Published in Journal of European Ceramic Society, 2005

Chemically induced disorder order transition in magnesium aluminium spinel.

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Abstract:

$MgAl_2O_4$ spinel powder was synthesized by nitrate citrate auto ignition route taking different ratios of nitrate and citrate solution. The 'as prepared' black ash was calcined at different temperatures in the range 650°C to 1250°C for 9 hours. Phase evolution of calcined powder samples as studied by X-ray diffraction indicates the presence of disorder at lower calcination temperatures, which transforms to an ordered structure at higher calcination temperatures. Finally, Raman spectroscopy confirms the order-disorder phase transition in spinel sample.

Keywords: Chemical preparation, X-ray methods, Spectroscopy, Spinels, Disorderness.

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1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) has attracted a great deal of attention as a technologically important advanced ceramic material owing to its high melting point (2135°C), high mechanical strength at elevated temperature, low electrical loss, good chemical inertness and thermal shock resistance [1, 2]. Because of these good properties, $MgAl_2O_4$ finds applications ranging from traditional refractories to some advanced usage like infrared and humidity sensors, armour materials, excellent transparent material for arc-enclosing envelopes and alkali-metal vapour discharge devices. Various authors have reported the preparation of this spinel by different chemical routes like sol-gel [3], spray pyrolysis [4], co-precipitation, precipitation from organometallic precursors, auto-ignition [5], microwave-assisted synthesis [6] etc. In general, all these synthesis routes require calcination of the amorphous product at high temperature to yield a perfect single-phase spinel.

Of particular interest is the phase evolution as a function of calcination temperature. The calcination, if done at different temperatures, may involve some alteration in phases present, relative amount of phases and (dis)order in spinel structure. The disorder in the spinel structure has been reported by various authors dealing with neutron irradiation [7], low energy/high energy ion-irradiation etc. The present paper discusses the formation and estimation of the disordered spinel phase, which is chemically induced.

Spinels are a special class of crystal structure (AB_2O_4) in the space group of Fd3m of which $MgAl_2O_4$ is the more common member having wide commercial applications. The cubic structucture containing a closed packed array of 32 oxygen atoms has cations in both octahedral and tetrahedral positions. In a normal spinel structure like $MgAl_2O_4$, 8 divalent cations (Mg) are in the tetrahedral sites and 16 trivalent cations (Al) are in octahedral sites. The ideal cell parameter is a = 0.808 nm. However, during chemical synthesis of spinel powder, disorder may occur in the spinel structure. The degree of disorder may change with calcination temperature.

In the present study, $MgAl_2O_4$ has been synthesised by the nitrate citrate auto ignition route using magnesium and aluminium nitrates (which acts as oxidisers) and citric acid (which acts as fuel). The stoichiometry of precursors (nitrate to citrate ratio) has been varied from 1:1 to 1:2 composition. The resulting powder was calcined at different temperatures ranging from 650 to 1250˚C. X-ray diffraction studies were carried out to study the phase evolution and disorder in spinel phase. The disorder has also been studied by Raman spectroscopy and the disorder as observed from Raman spectroscopy and X-ray diffraction has been correlated.

2. Experimental procedure:

2.1 **Powder preparations:**

Analytical reagent grade $Al(NO_3)_3.9H_20$ and $Mg(NO_3)_2.6H_2O$ (E-merck India) were dissolved separately in distilled water (concentration of each precursor was 0.5 mol/l). Citric acid ($C_6H_8O_7.H_2O$) was also dissolved in water in a separate beaker. All the three aqueous solutions were mixed together to form a nitrate-citrate solution. The concentration of citric acid was varied to obtain 1:1, 1:1.5 and 1:2 nitrate-citrate molar ratio in the mixed solution. The mixed nitrate-citrate complex solution was heated on a hot plate with magnetic stirrer. On heating the solution, its viscosity increased and it gradually transformed into a viscous gel with evolution of NO_x gases. Further heating causes ignition of the gel to a black residue called black ash. A detailed report on this synthesis of spinel is reported elsewhere [5].

The black ash of all three compositions was ground in an agate mortar and pestle for 2 hours followed by calcination at different temperatures ranging from 650 to 1250˚C with a hold time of 9 hours at the peak temperatures. The resulting calcined powder was used for further characterisation.

2.2 **XRD characterisation:**

The phase evolution in the calcined powders was studied by X-ray diffraction (Model PW 1830, Philips, Netherland) using Cu-Kα radiation (20mA/30kV). The samples were scanned in the 2θ range 20^o to 80^o (scan rate 2θ $=3^o$/min). Silicon was used as an internal standard for all the measurements. Science powder samples were used, the chances of texturing was less.

2.3 Raman spectroscopy:

Raman spectroscopy was performed on calcined powders of each composition for each of the three calcination temperatures (viz. 650^oC, 950^oC and 1250^oC). A small amount of powder (about 0.25 gms) was directly placed under the laser source and the Raman spectra was recorded. The spectra were taken using a Renishaw Ramascope-1000 multi-channel Raman spectrometer equipped with a CCD detector in a back scattering mode. In order to enhance the signal coming from spinel powder, a confocal hole coupled with the microscope was adjusted to its minimum value. For all samples, the 514.5 and 488 nm excitation laser lines were used (coherent argon-krypton ion laser) together to avoid the luminescence signal due to impurities. The laser beam was operated below 20 mW.

3. Results and Discussion:

3.1 Phase Analysis:

The X-ray diffractograms of the ash and calcined powders below 650^oC show amorphous characteristics. Peaks corresponding to $MgAl_2O_4$ spinel start appearing at 650^{o}C (Fig. 1). Although the'd' value of the peaks corresponds to a fully ordered spinel (ICDD 21-1152), closer observation reveals that the relative intensity of the strongest peaks viz. (311) and (400) differs from that of the standard values [8]. Table- 1 lists the relative intensities of the above two peaks. It is further observed that the intensity of the above two peaks changes for samples produced from different nitrate-citrate ratio as well as samples calcined at different temperatures. The changes in the peak intensity indicate the presence of a disorder spinel phase in the sample. Literature review on the formation of disordered spinel reveal that disorder spinel phase can form either due to a true change in the inversion parameter (Simone's theory) [7] or due to the formation of an intermediate phase of different or related structure (Sickafus's theory) [8]. Simone's analysis on the obtained X-ray pattern of unirradiated $MgAl_2O_4$ samples says that their spinel was nonstoichiometric (Mg/Al < 0.5). They also observed that the X-ray diffractogram of the irradiated samples was quite different from that of unirradiated one. Broad peaks were observed in the irradiated samples near 2θ value 35^{o} and 62^{o}, which indicated significant amorphisation of the $MgAl_2O_4$ samples on irradiation. Moreover, irradiation also induced the disappearance of peaks at $2\theta = 38^{o}$. On the other hand, the work by Sickafus [8] on the structural analysis of $MgAl_2O_4$ up on irradiation says that the lattice parameter changes from a = 0.808 nm (for unirradiated) to a = 0.404 nm (for irradiated) along with a change in space group from Fd3m to Fm3m. Moreover, an earlier report by Sickafus et al. [9] clearly mentioned that the X-ray diffraction pattern of an ordered $MgAl_2O_4$ should show higher intensity for all odd reflections like (311) etc., and it will be lower for all even reflections e.g. (222). However, if the samples contain both ordered and disordered spinel (rocksalt structure), the intensity of all even reflections (222) will increase because (111) reflections for disordered spinel also occur at the same 2θ thereby increasing the intensity of (222). Sickafus et al. [9] suggests that disordering takes place through a displacive transformation in which the atoms move to forbidden (interstitial) sites.

