MgAl_2O_4 at 1073 K is ~ 0.3 .^{12,13} The greater disorder observed in our sample synthesized at 1073 K is likely a result of an initially random mixture of cations in the freeze-dried precursor and mild calcination conditions.

B. Calorimetry. High-temperature drop solution calorimetry was used to study the evolution of the total energy of the material with heat treatment and elucidate the energetic pathway to product formation. The MgAl_2O_4 samples readily dissolved in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at ~ 975 K, and the calorimeter signal usually returned to a stable baseline in less than 1 h after dropping a sample into the solvent. As discussed above, the heat effect measured by drop solution calorimetry has three contributions; the heat content of MgAl_2O_4 between 298 and 975 K, the heat of desorbing and heating of H_2O to 975 K, and the heat of solution of the MgAl_2O_4 in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 975 K. The equilibrium adsorbed H_2O content of the samples is given in Table 1. Once the calorimetric data is corrected for heat effects due to removal of this H_2O , the final state of all experiments is the same (i.e., a dilute solution of MgO and Al_2O_3 in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at 975 K). Any difference in the corrected enthalpy of drop solution, ΔH_{cds} , then gives directly the enthalpy difference between the samples at room temperature. In general, ΔH_{cds} became more endothermic with increasing calcination temperature. The major factors contributing to this increase were crystallization, changes in cation distribution, and decreases in surface area. To evaluate these factors further, it is necessary to discuss the correction of the calorimetric data for the heat of removal of H_2O , $\Delta H_{\text{H}_2\text{O}}$.

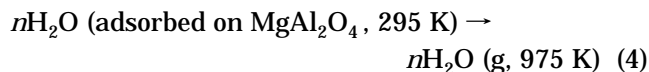
1. *Correction for Adsorbed H_2O .* The enthalpies of drop solution of MgAl_2O_4 samples from the dehydrated precursor calcined at varying temperatures appear in Table 1. Also included are the equilibrium weight percentages of adsorbed H_2O on the samples as determined by TGA. To determine $\Delta H_{\text{H}_2\text{O}}$ and to correct the data for heat effects due to adsorbed H_2O , transposed temperature drop calorimetry was performed on samples calcined for 1 h at 1073 and 1173 K. As these samples had been calcined at a temperature more than 100 K higher than the calorimeter temperature, little to no grain growth or cation ordering would be expected to occur during transposed temperature drop calorimetry, and heat effects due to dehydration can be isolated. In these experiments, pellets of nanophase $\text{MgAl}_2\text{O}_4\cdot n\text{H}_2\text{O}$ were dropped into the calorimeter in the absence of solvent. The measured heat effect, ΔH_{tid} , which corresponds to the reaction



was 171.9 ± 2.2 kJ per mole of $\text{MgAl}_2\text{O}_4\cdot 0.722$ H_2O for the 1073 K sample and 118.7 ± 0.6 kJ per mole of $\text{MgAl}_2\text{O}_4\cdot 0.160$ H_2O for the 1173 K sample. These heat effects contain two contributions. The first is the heat content of anhydrous MgAl_2O_4



