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Chemically induced order disorder transition in magnesium aluminium spinel

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Abstract

Magnesium aluminate spinel ($MgAl_2O_4$) 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 650–1250 °C for 9 h. 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.

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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 structure 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

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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 $Al(NO_3)_3 \cdot 9H_20$ and $Mg(NO_3)_2 \cdot 6H_2O$ (E-merck India) were dissolved separately in distilled water (concentration of each precursor was 0.5 mol/l). Citric acid ($C_6H_8O_7 \cdot H_2O$) 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 h followed by calcination at different temperatures ranging from 650 to 1250 °C with a hold time of 9 h 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 (20 mA/30 kV). The samples were scanned in the 2θ range 20–80° (scan rate $2\theta = 3°/\text{min}$). Silicon was used as an internal standard for all the measurements. Since 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, 950 and 1250 °C). A small amount of powder (about 0.25 g) 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 °C show amorphous characteristics. Peaks corresponding to $MgAl_2O_4$ spinel start appearing at 650 °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. (3 1 1) and (4 0 0) 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 non-stoichiometric ($Mg/Al < 0.5$). 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 and 62°, which indicated significant amorphisation of the $MgAl_2O_4$ samples on irradiation. Moreover, irradiation also induced the disappearance of peaks at $2\theta = 38°$. 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 (3 1 1), etc., and it will be lower for all even reflections e.g. (2 2 2). However, if the samples contain both ordered and disordered spinel (rocksalt structure), the intensity of all even reflections (2 2 2) will increase because (1 1 1) reflections for disordered spinel also occur at the same 2θ thereby increasing the intensity of (2 2 2). 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 (4 0 0) and (4 4 0) reflections in the disordered spinel (Fig. 1).

