

# Synthesis of magnesium–aluminium spinel from autoignition of citrate–nitrate gel

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## Abstract

Magnesium–aluminium spinel has been synthesized by citrate–nitrate route using hydrated nitrates of Mg and Al as the precursors with a citrate–nitrate ratio of 1:1. Self-ignition of the gel-like mass yielded a black mass, which crystallized to Mag–Al spinel on calcination at 650 °C for 9 h. The crystallized mass was a mixture of ordered and disordered phases of Mag–Al spinel. Phase pure-ordered spinel could be obtained for powders calcined at 1100 °C and above. The green compacts of the spinel powders could be sintered to near theoretical density at 1150 °C for 30 min. The activation energy for densification was calculated (16.4 kcal/mol) assuming Arrhenius type behaviour. The densification mechanism could be assigned to the ordering of the disordered spinel involving vacancy diffusion through the surface.

*Keywords:* Autoignition; Citrate–nitrate gel; Black ash; Order–disorder Mag–Al spinel

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## 1. Introduction

Magnesium–aluminium spinel (Mag–Al spinel) is an important advanced ceramic material possessing useful mechanical properties and wide range of applications even up to very high temperatures. Apart from being an important refractory material, it is also used in advanced areas like high-temperature arc-enclosing envelopes, humidity and infrared sensors, transparent windows, domes, and as armour materials [1]. Various chemical synthesis routes have been adopted for production of single-phase spinel powders such as flame spray pyrolysis [2], precipitation from organo-metallic precursors [2,3], combined gelation and precipitation from inorganic salt solutions [4], etc. However, all of the above processes involve a high-temperature calcination step for crystallization. Moreover, the processing of high-density single-phase stoichiometric Mag–Al spinel is rather difficult. High-density spinel is usually prepared either by employing high sintering temperature and/or use of oxygen ambient [5] or by the use of specialized and expensive techniques like hot pressing [5], cold isostatic pressing followed by sintering [6], and hot isostatic pressing [7].

It is well known that low-temperature densification of single-phase spinel requires ultrafine and chemically homogeneous powder. Combustion synthesis processes, characterized by high temperatures, fast heating rates, and short reaction times, have been found suitable for synthesizing ceramic powders for advanced applications [8]. Ultrafine oxide ceramic powders of Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, BaTiO<sub>3</sub>, LaCrO<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> have been produced by Combustion Synthesis [8–10] utilizing the exothermic redox reactions between an oxidizer (metal nitrates) and a fuel (amides, urea, hydrazine, etc). The fuels used are sources of C and H and liberate heat. At the same time, they form complexes with the metal ions facilitating homogeneous mixing of the cations in solution [8]. Bhaduri et al. [9,10] prepared both stoichiometric and nonstoichiometric Mag–Al spinel by combustion synthesis using urea as a fuel and metal nitrates as oxidizers.

The present paper discusses the processing and sintering of phase pure Mag–Al spinel by autoignition process. Magnesium and aluminium nitrates have been used as the oxidizers and citric acid as the fuel. Addition of citric acid to the mixture of magnesium and aluminium nitrate results in a series of redox reactions to form a citrate–nitrate complex which subsequently crystallizes to form spinel at a lower temperature. Results on the phase evolution and powder sinterability have been reported. A

probable mechanism for low-temperature densification has also been suggested.

## 2. Experimental

The precursors were analytical reagent grade  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and citric acid (E-merck, India). The nitrate salts were dissolved separately in doubly distilled water, concentration of each nitrate solution being 0.5 mol/l. For preparing a stoichiometric spinel, the two solutions were mixed in a ratio so as to yield a 2:1 molar ratio of Al and Mg, respectively. Aqueous solution of citric acid was added to the mixed nitrate solution. The molar ratio of citrate to nitrate ions in the solution was maintained at 1:1 so as to bind all metal ions to form a citrate–nitrate complex. The mixed citrate–nitrate precursor solution was continuously stirred on a hot plate, which resulted in a thickened brown viscous gel-like mass along with the evolution of brown gases (probably  $\text{NO}_x$  type). Further heating caused slow ignition of the gel forming a black residue called black ash.