In our present study, we have observed higher intensity for (400) and (440) reflections in the disordered spinel (Fig.1). The increase in peak intensity of these two peaks occurs due to the presence of disorder phase in the spinel structure as discussed above. This is because the intensity of (400) order phase and (200) disorder phase occur at same 2θ. Similarly, peak intensity of (440) order and (220) disorder spinel phase also occur at the same 2θ value. With increasing calcination temperature the disordered in the sample decreases and thus the intensity of (400) and (440) decreases due to lower intensity of (200) and (220) disordered reflections. Thus a lowering of intensity of all even reflections with increase in calcination temperature was observed for our samples. Thus in the light of the above discussion, it appears that (a) the disorder structure observed in our spinel sample results from the formation of an intermediate phase of different but related structure of rock salt type [8], (b) spinel samples have disorder at lower calcinations temperature i.e. 650^{o}C to 950^{o}C and (c) the disorder phase decreases on increasing the calcination temperature.

Disorder in spinel samples has been reported earlier, which is usually observed after ion-irradiation or neutron irradiation. But here, formation of disorder $MgAl_2O_4$ due to chemical processing route (auto ignition) is presented in detail, which was briefly reported elsewhere by the same authors [5]. Although the nitrate citrate autoignition route provides a milder experimental condition than the ion irradiated treatment, the existence of disordered spinel structure has been noticed in our samples. We think that it may be combined effect of chemical composition and the heat of exothermic reaction involved in nitrate citrate autoignition route. This type of chemically induced disordered has also been reported earlier by Sickafus et al. [9]. We have also observed this type of disorder spinel prepared by gel precipitation route.

A semi-quantitative measurement of order spinel phase in the sample can be done by comparing the peak intensity of {311} and {400} reflections using the formula [10].:

Degree of order in the spinel powders = $[I_O/(Io + I_D)]$…………(1)

where Io = intensity of {311} plane (order phase), $I_D = Ic_{,400} - Io_{,400}$ = intensity of disorder spinel phase in {400} plane; $Ic_{,400}$ = intensity of {400} plane having both order and disorder phase and $Io_{,400}$ = intensity of order phase in {400} plane. All the intensity values used in this calculation were absolute intensities (cps) after subtracting the background intensity. In the present calculation only (311) and (400) peaks are considered following the models proposed by Sickafus wherein the intensity of (311) peak (pertaining to completely ordered spinel) has 100% relative intensity. For the same order spinel the relative intensity of (400) peak is 57.18. However, for completely disorder spinel the intensity of (400) is 100%, while that of (311) is zero. Therefore, if the observed relative peak intensity of (400) reflection is higher than 57.18% then the higher peak intensity results from the contribution of disorder structure of the spinel. Moreover, as we are using the most intense peak of both order and disorder phase, determination of degree of order involving any other combination of peaks may give a less reliable value. At this point it may be noted that we have also verified our results by considering a different combination of peaks of the order and disorder phase as cited by Sickafus and have found that the new result agrees well with the results that we have reported.

Further, although the present data of order phase fraction is calculated on the basis of peak intensity, we have also calculated the fraction of order phase fraction on the basis of integrated peak intensity. It was observed that the two results were in good agreement. Thus our method of order phase calculation on the basis of peak intensity is accurate.

The calculated amount of order (based on the Rocksalt model) in samples prepared by different nitrate to citrate ratio and calcined at different temperatures (650˚, 950˚ and 1250˚C for 9 hrs each) is given in Table- 2 and the same data are presented graphically in Fig. 2.

3.2 Raman spectroscopy:

The number of expected Raman peaks for $MgAl_2O_4$ spinel can be determined from group theory [11]. The factor group analysis predicts that the following modes are observed for ordered spinel (S.G. Fd3m):

$$3F_{2g} + A_{1g} + E_g + F_{1g} + 4F_{1u} + 2F_{2u} + 2E_u + 2A_{2u}$$

Although only five optic modes are Raman active and four are infrared active, there are reports of six and seven bands in Raman spectra for stoichiometric and non stoichiometric spinel [12]. Raman spectra for spinel samples of differing nitrate to citrate ratio (1:1, 1:1.5, 1:2) and calcined at different temperatures (650˚, 950˚ and 1250˚C for 9 h each) are presented in Fig. 3. The Raman peaks in different modes for the spinel samples of all compositions are presented in Fig. 3 and Table- 3. Table- 3 also includes the data obtained by Simone et al. [7] in ion irradiated spinel samples. In the Raman spectra of spinel calcined at 650^{o}C, no peaks of any Raman active mode could be detected. However, the spectrum shows a sharp negative peak at 392.46 cm^{-1} and a small negative peak at 491 cm^{-1} in all the three compositions.

Usually this kind of negative peak is rare in Raman spectra. However, it is also reported in the literature [13] that some materials had both Raman and infrared active (IR) mode and depending on the conditions either a Raman active mode or an IR active mode are detected.

As the spinel is produced by nitrate-citrate combustion, it is possible that the reaction is not totally complete on calcination at 650˚C leaving behind some unreacted complex of nitrate-citrate type. The presence of the unreacted complex phase probably causes a negative peak in the spectra. Moreover, higher scattered intensity of IR active mode probably masks the peaks corresponding to Raman active mode.