and the second is due to the removal and heating of adsorbed H_2O



The heat content of anhydrous MgAl_2O_4 (reaction 3) was determined from transposed temperature drop calorimetry on a sample calcined for 24 h at 1773 K to be $+103.29 \pm 0.71$ kJ mol^{-1} , which is slightly smaller than the reported value, $+106.95$ kJ mol^{-1} MgAl_2O_4 .²⁵ Some of this difference could be due to the nonstoichiometry. To determine $\Delta H_{\text{H}_2\text{O}}$, we subtracted our value for the heat content from the ΔH_{tid} obtained from the hydrated samples and attributed the remaining heat effect to the removal and heating of the adsorbed H_2O . The resulting average value for both samples was then $\Delta H_{\text{H}_2\text{O}} = +96.6 \pm 4.3$ kJ $(\text{mol H}_2\text{O})^{-1}$. As in our previous study of nanophase aluminas,²⁶ TGA revealed that $\sim 5\%$ of the equilibrium adsorbed H_2O content was not removed after a 1 h heat treatment at 975 K. It is therefore likely that all of the adsorbed H_2O was not removed during transposed temperature drop calorimetry. The integral heat of H_2O desorption for the entire equilibrium coverage is then at least 5% greater than our measured value, and we adopt 101.4 kJ $(\text{mol H}_2\text{O})^{-1}$ with an estimated uncertainty of ± 10 kJ $(\text{mol H}_2\text{O})^{-1}$ for $\Delta H_{\text{H}_2\text{O}}$. This correction was then applied to the ΔH_{ds} data from all hydrated samples to yield the corrected enthalpy of drop solution calorimetry, ΔH_{cds} (Table 1). Evolved gas analysis of the sample calcined at 873 K showed the presence of adsorbed NO and NO_2 . Calorimetry was performed on this sample, but these results should be considered suspect as the presence of NO_x introduces some uncertainty into the initial and final states (before and after solution in $2\text{PbO}\cdot\text{B}_2\text{O}_3$) of the material. Samples calcined at higher temperatures evolved no detectable NO_x .

2. *Energetic Trends with Increasing Calcination Temperature.* Navrotsky et al.²⁷ directly measured the enthalpy of solution in $2\text{PbO}\cdot\text{B}_2\text{O}_3$ at ~ 975 K of conventionally synthesized MgAl_2O_4 to be $+61.07 \pm 0.92$ kJ mol^{-1} , and earlier Charlu et al.²⁸ measured this value as $+59.58 \pm 0.58$ kJ mol^{-1} . Adding our measured heat content of $\text{Mg}_{0.957}\text{Al}_{2.028}\text{O}_4$, 103.29 ± 0.72 kJ mol^{-1} , places these values in fair agreement with the fully crystallized samples in this study (those calcined at $T \geq 1573$ K). Samples calcined below 1573 K gave lower values of ΔH_{cds} , which indicates metastability in these samples. Figure 5 shows a fairly regular increase in ΔH_{cds} with increasing calcination temperature. A large jump in ΔH_{cds} occurs between the samples calcined at 973 and 1073 K. On the basis of the TGA/DTA and XRD studies mentioned above, we can attribute this jump to crystallization of MgAl_2O_4 from an X-ray amorphous phase. The enthalpy difference between these samples,

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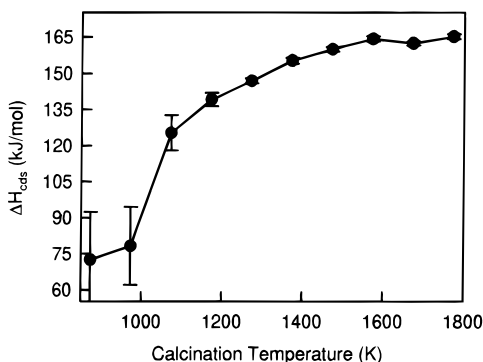
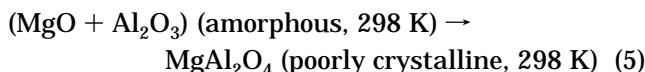
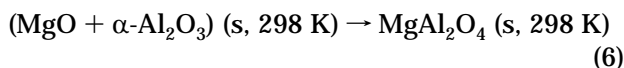


Figure 5. The corrected enthalpy of drop solution data, ΔH_{cds} , as a function of calcination temperature.