DTA of the gel was conducted till 1200 °C in air using  $\alpha\text{-Al}_2\text{O}_3$  as diluent. A computerized data acquisition system (Agilent Tech, USA) was used for recording and analyzing the data. The heating rate was 10 °C/min. TG analysis of the dried gel was also carried out up to 1200 °C in air. X-ray diffractometer (Model PW 1730, Philips, Holland) was used for the phase analysis of the powders calcined at different temperatures using  $\text{Cu-K}\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at an accelerating voltage of 30 kV and 25 mA and a scan rate of  $2^\circ \text{ min}^{-1} 2\theta$ . The powder samples were mounted on a flat XRD plate and scanned at room temperature in the range  $20^\circ \leq 2\theta \leq 80^\circ$ . The calcined powders were mixed with 2 wt.% PVA solution and granulated. The granulated powders were uniaxially compacted at 300 MPa into cylindrical pellets of 12.5-mm diameter and 3-mm thickness. These pellets were sintered for 30 min in the temperature range of 650–1300 °C. Bulk density of the sintered pellets was measured using Archimedeian principle with a Toledo microbalance. Densification behaviour of the sintered pellets was studied as a function of sintering temperature. For studying the densification kinetics, some other pellets were sintered between 1000 and 1200 °C for holding time ranging between 30 min and 2 h.

## 3. Results and discussion

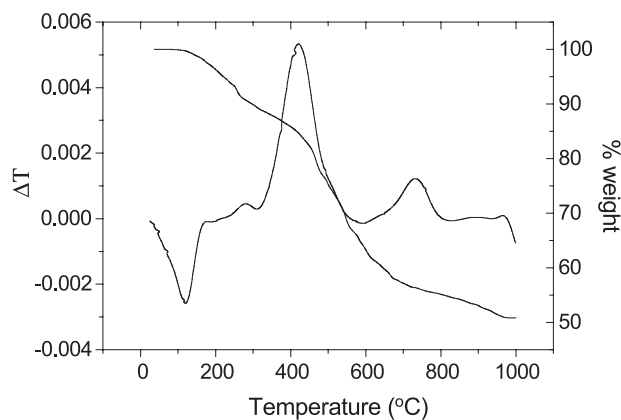
The citrate–nitrate gel synthesis follows a series of oxidation and redox reactions to finally yield an ash. When the precursor solution (mixed solution of the metal nitrate and citric acid) is heated at around 80–100 °C, dehydration takes place followed by gelation. The gelation probably results due to the formation of a metal–citrate–nitrate complex. On continued heating, the decomposition

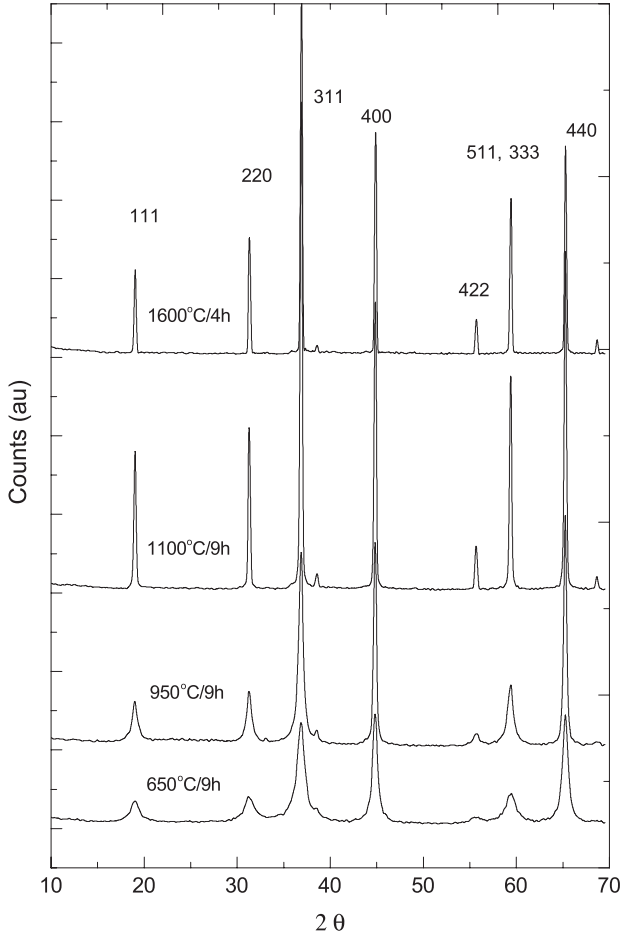
of the nitrates takes place with the evolution of gases like  $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}_5$ . The resulting swelling and effervescence of the gel is accompanied by the evolution of brown gases ( $\text{NO}_x$  type) during this stage. This reaction is followed by the formation of a metal–citrate complex in the form of a black ash, which is the end product of the synthesis.