The peaks near 721, 723 and 727 cm^{-1} are associated with the stretching of AlO_4 tetrahedra [11], which is in agreement with Rietveld analysis done by Simeone et al. [7]. The peak at 723 cm^{-1} is observed for samples calcined at 950˚C for all composition, which is also due to Al-O stretching vibration of AlO_4 tetrahedra [11]. All these indicate the occupancy of some Al ions in tetrahedral sites making it a disordered structure. The peaks corresponding to AlO_4 tetrahedral vibrations become sharper with increaseing nitrate-citrate ratios as well as higher calcination temperatures. Thus the transition from a broad to a sharp peak indicates a corresponding decrease in the disorder, which is in accordance with the result obtained by XRD analysis (Fig.1). Further, the 723 cm^{-1} peak either disappear or decrease in intensity for higher calcination temperature (1250^{o}C) indicating more order at higher temperature, which is also in accordance with the XRD results.

The peaks found near 410 cm^{-1} for samples calcined at 950 and 1250˚C (for all composition) are assigned to AlO_4 bending. The shoulder peak on the low wave number side of 410 cm^{-1} peak (i.e. around 381 cm^{-1}) corresponds to additional bending vibrations for Al ions in tetrahedral site [14]. The presence of these additional peak of AlO_4 tetrahedra also correspond to disorder spinel structure. Further, these peaks get sharper from 950 to 1250 ˚C for all composition indicating improved order in the structure. This result is also in accordance with the XRD data presented. However, the presence of peaks corresponding to AlO_4 bending even at the highest calcination temperature indicates that some disorder exists till 1250^{o}C. This disorder could not be detected by XRD. The existence of a peak near 770 cm^{-1} corresponds to the Mg-O stretching vibration. Observation of Raman spectra reveals the Mg-O stretching peak gets sharpened with higher temperature for all compositions. It hints at ordering of spinel with higher temperature. In accordance with the proposed Rocksalt structure [8] initially all cations (including Mg) are in octahedral interstices. But with ordering of spinel, the Mg atoms should go to tetrahedral interstices involving less number of MgO bonds in octahedral sites. Hence, the overall MgO stretching decreases giving sharper peak with less intensity near 770 cm^{-1}. This ordering behaviour agrees with the XRD data and the Rocksalt structure proposed by Sickafus et.al [8].

Thus this study reveals that there is a close agreement between the X ray diffraction data and Raman spectra. It is evident that spinel produced by lower nitrate-citrate ratio gives rise to some disorder in spinel structure at lower temperature. This disorder decreases with increasing nitrate-citrate ratio (from 1:1 to 1:2) resulting in a crystallographic ordering of the structure. This trend in ordering can be attributed to the combined effect of heat and chemical composition. The large exothermic heat associated with nitrate-citrate combustion reaction increases with decreasing nitrate-citrate ratio. With increasing amount of nitrate in the initial composition, the exothermicity of the reaction increases giving rise to more and more heat which leads to a more complete reaction between the precursors giving rise to a more ordered spinel structure. On the other hand, in samples with a lower nitrate citrate ratio, the reactions remain incomplete at lower temperature on account of the low exothermicity. Thus the incomplete reaction gives rise to a complex disordered spinel with a trace of complex intermediate phases. Hence, a generally increasing trend in ordering of spinel is marked from 1:1 to 1:2 compositions.

Further, it is seen that for the same nitrate-citrate ratio in the initial precursor, the powder obtained at different calcination temperatures shows different degrees of ordering. In general, the ordering increases steadily with an increase in calcination temperature. This can be again attributed to the effect of heat i.e., with increasing calcination temperature, more heat is supplied to the powder which facilitates more complete chemical reaction among the metastable phases and unreacted phases giving rise to a more ordered spinel phase. This is in accordance with the XRD and Raman data presented. However, it may be noted that the fraction of disordered phase calculated from X-ray diffraction measurement gives only a rough quantitative estimation. The results of Raman spectroscopy although provides a better insight about the co-ordination state of Al and Mg ions, cannot provide a quantitative estimation. A better and more accurate quantitative result will be provided by ^{27}Al solid state MAS NMR study to determine the octahedral:tetrahedral Al ratio which is under study.

4. Conclusions:

The following conclusions can be drawn from the current study:

(1) A disorder-order phase transition was found in $MgAl_2O_4$ spinel due to combined effect chemical composition and the associated exothermicity of the reaction. So,

the disordering is chemically induced. The phase transition was probably due to formation of an intermediate phase having different but related structure.

(2) With increase in citrate content in the precursors the spinel gets increasingly order. This effect can be related to higher exothemicity of the reaction.

(3) The disorder-order phase transition is confirmed by X-ray diffraction analysis and Raman spectroscopy. The spinel transforms to a more order structure at higher calcinations temperature.

(5) Raman spectroscopy revealed that even at 1250^{o}C the samples remains partially disordered. However, the degree of disorder is dependent on the nitrate-citrate ratio.

Acknowledgements:

The authors are grateful to Dr D. Roy, Dr K. Yates and Dr V. Adyam of Materials Science, Cambridge for their help in Raman spectroscopy and to Prof. T. W. Clyne, Director of Gordon Laboratory, for his kind permission to use the Raman spectroscopy facility. The first author (PB) is grateful to Shell Centenary Chevening Fund (British Council) for a scholarship at Cambridge.