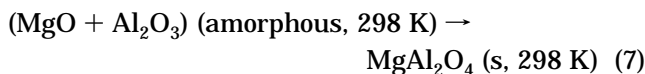
$-47.1 \pm 17.9 \text{ kJ mol}^{-1}$, which represents the reaction



may be compared to the enthalpy of the reaction



where “s” refers to well-crystallized solids, $-36.5 \pm 1.1 \text{ kJ mol}^{-1}$.⁴ The material synthesized at 1073 K is still $39.9 \pm 7.4 \text{ kJ mol}^{-1}$ less stable energetically than that synthesized at 1773 K. Therefore the reaction



is accompanied by an enthalpy change of $-87.0 \pm 16.3 \text{ kJ mol}^{-1}$. This shows that the energetic pathway to fully crystallized MgAl_2O_4 from the amorphous material is highly exothermic compared to the reaction of a mechanical mixture of MgO (periclase) and Al_2O_3 - (corundum), suggesting that there are thermodynamic benefits to synthesis of materials through freeze-drying in addition to the well-documented kinetic enhancements.^{7,16} As the products of reactions 6 and 7 are identical (well-crystallized MgAl_2O_4), the extra enthalpy of reaction 7 is solely due to the energetic instability of the poorly crystalline reactants relative to corundum and periclase. This instability places the amorphous phase obtained from freeze-dried nitrates higher in the system's potential energy diagram, which makes accessible any metastable states lying energetically above a mechanical mixture of coarse-grained $\alpha\text{-Al}_2\text{O}_3$ and MgO. The MgAl_2O_4 calcined at 1073 K is actually metastable (or only entropy-stabilized) with respect to a mixture of coarse-grained $\alpha\text{-Al}_2\text{O}_3$ and MgO, and such material would not be accessible through conventional ceramic processing of coarsely crystalline reactants.

3. Energetic Trends with Variation in Cation Distribution and Particle Size. Some of the increase in ΔH_{cds} for the MgAl_2O_4 samples with increasing calcination temperature can be attributed to changes in cation distribution. The interchange enthalpy was approximated by Navrotsky and Kleppa²⁹ to be about -46 kJ mol^{-1} . ΔH_{cds} decreases fairly regularly with increasing

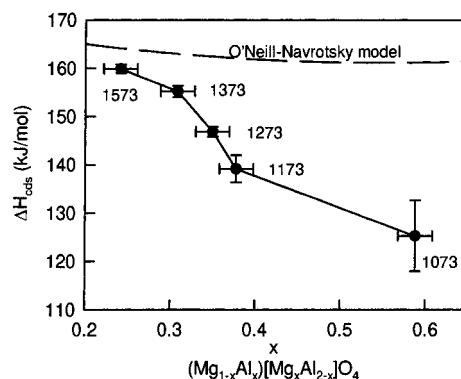


Figure 6. The corrected enthalpy of drop solution data, ΔH_{cds} , as a function of the order parameter, x , determined by ^{27}Al MAS NMR. The dashed line shows how the ΔH_{cds} should vary with the O'Neill-Navrotsky³⁰ model and Maekawa's³¹ coefficients (see text).

x . Following Navrotsky and Kleppa²³ and assuming a constant dependence of the enthalpy of disordering, ΔH_{D} , a linear fit through the data yields $\sim 100 \text{ kJ mol}^{-1}$ as the interchange enthalpy of Mg^{2+} and Al^{3+} in the spinel structure, which is over twice the value estimated by Navrotsky and Kleppa.²³ O'Neill and Navrotsky³⁰ suggested that ΔH_{D} in simple spinels can be expressed as a quadratic function of the type

$$\Delta H_{\text{D}} = \alpha x + \beta x^2 \quad (8)$$

where x is again the order parameter and α and β are empirically determined coefficients that depend on the charge and ionic radii of the metal ions under consideration. The coefficients for MgAl_2O_4 were recently evaluated by Maekawa et al.³¹ as $\alpha = 35 \text{ kJ mol}^{-1}$ and $\beta = -32 \text{ kJ mol}^{-1}$. Attempts at fitting our data (Figure 6) to this model yield coefficients which are 1 order of magnitude greater than these values. These problems may occur because coarsening occurs simultaneously with cation ordering, making it impossible to separate their energetics.