The DTA of the gel (Fig. 1) shows an endothermic peak at around 100 °C, resulting from the dehydration of the gel. The TG curve also shows a corresponding small weight loss at that temperature. A very large exothermic peak is observed at about 420 °C with a corresponding weight loss in the TG curve, which may be due to the oxidation of the metal–citrate complex. The broad nature of the peak indicates that the ignition takes place over a range of temperature. Further heating produces a small and broad exothermic peak at 700 °C with an onset temperature of 600 °C, which corresponds to the crystallization of  $\text{MgAl}_2\text{O}_4$  spinel from black ash. Usually, crystallization peaks are sharp and without any weight loss. However, in this case, a broad peak is observed with an associated weight loss as observed in TG. Thus, the exothermic peak represents two simultaneous processes, one being the crystallization of spinel and the other being the oxidation of carbonaceous matter present in the black ash.

The X-ray analyses of the calcined powders are in support of this above argument (Fig. 2). The X-ray diffractogram of the black ash showed a broad and diffused peak confirming amorphous nature of the ash (not shown in Fig. 2). The powder remains amorphous even after calcination at 550 °C. However, peaks corresponding to  $\text{MgAl}_2\text{O}_4$  spinel start appearing in the powders calcined at 650 °C. The phase evolution of calcined powders can be deliberated with reference to the diffraction patterns of a fully ordered spinel (ICDD File Card no. 21-1152) and a simulated powder X-ray diffraction model for disordered spinel as proposed by Sickafus [11].

The X-ray powder diffraction patterns for powders calcined at 650 °C for 9 h showed intensity peaks corres-





ponding to that of  $\text{MgAl}_2\text{O}_4$  spinel. The lattice constant was also calculated to be 8.089 Å which is the same as the lattice constant of a fully ordered spinel. However, the reported value for the 100% peak of a fully ordered spinel is  $36.85^\circ$  in contrast to the present study where the maximum peak was observed at a  $2\theta$  of  $44.88^\circ$ . The referred simulation model by Sickafus suggests that there could be a host of disordered spinel phases (also called metastable spinels), either having cation vacancies or different cation arrangements inside the FCC anion lattice. The reflections from  $\{222\}$ ,  $\{400\}$ , and  $\{440\}$  planes only (considering an anion lattice of size 8.089 Å) account for the diffraction patterns of a metastable spinel. The model also suggests that all-odd-indices reflections (e.g. the reflections from  $\{111\}$ ,  $\{311\}$ ,  $\{331\}$ , and the like planes) are forbidden in the disordered spinel structure and are found only in ordered spinels. The presence of all-odd-indices reflections along with higher peak intensities of 440 and 400 reflections is suggestive of the fact that the powder calcined at  $650^\circ\text{C}$  contains a mixture of ordered as well as disordered spinel phases. This is an interesting observation as the formation of disordered spinel is normally observed in neutron-irradiated/ion-irradiated processes. Although disordered phase formation due to

chemically induced phase transformation has also been reported for spinel-like compounds [12], formation of disordered Mag–Al spinel from an autoignition process has not been reported previously.

In the present study, the peak intensity of 311 reflection ( $2\theta = 36.85^\circ$ ) accounts only for the ordered spinel, whereas the peak from 400 reflection has contributions both from the ordered as well as the disordered spinel in the calcined powders (Fig. 2), which probably accounts for the higher intensity of the 400 reflection ( $2\theta = 44.83^\circ$ ). The same argument can be applied to the 440 reflection ( $2\theta = 65.24^\circ$ ), in which case also X-ray peak appears from the combined effect of ordered as well as disordered spinels. Based on the simulated model for different types of disordered spinel structures as proposed by Sickafus [11], it can be inferred that the disordered spinel phase is one of the cation-deficient metastable spinel structures. At the same time, the absence of an intense peak for the 222 plane ( $2\theta \sim 38^\circ$ ) suggests that the disordered phase may be of the metastable rock salt-type spinel with disorder in the cation arrangements in the oxygen sublattice [11]. This type of metastable structure has also been found for irradiation-induced spinels by Ishimaru et al. [13].

For powders calcined at higher temperatures (Fig. 2), the intensity ratios of the peaks show gradual change. The gradual increase in the 311 peak ( $2\theta = 36.85^\circ$ ) indicates that ordering takes place in the spinel powders with higher calcination temperature. Similar trend is observed for all-odd-indices planes. A quantitative estimation on the amount of ordered phase present is attempted in our study by comparing the peak intensity at  $2\theta$  of  $36.85^\circ$  (i.e. 311 plane, the maximum peak position for a fully ordered spinel) to that at  $2\theta$  of  $44.83^\circ$  (i.e. 400 plane, the maximum peak position of the rock salt-type metastable spinel) with the following formula, adopted in a way similar to that proposed by Toroya et al. [14] for  $\text{ZrO}_2$  system.