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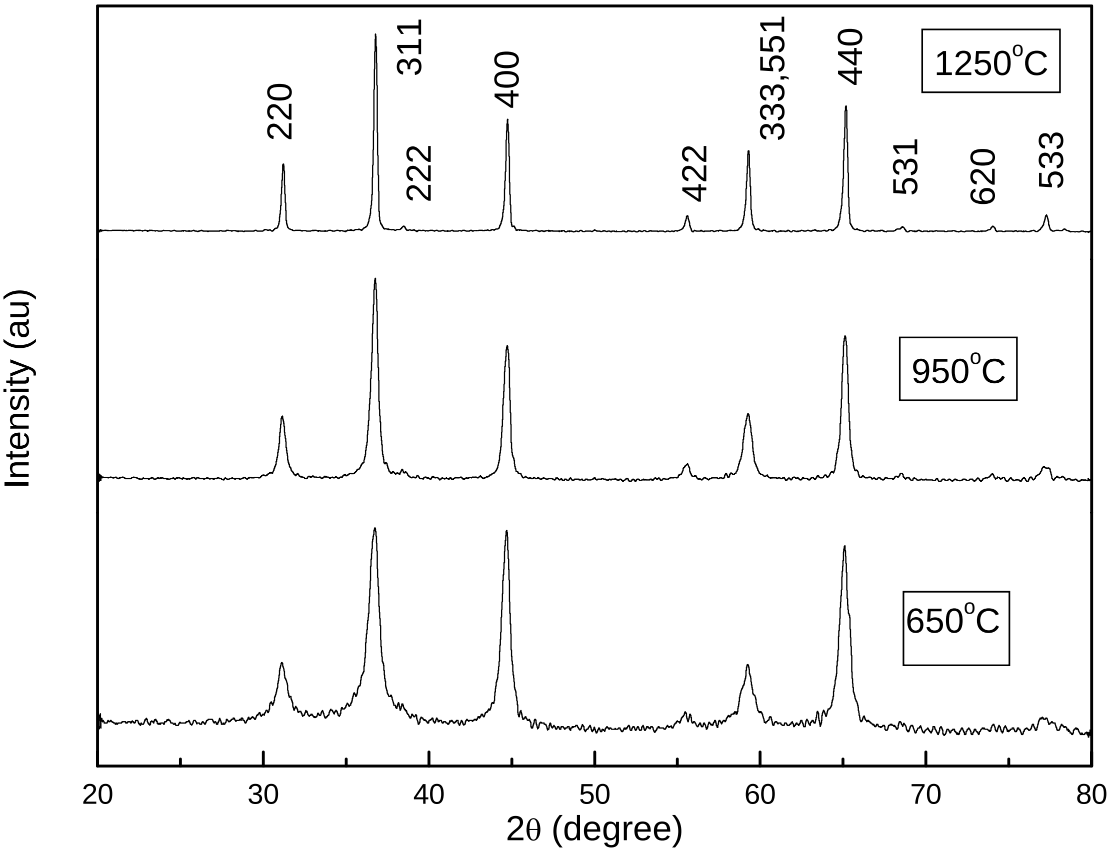
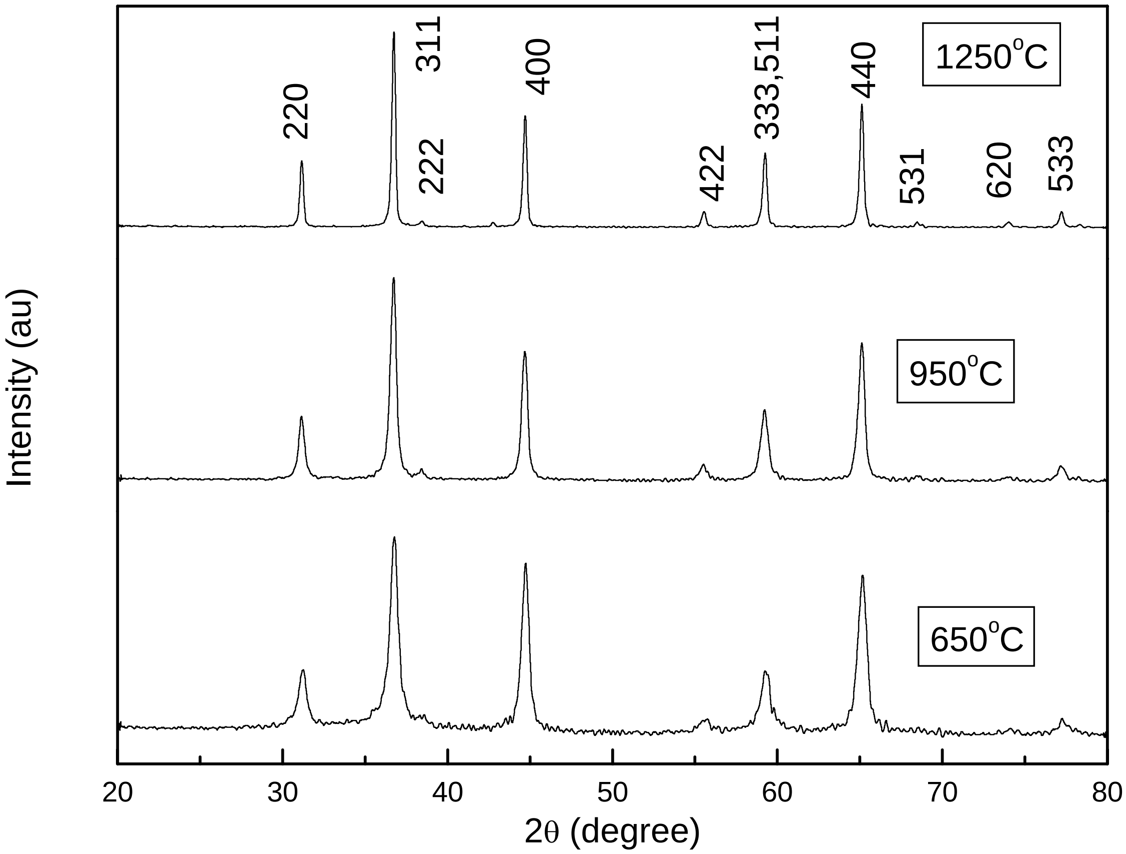
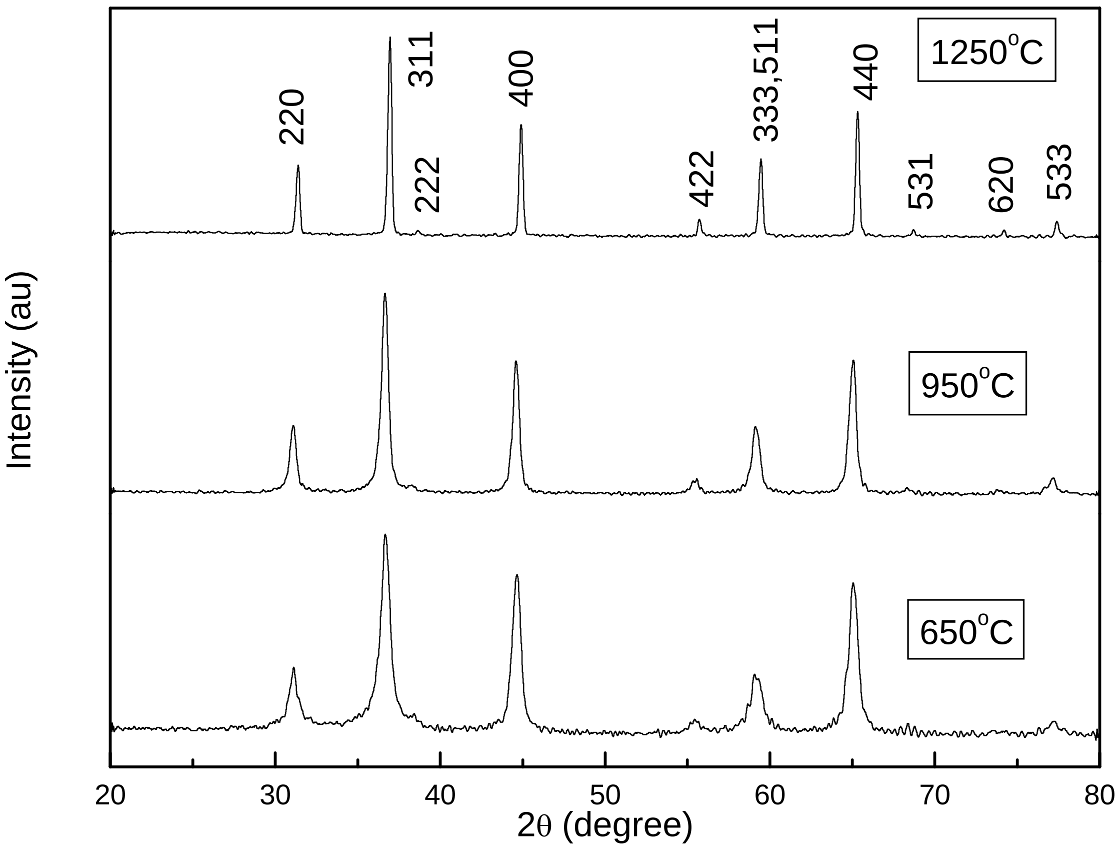