Assuming negligible surface energy in the 1573 K sample, Figure 6 shows how ΔH_{cds} should vary, as calculated using the O'Neill-Navrotsky model and Maekawa's³¹ coefficients. The difference between the predicted and observed values should then be due to excess surface energy. This difference (Figure 7) is a nearly linear function of the fwhm of the 311 XRD peak, strongly supporting such a role of the surface energy. Due to a limited supply of material we did not quantitatively determine the specific surface area of these samples. However, if one assumes a uniform distribution of spherical particles of diameter d , (or cubes with side of length d) the specific surface area, A_{surf} , can be estimated via simple geometric arguments such as

$$A_{\text{surf}} = 6/\rho d \quad (9)$$

where ρ is the density of the material ($3.58 \times 10^6 \text{ g m}^{-3}$ for MgAl_2O_4). Because the broadening of a diffraction peak is inversely proportional to the particle size of the material, it is directly proportional to the specific surface

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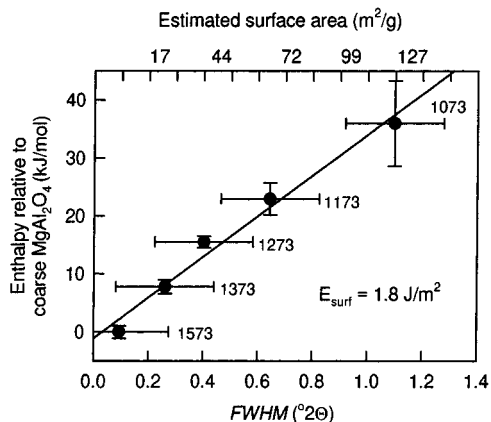


Figure 7. The enthalpy difference between the MgAl_2O_4 samples and the predictions of the O'Neill-Navrotsky³⁰ model and Maekawa's³¹ coefficients as a function of the order parameter, x . Upper axis is the estimated surface area of the samples based on the fwhm (see text). The error bars on the ordinate correspond to the uncertainty in estimated surface area. The surface energy calculated from the slope of the line is $1.8 \pm 0.3 \text{ J m}^{-2}$.

area

$$\text{fwhm} \propto \frac{1}{d} \propto \frac{\rho A_{\text{surf}}}{6} \propto A_{\text{surf}} \quad (10)$$

By comparison with the amount of H_2O adsorbed on $\gamma\text{-Al}_2\text{O}_3$ samples of known specific surface area under the same humidity and temperature conditions,²⁶ we estimate the surface area of the sample calcined at 1073 K to be $140 \pm 15 \text{ m}^2 \text{ g}^{-1}$. Assuming spherical crystallites, this corresponds to particle dimensions of $\sim 15 \text{ nm}$, which is in fairly good agreement with our TEM observations. The fwhm of the 311 XRD peak of this

sample is $1.098^\circ 2\theta$. Thus, we can estimate the surface areas of the other samples based on the excess broadening (i.e., the difference between the respective fwhm and the fwhm obtained from the coarse sample calcined at 1773 K, $\text{fwhm}_{1773\text{K}}$) of the 311 diffraction peaks as

$$A_{\text{surf}} = [(\text{fwhm} - \text{fwhm}_{1773\text{K}})/(1.098^\circ 2\theta - \text{fwhm}_{1773\text{K}})]140 \text{ m}^2 \text{ g}^{-1} \quad (11)$$

Table 1 and the upper axis in Figure 7 show the resulting estimated surface areas. From the slope of the line in Figure 7 we calculate the specific surface energy of the MgAl_2O_4 as $1.8 \pm 0.3 \text{ J m}^{-2}$. This is a reasonable value for a metal oxide surface energy³² and fairly close to the 1.67 J m^{-2} we recently determined for $\gamma\text{-Al}_2\text{O}_3$,²⁶ which is chemically and structurally similar to MgAl_2O_4 . Since we do not know the specific surface areas accurately, this surface energy should be viewed cautiously. However, its magnitude does suggest that the increase in ΔH_{cds} with increasing calcination temperature is dominated by the surface energy term.

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