Fraction of ordered phase in the powders

$$= [I_{\text{O}} / (I_{\text{O}} + I_{\text{D}})] \quad (1)$$

where  $I_{\text{O}}$  = intensity of the 311 plane (ordered phase),  $I_{\text{D}} = I_{\text{C},400} - I_{\text{O},400}$  = contribution of the intensity of the disordered phase in the 400 plane,  $I_{\text{C},400}$  = intensity of the 400 plane (containing both ordered and disordered phase), and  $I_{\text{O},400}$  = contribution of the intensity of the ordered phase in the combined 400 plane.

The amount of ordered spinel phases present in powders calcined at different temperatures is presented in Table 1. Powders calcined at  $1100^\circ\text{C}$  for 9 h and at higher temperatures showed complete orderness (Fig. 2). All the peaks in these powders not only corresponded to that of fully ordered spinel phase (ICDD file card no 21-1152), but also the relative intensities of peaks corresponding to the reflections from different planes matched with the referred pattern. Powders calcined at  $1600^\circ\text{C}$  also showed

Table 1  
Variation in degree of orderness of Mag–Al spinel as a function of calcination temperature

Calcination condition of the powders	Degree of orderness	Phases present
650 °C for 9 h	0.65	ordered spinel, metastable spinel
950 °C for 9 h	0.86	ordered spinel, metastable spinel
1100 °C for 9 h	1	fully ordered spinel
1600 °C for 4 h	1	fully ordered spinel

complete orderness and it may be inferred from this observation that the spinel powders synthesized by this route are thermally stable up to 1600 °C and that no decomposition or second-phase formation occurs till this temperature.

The kinetics of crystallization of MgAl<sub>2</sub>O<sub>4</sub> is related to temperature in a complex way. Crystallization of spinel from MgO and Al<sub>2</sub>O<sub>3</sub> powders by mixed oxide route is difficult due to the lower free energy of the calcined oxides. However, powders synthesized through most chemical routes are amorphous in nature and are therefore easy to crystallize. In a citrate–nitrate gel process, cations are contained in the gel as a homogeneous mixture which results in oxides with uniform composition on the molecular scale. Moreover, the extremely high exothermicity of the oxidation of metal–citrate complex not only sustains the reaction, but also brings down the crystallization temperature of the spinel.

The peaks were broad indicating the fineness of the powders. Calcination at higher temperatures did not change the peak position, but the peaks became sharper and higher in intensity indicating an increase in crystallite size. The average crystallite size was calculated from peak broadening using Scherrer's formula [15] with silicon as internal standard:

$$D \text{ (nm)} = \frac{0.89\lambda}{B\cos\theta_B} \quad (2)$$

where  $D$ =average crystallite size,  $\lambda$ =wavelength of the X-ray radiation,  $\theta_B$ =Bragg angle, and  $B$ =full width at half maximum intensity.

The crystallite size was found to be 12 nm for the powders calcined at 650 °C for 8 h. The crystallite size increased with higher calcination temperatures and the maximum size was found to be 32 nm for powders calcined at 1100 °C.

Fig. 3 shows the variation of sintered density of pellets as a function of sintering temperature for a holding period of 30 min at each temperature. It can be seen that even at 650 °C, the density increased from a green density of 2.18 to 3.19 g/cm<sup>3</sup>. The increase in density becomes rapid at higher temperatures, and maximum density of 3.58 g/cm<sup>3</sup> (i.e. 99% of theoretical density) could be achieved at 1150 °C with

30-min holding. This is a significant reduction in sintering temperature as compared to the reported works where theoretical density is achieved at 1450 °C for powders synthesized by combined gel precipitation routes [4] and 1500 °C for powders from alkoxide route with hot isostatic pressing [3].