(a) 1:1 composition



(b) 1:1.5 composition



(c) 1:2 composition

Figure 1: P. Barpanda et al

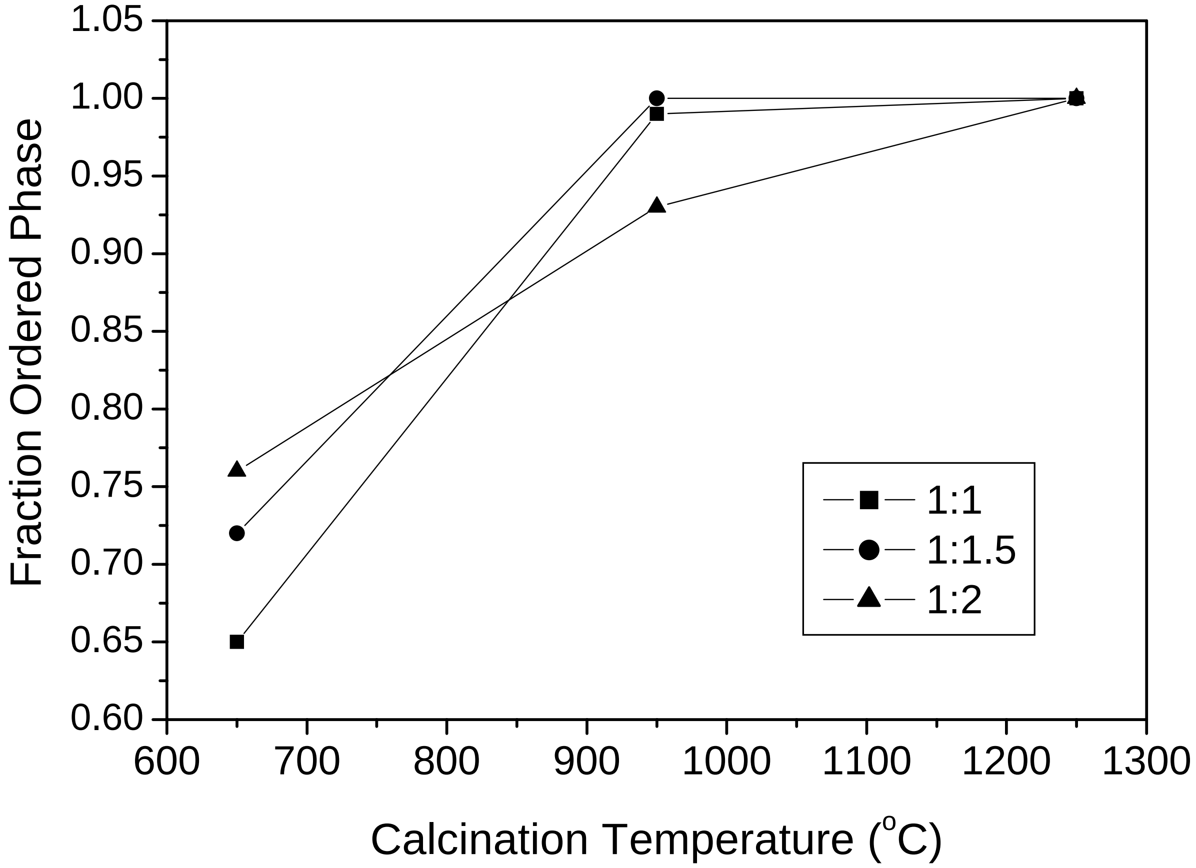
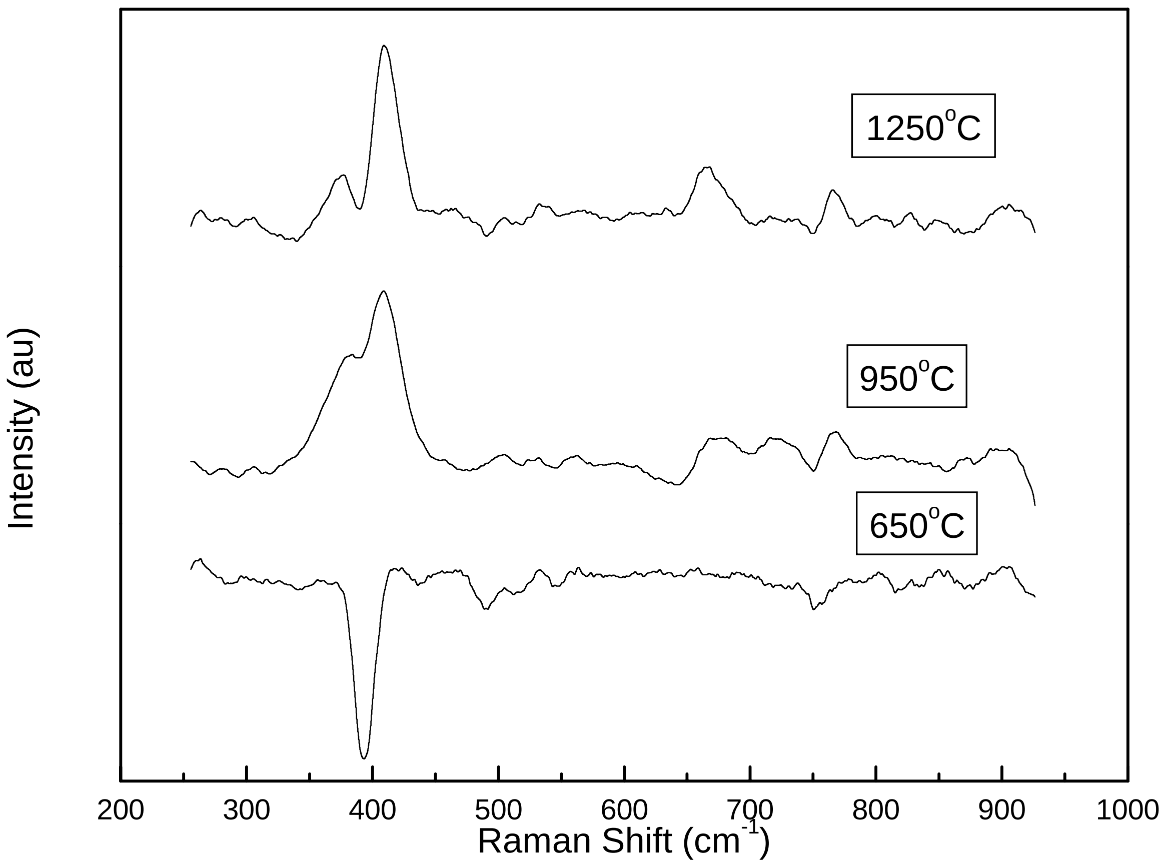
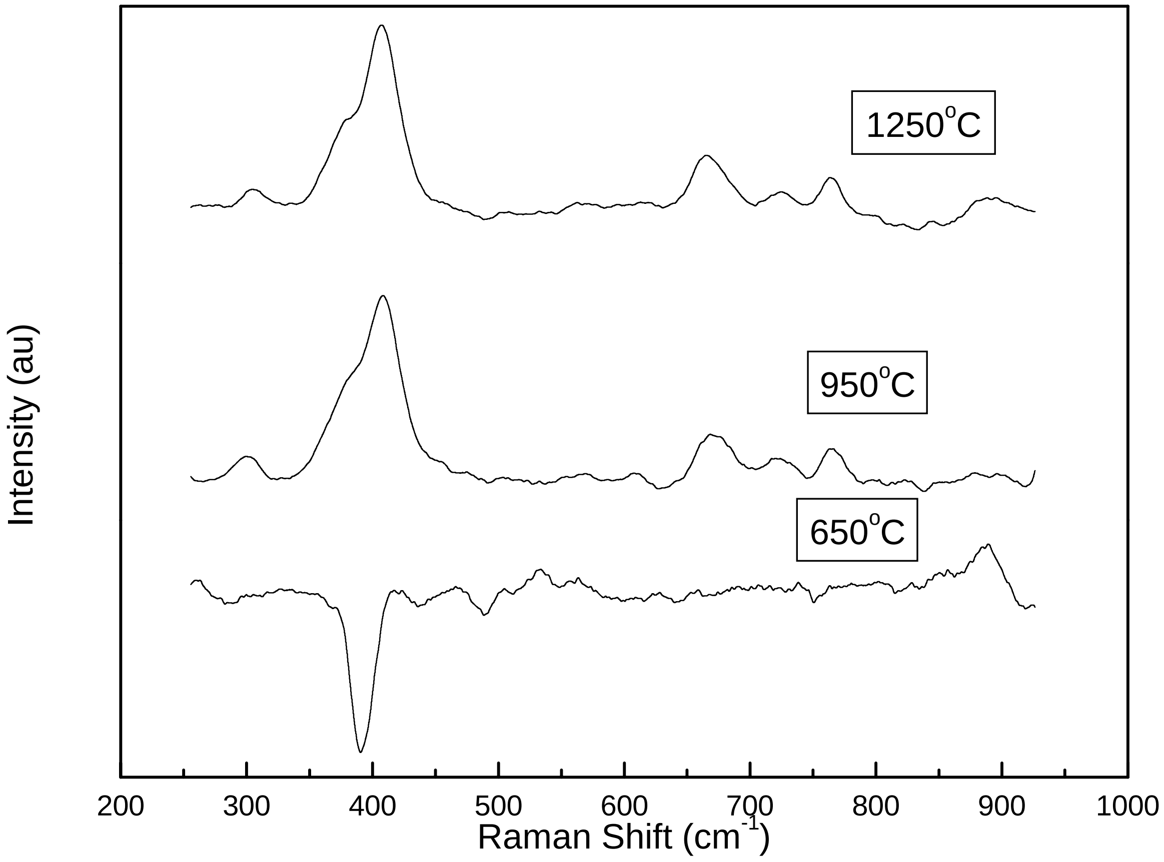