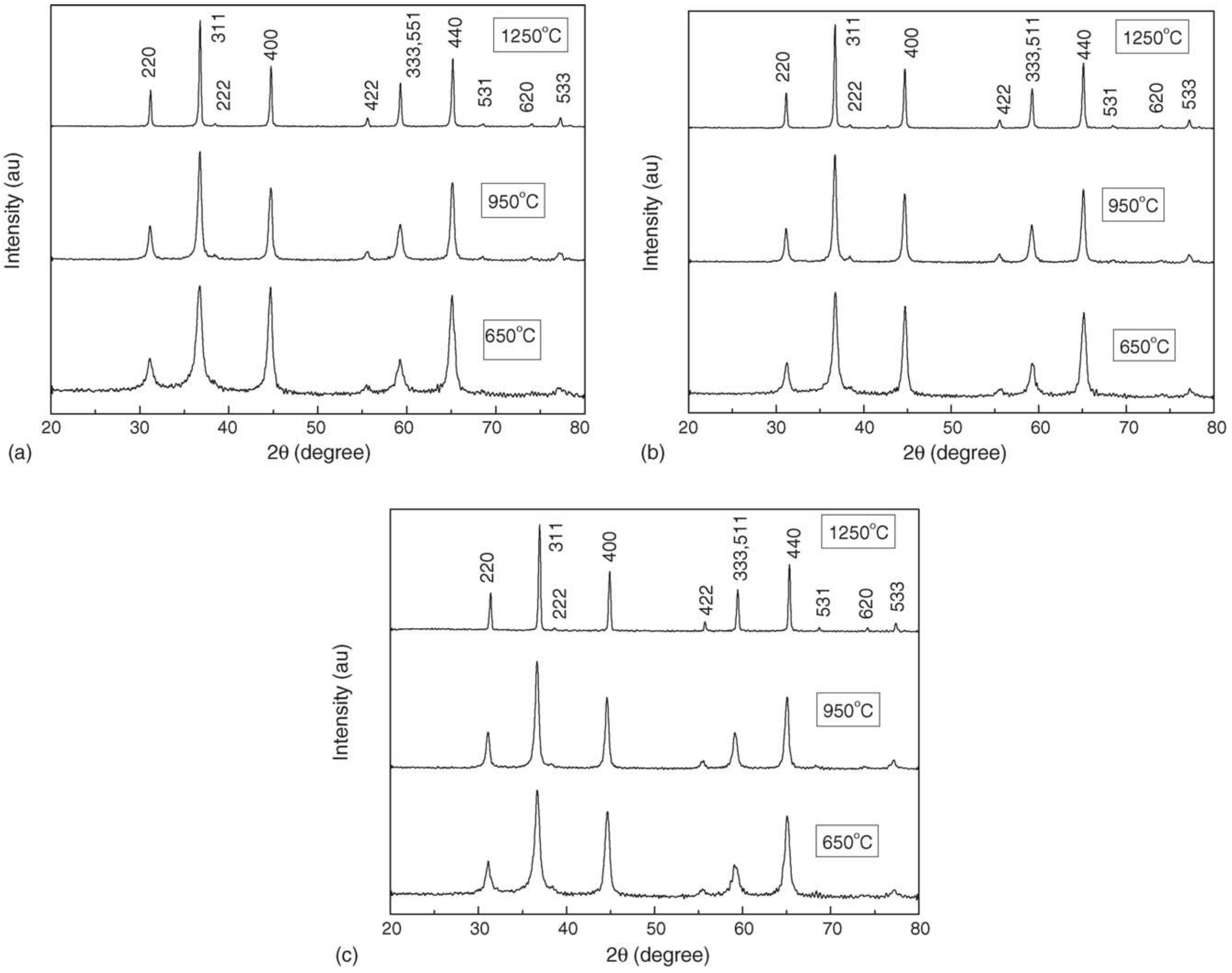

Fig. 1. X-ray diffractograms of spinel as a function of nitrate–citrate ratio: (a) 1:1; (b) 1:1.5; and (c) 1:1.

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 (4 0 0) order phase and (2 0 0) disorder phase occur at same 2θ. Similarly, peak intensity of (4 4 0) order and (2 2 0) disorder spinel phase also occur at the same 2θ value. With increasing calcination temperature, the disorder in the sample decreases and thus the intensity of (4 0 0) and (4 4 0) decreases due to lower intensity of (2 0 0) and (2 2 0) 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. 650–950 °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

Table 1
Relative intensity of {3 1 1} and {4 0 0} planes

Temperature (°C)	Nitrate–citrate ratio						Ordered spinel[8]		Metastable spinel[8]	
	(1:1)		1:1.5		1:2					
	3 1 1[a]	4 0 0[a]	3 1 1[a]	4 0 0[a]	3 1 1[a]	4 0 0[a]	3 1 1[a]	4 0 0[a]	3 1 1[a]	4 0 0[a]
650	1 0 0	90.85	1 0 0	83.44	189.16	79.89	1 0 0	57.18	–	1 0 0
950	1 0 0	67.57	1 0 0	66.18	268.75	64.85				
1250	1 0 0	52.71	1 0 0	56.49	347.01	53.79				

[a] Reflection planes.

Table 2
Variation of ordered $MgAl_2O_4$ spinel as a function of nitrate–citrate ratio and calcination temperature

Nitrate–citrate ratio	Calcination temperature (°C)	Fraction order phase	Phases present
1:1	650	0.65	Ordered and metastable spinel
	950	0.99	Ordered and metastable spinel
	1250	1.00	Fully ordered spinel
1:1.5	650	0.72	Ordered and metastable spinel
	950	1.00	Fully ordered spinel
	1250	1.00	Fully ordered spinel
1:2	650	0.76	Ordered and metastable spinel
	950	0.93	Ordered and metastable spinel
	1250	1.00	Fully ordered spinel

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 auto-ignition 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 auto-ignition route. This type of chemically induced disorder 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 $\{3\,1\,1\}$ and $\{4\,0\,0\}$ reflections using the formula:[10]

$$\text{Degree of order in the spinel powders} = \left[\frac{I_\mathrm{O}}{(I_\mathrm{O}+I_\mathrm{D})}\right] \quad (1)$$

where I_O = intensity of $\{3\,1\,1\}$ plane (order phase); $I_\mathrm{D} = I_{\mathrm{C},400} - \mathrm{I}_{\mathrm{O},400}$ = intensity of disorder spinel phase in $\{4\,0\,0\}$ plane; $I_{\mathrm{C},400}$ = intensity of $\{4\,0\,0\}$ plane having both order and disorder phase; and $I_{\mathrm{O},400}$ = intensity of order phase in $\{4\,0\,0\}$ plane. All the intensity values used in this calculation were absolute intensities (cps) after subtracting the background intensity. In the present calculation, only (3 1 1) and (4 0 0) peaks are considered following the models proposed by Sickafus wherein the intensity of (3 1 1) peak (pertaining to completely ordered spinel) has 100% relative intensity. For the same order spinel, the relative intensity of (4 0 0) peak is 57.18. However, for completely disorder spinel the intensity of (4 0 0) is 100%, while that of (3 1 1) is zero. Therefore, if the observed relative peak intensity of (4 0 0) 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 h 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. *Fd*3*m*):

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

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

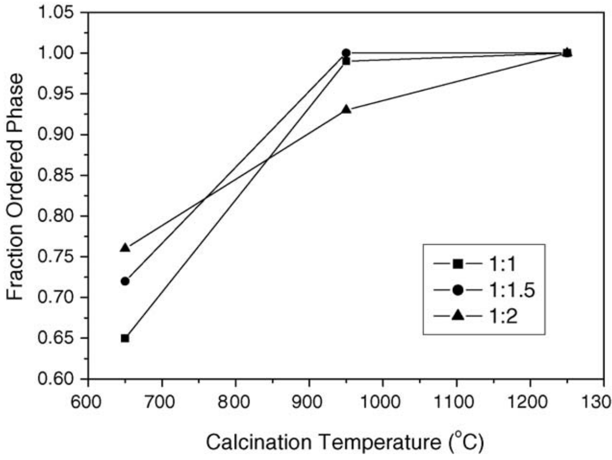

Fig. 2. Variation of ordered spinel phase with nitrate–citrate ratio and calcination temperature based on Rocksalt model.