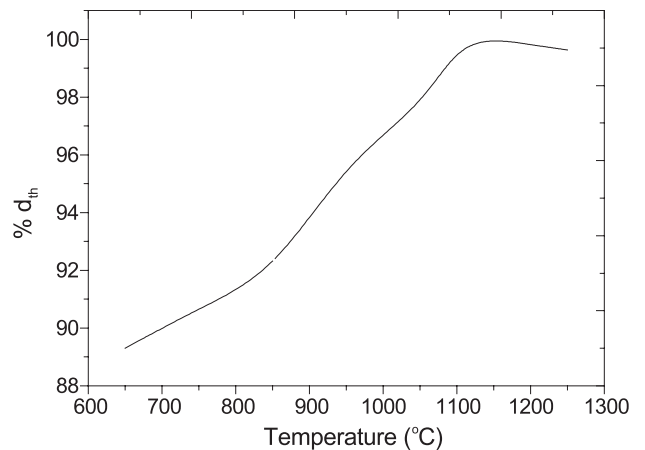
The variation of density with sintering time has been studied in the temperature range of 1100–1300 °C. The density of the sample was found to have rather a strong dependence on the sintering temperature than with sintering time. The density variation at a particular sintering temperature as a function of sintering time could be described by the equation [16]:

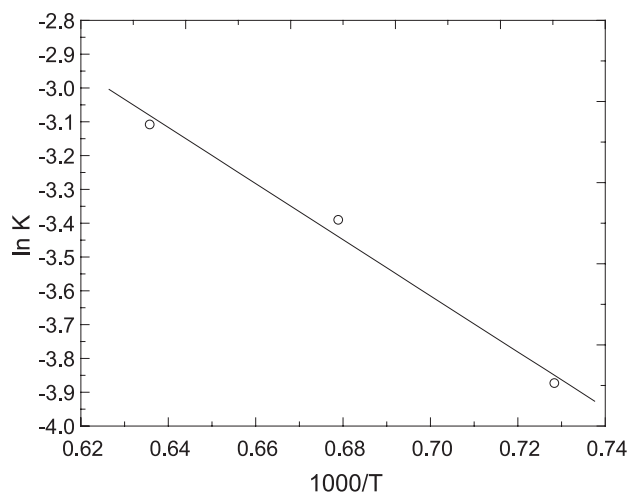
$$\rho = \rho_o + K\ln(t - t_o) \quad (3)$$

where  $\rho_o$  is the density at the initial time  $t_o$  and  $\rho$  is the density of the sample at a particular time  $t$ .  $K$  is a temperature-dependent constant having a relationship with the activation energy for densification  $Q_a$  by the following equation [13]:

$$K = K_o\exp(-Q_a/RT) \quad (4)$$

The variation of sintered density ( $\rho$ ) of samples with  $\ln(t)$  at a particular sintering temperature could be fitted to a straight line, the slope of which represents the value of  $K$  for that temperature. Activation energy for densification is calculated from the slope of the plot of  $\ln K$  vs.  $1000/T$  (Fig. 4). The calculated activation energy for densification for this system was found to be 16.43 kcal/mol. Since densification is influenced by heating rate, particle size, and size distribution of the powders, a detailed study involving isothermal sintering is required to figure out the sintering mechanisms involved and their relative contribution. Since our work is done on the basis of non-isothermal sintering, it is difficult to specify the transport mechanisms involved. However, the low activation energy of 16.43 kcal/mol obtained for our samples suggests that





densification is predominantly controlled by vacancy diffusion. This is further supported by the presence of disordered spinel phase in the powders that gradually become ordered with increase in calcination temperature. Ordering of the disordered phase involves migration of cations (and therefore migration of vacancies) from a disordered arrangement to the lattice positions of a perfectly ordered spinel unit cell. Since in the present study fully ordered spinel phase is obtained in powders calcined at 1100 °C for 9 h and the pellets could be sintered to theoretical density at 1150 °C for 30 min, the results suggest that ordering and densification might have occurred simultaneously involving the migration of cations through the surface of the ultrafine powders during the sintering process.

#### 4. Conclusion

Phase pure spinel is synthesized from metal nitrate solutions by an autoignition process using citric acid as the fuel and metal nitrates as oxidizers. The black ash

formed by the process is a metal–citrate complex, which produces ultrafine powders of ordered and disordered spinel. Calcination of the powders at higher temperatures brought about an increase in ordering of the spinel. The high degree of exothermicity produced by the oxidation of the metal citrate complex sustains the reaction, helps disintegrating the agglomerates to produce fine powders, and also brings down the crystallization temperature of the spinel. These fine powders could be sintered to theoretical density at a sintering temperature of 1150 °C held for 30 min. The sintering of the pellets is thought to be a simultaneous process with ordering of the spinel, which involves diffusion of cations through the surface of the ultrafine powders. The exact reason for the formation of disordered spinel in a chemically induced process, however, is unclear and is being studied by the authors in detail.

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