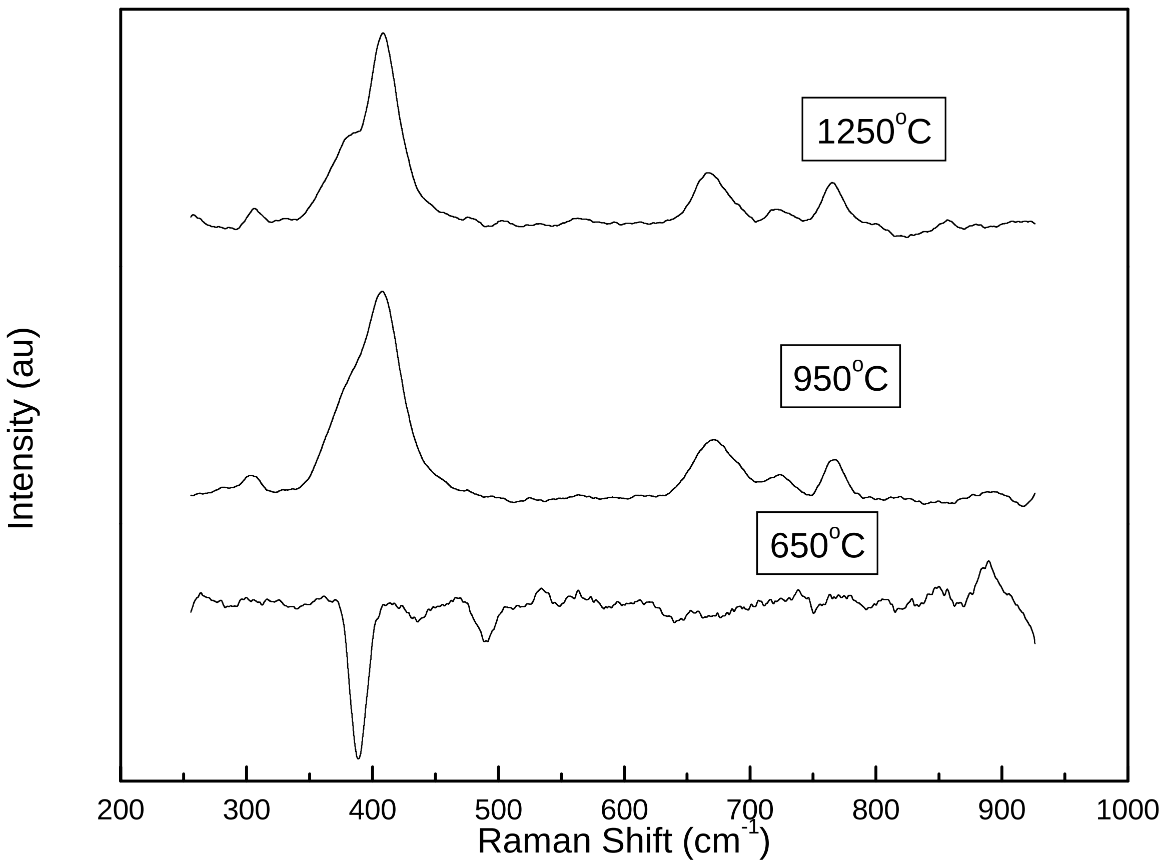
Figure 2: P. Barpanda et. al.