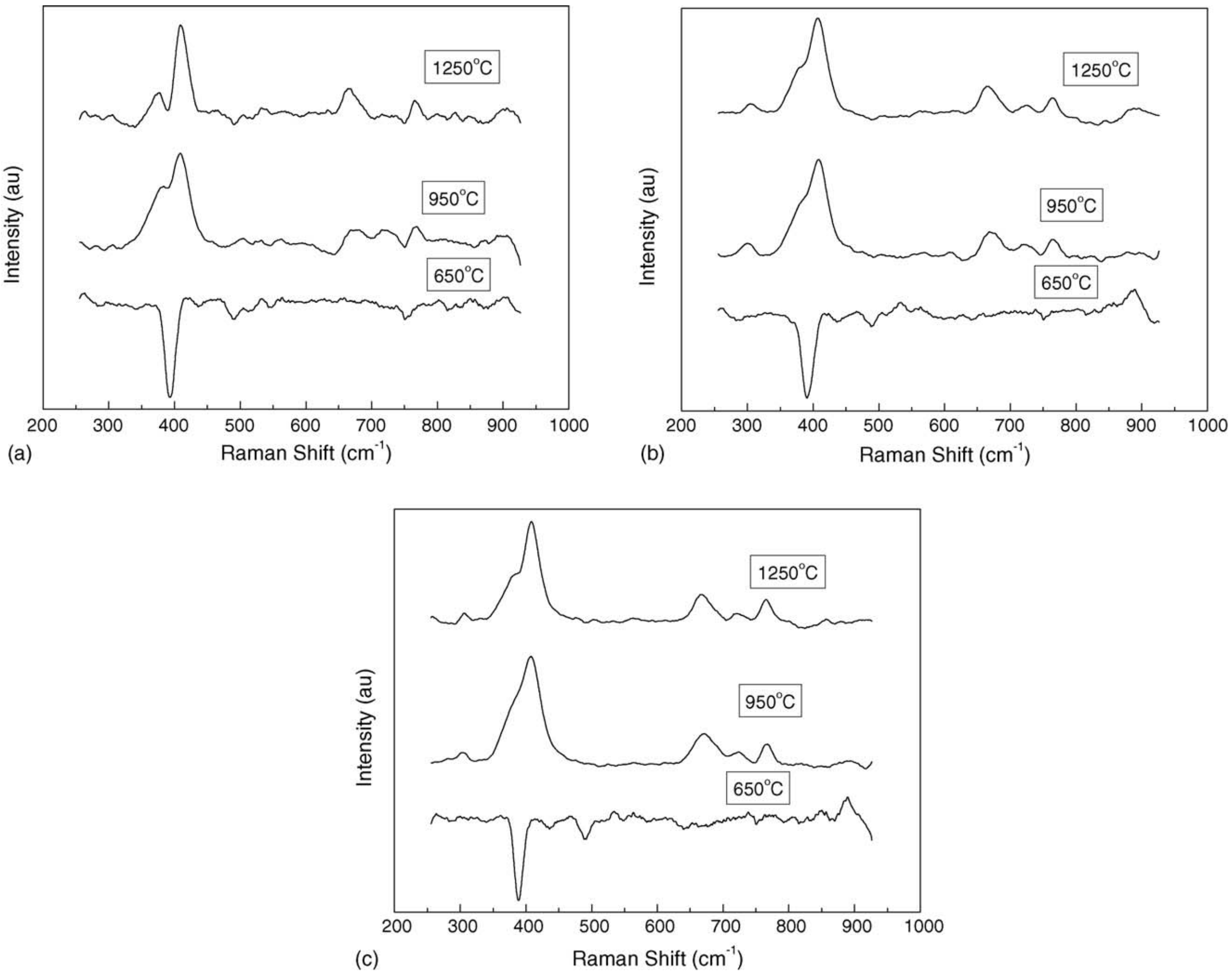

Fig. 3. Raman spectra of spinel as a function of nitrate–citrate ratio: (a) 1:1; (b) 1:1.5; and (c) 1:2.

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 °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.

Table 3

Comparison of Raman peaks in $MgAl_2O_4$ spinel as a function of nitrate–citrate ratio and calcination temperature

IR Peak position (cm^{-1})[7]→		F_{2g} 306.90		E_g 406.00	F_{2g} 670.00	A_{1g} 723.00	A_{1g} 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

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 increasing 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 °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 °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 exothermicity 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 calcination temperature.

(4) Raman spectroscopy revealed that even at 1250 °C, the samples remains partially disordered. However, the degree of disorder is dependent on the nitrate–citrate ratio.

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