(a) 1:1 composition



(b) 1:1.5 composition



(c) 1:2 composition

Figure 3: P. Barpanda et. al.

Temperature (^{o}C)	Nitrate/Citrate Ratio						Ordered Spinel [8]		Metastable Spinel [8]	
	(1:1)		1:1.5		1:2					
	Reflection planes									
	311	400	311	400	311	400	311	400	311	400
650	100	90.85	100	83.44	189.16	79.89	100	57.18	-	100
950	100	67.57	100	66.18	268.75	64.85				
1250	100	52.71	100	56.49	347.01	53.79				

Table 1: P.Barpanda et. al.

Nitrate/citrate ratio	Calcination Temperature (^oC)	Fraction order phase	Phases present
1:1	650	0.65	ordered & metastable spinel
	950	0.99	ordered & metastable spinel
	1250	1.00	fully ordered spinel
1:1.5	650	0.72	ordered & metastable spinel
	950	1.00	fully ordered spinel
	1250	1.00	fully ordered spinel
1:2	650	0.76	ordered & metastable spinel
	950	0.93	ordered & metastable spinel
	1250	1.00	fully ordered spinel

Table 2: P.Barpanda et. al.

IR		F_{2g}		E_g	F_{2g}	A_{1g}	A_{1g}
Peak Position (cm^{-1}) [7] →		306.90		406.00	670.00	723.00	766.00
Nitrate/citrate ratio	Calcination Temperature (°C)						
1:1	650	-	-	-	-	-	-
	950	307.10	378.38	408.74	680.94	721.83	766.22
	1250	307.10	374.86	409.90	662.24	724.16	766.22
1:1.5	650	-	-	-	-	-	-
	950	298.92	381.87	407.57	669.25	718.49	766.22
	1250	305.93	377.19	406.40	664.58	723.00	765.05
1:2	650	-	-	-	-	-	-
	950	303.59	379.53	407.57	669.25	723.00	766.22
	1250	305.93	378.36	409.90	664.58	719.49	766.22

Table 3: P.Barpanda et. al.

We are thankful to you and the reviewers for providing critical assessment and positive suggestions in improving the quality of the paper.

Answer to Q.1

(a)General

This paper reports the synthesis of solid $MgAl0_4$ by a nitrate/citrate route, and presents results interpreted by the authors to indicate that the degree of order in the product can be controlled both by the composition of the initial mix (which they suggest influences the liberated heat of the reaction) and by the calcination temperature. While it is well known from thermodynamic considerations and experimental studies that high-temperature heat treatment with strictly-defined quenching regimes can change the degree of disorder of this compound, the present experimental conditions appear to be much milder than the high-temperature quenching or radiation damage normally required to produce these effects. Therefore the present results are of considerable interest *if proven,* but a higher standard of proof is desirable.

Yes, while we agree that although citrate-nitrate autoigition route is a highly exothermic process we are not comparing this method with the thermal quenching which is reported to be of severe type. It is possible that the present experimental conditions are milder than the ion irradiation treatment. But, we have observed the disordered $MgAlO_4$ for this case. The reviewer had suggested that part of this result might be because of texturing the samples. Since we have used powder samples, the possibility of texturing is minimal. We would also like to mention that similar kind of disordered spinel was observed in samples prepared through wet chemical routes like precipitation. Thus it appears that this detection of disordered spinel to be general phenomenon for spinels which crystilizes from amorphous matrix.

Part of the difficulty with this paper lies in its English expression, which may not do full justice to the authors' arguments. In particular, it is not very clear what they mean by "orderness" and "disorderness" (which would be better changed to "order" and "disorder").

We accept the suggestion of the reviewer. We have changed all the orderness and disorderness to ordered and disordered respectively in the text.

It is also not clear whether they appreciate the nature of the difference between the two groups whose work they cite on the crystallographic effects of radiation damage in spinel. It would be of assistance to the reader if in their discussion they were to summarise the two different points of view and indicate on which side they find themselves. It is important for the authors to clearly state, with reasons, whether they believe that the phenomenon described here represents a true change in the inversion parameter, or results from the formation of an intermediate phase of different but related structure.

Thank you for pointing a major drawback of our manuscript. As per the suggestion we have critically analyzed our result in the light of both Simone's theory (true change in the inversion parameter) and Sickfus's theory (formation of an intermediate phase of different but related structure). The analysis has been elaborated in the following paragraph:

Simone's analysis on the obtained X-ray pattern of unirradiated $MgAl_2O_4$ samples says that their spinel was nonstoichiometric (Mg/Al < 0.5). They also observed that the XRD pattern of the irradiated samples was quite different from that of unirradiated one. Broaden peaks were observed in the irradiated samples near 2θ value 35^o and 62^o which indicated significant amorphisation of the $MgAl_2O_4$ samples. Moreover, irradiation also induced the disappearance of peaks at $2\theta = 38^o$. On the other hand, the work by Sickafus on the structural analysis of $MgAl_2O_4$ up on irradiation says that the lattice parameter changes from a = 0.808 nm (for unirradiated) to a = 0.404 nm (for irradiated) along with a change in space group from Fd3m to Fm3m. An earlier report by Sickafus et al. also clearly mentioned that the XRD pattern of an ordered $MgAl_2O_4$ should have higher intensity for all odd reflections like (311) etc., and it will be lower for all even reflections e.g. (222). However, in samples having both ordered and disordered spinel (rock salt structure) the intensity of all even reflections (222) will increase because (111) reflections for disordered spinel will also occur at the same 2θ value thereby increasing the intensity of (222).

The disordering as discussed by Sickafus et al. takes place through a displacive transformation in which the atoms move to forbidden (interstitial) sites.

In our present study, we have observed that higher intensity for (400) and (440) reflections in the disordered spinel (Fig.1) the increase in peak intensity of these two peaks occur due to disordered in the spinel structure. This is because the intensity of (400) ordered and (200) disordered occur at same 2θ. Similarly peak intensity of (440) ordered and (220) disordered spinel also occur at the same 2θ value. With increasing calcination temperature the disorder in the sample decreases and thus the intensity of (400) and (440) decreases due to lower intensity of (200) and (220) disordered reflections. Thus lower intensity of all even reflections with increase in calcinations temperature was observed for our samples. This lead to the following conclusions:

a) The disordered structure observed in our spinel sample results from the formation of an intermediate phase of different but related structure of rock salt type
b) spinel samples have disorder at lower calcination temperature i.e., 650°C to 950°C.
c) the disorder decreases on increasing the calcinations temperature.

Specific points.

X-ray measurements.

Following on from the above comment, the authors should provide considerably more detail about the X-ray measurements and their interpretation, in particular, justifying their use to determine the degree of order or disorder in their samples.

The reviewer and the details of X-ray measurement have been incorporated in the revised text at page 4.

Since relative peak intensities are used, what precautions were taken to eliminate preferred orientation in the samples?

We would like to mention that we have not used the relative peak intensity for determining disorder, we have used actual intensity value. The table-2 which lists the relative peak intensity is included in the manuscript shows only the changes in the relative intensity of (311) and (400) peak of the prepared spinel samples in comparison to the completely ordered and disordered spinel. No disorder calculation was done from the Table. Disorder has been calculated from the absolute intensity after background subtraction.

Would the method be more reliable if more than one pair of peaks was used in the measurement?

We have taken only (311) and (400) peaks for calculating the order and disorder in the spinel samples due to the following reasons:

In the light of the methods proposed by Sickafus (311) peak pertaining to completely ordered spinel and its relative intensity is 100. For the same ordered sample the relative intensity of (400) peak is 57.18. However, for completely disordered spinel the intensity of (400) is 100%, while that of (311) is zero. Thus if the observed peak intensity of (400) samples is higher than 57.18% (the reported relative intensity for a completely ordered sample) then the higher peak intensity arises out of disorder in the sample. This forms the basis of our calculation. Since we are using 100% of peak intensity of ordered and disordered phase, calculation involving nay other combination of peaks may give a less reliable value. However, for verification we have used a different peak combination of the disordered phase and we have found that new results matches well with our previous results.

There is a discrepancy between page 5, where the use of the intensities of the rocksalt spinel peaks is said to provide a "rough quantification" and page 6 where the implication is that this procedure is fully quantitative.

We thank the reviewer for pointing out the discrepancy. In fact on reviewing our manuscript we have found there was a typographical error. Actually it should have been semi quantitative instead of quantitative.

Were these intensity measurements based on peak heights or integrated peak intensities?

The peak intensities given in our manuscript refers to peak heights. However, we have also estimated the disorder on the basis of integrated peak intensity and found good agreement between the two results.

The diagram showing these changes in relative peak intensity (Fig. 1) truncates both peaks of interest in the diffractograms of samples heated at 650°C, making it impossible for the reader to see what is going on.

We have change the order of diagram in our revised manuscript so that no peaks are truncated.

Raman measurements.

The interpretation of these spectra is based on cited work by Simone et al. which, although stated on page 7 to be included in Fig. 3 and Table 3, has been omitted from both. The explanation of the negative peak at about 380 wavenumbers in all the low-temperature samples is unsatisfactory. The authors suggest two possibilities; which one do they favour and why? If this moiety is a nitrate-citrate complex, why is the peak negative? If it is magnesium nitride, would the authors expect this phase at 650°C, and would they like to suggest a mechanism by which it might be formed in the gel? There is a problem with the reasoning on page 7 regarding the appearance and disappearance of peaks at 721, 723 and 727 wavenumbers, all of which are assigned to tetrahedral Al vibrations (since these peaks cannot be visually discriminated in the spectra presented in Figure 3 this discussion is unconvincing). Although the 723 peak is said to disappear from the spectra at higher calcination temperatures, this is not supported by Fig. 3(b) and (c). Furthermore, the authors equate the presence of this peak with disorder, but in the work they cite by Simone et al., this peak occurs strongly in unirradiated (ordered) spinel, and disappears in irradiated (disordered) samples. These discrepancies suggest that Raman spectroscopy may not be sufficiently reliable a technique to support the authors' conclusions. A more robust and widely-used spectroscopic method for determining the inversion parameter of aluminate spinels is to measure the octahedral:tetrahedral Al ratio by $_{27}$ Al solid-state MAS NMR (see, for example, MacKenzie and Smith, Multinuclear Solid State NMR of Inorganic Materials, Pergamon/Elsevier, Oxford, 2002).

In the light of the above suggestions provided by the reviewer we have rewritten the results and discussion part of Raman spectra and also we have redrawn the Raman spectra (Fig. 3 (a, b and c)) after background correction. The redrawn Raman spectra shows better clarity of the concerned peaks.

Other points.

The occasional use of the term oxidant/fuel ratio for nitrate/ citrate ratio has a strange and unfamiliar ring; from the point of view of readers with a chemistry background it would be better to use the latter throughout.

We have changed fuel/oxidant ratio to nitrate/citrate ratio in the text.

To
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Ref: Your letter RJB/Do 26.02.2005

Dear Professor Brook,

This has reference to the reviewer's comment for our manuscript JECS 533/04 entitled "Chemically induced disorder order transition in magnesium aluminium spinel". We have carefully gone through all the comments and we express our sincere thanks for providing us with very constructive suggestions in order to improve the quality of the paper. In the light of the reviewer's suggestion, we have revised the manuscript. Our answers to the reviewer's queries/suggestions have also been provided separately. Please find enclosed herewith a copy of the revised manuscript and a copy of out answers to the reviewer's queries for your consideration for publication in the Journal of the European Ceramic Society.

With warm regards

Yours sincerely

(S. Bhattacharyya)

Encl.

1. Revised manuscript
2. Answers to reviewer's comments