

DEVELOPMENT OF SPINEL MAGNESIUM ALUMINATE BY SOLUTION COMBUSTION ROUTE USING THIOUREA AND UREA AS FUEL

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Abstract: In the present article spinel phase magnesium aluminate was synthesized using Magnesium nitrate, Al-nitrate precursors in 1:2 molar ratio using urea and thiourea as fuel and reducing agent. Nitrate salts were mixed in a stoichiometric ratio in distilled water with three different molar ratios of two different fuels: urea and thiourea. The temperature of crystallization was obtained after thermal analysis followed by annealing at a fixed temperature, fixed soaking period for urea as fuel while variable temperature and soaking period were required for thiourea as fuel. FTIR analyses were carried out of the samples to verify the M-O co-ordinations for the phase formation. Prominent octahedral M-O stretching was noted at about 609 cm⁻¹ while that of Al-Mg-O stretching was noted at about 1100 cm⁻¹ for thiourea based samples. Using Urea as fuel Al-O stretching was noted at about 539cm⁻¹ while that of Al-Mg-O vibration was noted at about 677cm⁻¹. Morphological features of the synthesized samples were observed by SEM. Agglomeration was noted for both urea and thiourea as fuel having irregular polygon shape. Using thiourea as fuel, a bit of porous structure was noted while for urea as fuel negligible porosity was noted.

Keywords: Magnesium Aluminate; Thermal analysis; Phase analysis; M-O co-ordinations; Morphology

تحضير معدن السبينيل ذو الومينات المغنيسيوم عن طريق حرق المحلول باستخدام الثيوريوريا واليوريا كوقود

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المخلص: تم خلال هذه الدراسة تصنيع ألومينات المغنيسيوم في طور الإسبينيل باستخدام نترات المغنيسيوم وسلانف النترات بنسبة 1: 2 مولارية باستخدام كلا من اليوريا والثيوريوريا كوقود وعوامل اختزال. تم خلط أملاح النترات بنسب متكافئة في الماء المقطر مع ثلاث نسب مولارية مختلفة لنوعي الوقود المذكورين اعلاه. اسفرت الدراسة بعد التحليل الحراري والتلدين لليوريا والثيوريوريا إلى أن فترة نفع اليوريا ودرجة حرارة تبلوره ثابتتين، بينما تطلب استخدام وقود الثيوريوريا وجود درجة حرارة وفترة نفع متغيرتين، وتم إجراء التحليل الطيفي للعينات للتأكد من تنسيقات M-O لتشكيل الطور. لوحظ تمدد M-O ثماني السطوح البارز عند حوالي 609 سم-1 بينما لوحظ امتداد Al-Mg-O عند حوالي 1100 سم-1 للعينات القائمة على الثيوريوريا. وفي حالة استخدام اليوريا كوقود لوحظ تمدد Al-O عند حوالي 539 سم-1 بينما لوحظ استخدام اهتزاز Al-Mg-O عند حوالي 677 سم-1. تمت ملاحظة السمات المورفولوجية للعينات المركبة بواسطة المجهر المسحي الإلكتروني. كما لوحظ من نتائج التجارب أن تكتل كل من اليوريا والثيوريوريا له شكل مضلع غير منتظم، كما أن للثيوريوريا بنية مسامية تؤخذ بعين الاعتبار بينما كان لليوريا بنية أقل مسامية.

الكلمات المفتاحية: الومينات المغنيسيوم، تحليل حراري، يوريا، ثيوريوريا، وقود.

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1. INTRODUCTION

Magnesium aluminate has lots of industrial applications due to its high melting point (2135°C), high-temperature mechanical strength, chemical inertness, thermal shock resistance, chemical resistance, and low thermal expansion coefficient. (C Păcurariu *et al.* 2007; S.R. Ghosh *et al.* 2018; Ali Saberi *et al.* 2008; P V Marakkar Kutty *et al.* 2013) The presence of such properties makes the compound suitable as high-temperature refractory material for both cement rotary kiln, and steel ladle. In the initial decades, chromite-based spinel is extensively used for steel making, glass tank regenerators, rotary kiln and even for copper industry. However, environmental concern regarding Cr+6 species from the chromite spinel is a hindrance to its applications. (Chandrima Ghosh *et al.* 2015) The above compound has spinel structure represented by the formula AB_2O_4 where A is the divalent ion, B is the trivalent ion and O represents the anion. Divalent Mg and trivalent Al ions occupy tetrahedral (1/8 of available) and octahedral sites (1/2 of available) respectively. (Shiva Salem 2015) The particular spinel ceramic also has excellent optical properties and can be used for transparent ceramics. The optical property enhances its eligibility as a prominent candidate material for transparent armour and visible-infrared windows. It is also utilized for ceramic paints and for making catalyst support, membranes, dye absorbent and as sensors. For the successful application of spinel aluminate as dye absorbent, catalyst, sensors, spinel fabricated needs to possess high purity, controlled particle size, high surface area and uniform pore size distribution. (Narges Habibi *et al.* 2017) Spinel magnesium aluminate also acts as a potential candidate for humidity sensors. In recent researches, it is noted that spinel magnesium aluminate as one potential candidate for photocatalyst to decompose reactive red methylene used as a dye for industrial operations. (Mostafa Y Nassar *et al.* 2014) Purity, particle size, chemical homogeneity, and reactivity of spinel magnesium aluminate are influenced by the synthesis route. (Ali Saberi *et al.* 2008) The material is found to be synthesized by various methods in addition to solid-state reaction like sol-gel (Debsikdar J.C 1985; Naskar M.K. *et al.* 2005) precipitation (Li J-G *et al.* 2000), aerosol method (Yang N *et al.* 1992), co-precipitation (Guo J *et al.* 2004), combustion synthesis, freeze-drying, decomposition of an organometallic complex in super critical fluids, hydrothermal route, plasma spray decomposition of powders, (Bickmore R Clint *et al.* 1996; Bratton R.J. 1969; Barj M. *et al.* 1992; Pommier C. *et al.* 1990; Yang Ning *et al.* 1992; Varnier Olivier *et al.* 1994) microwave-assisted combustion route (Torkian Leila *et al.* 2011), polymerized complex method (Lee P.Y *et al.* 2006; Du Xuelian *et al.* 2014), mechanochemical route (Domanski D. *et al.* 2004), self-propagating high-temperature synthesis (Gorshov V. A. *et al.* 2017) and others.

In the present article, spinel magnesium aluminate is synthesized using urea and thiourea as fuel and reducing agent for three molar ratios along with nitrate precursors. The annealing temperature is confirmed after carrying thermal analysis of mixed solutions followed by phase analysis, bonding analysis and morphological studies.

2. EXPERIMENTAL METHODS

AR grade of magnesium nitrate, aluminium nitrate, urea and thiourea were used as precursors for synthesizing spinel. The stoichiometric ratio of magnesium nitrate, aluminium nitrate were taken in 1:2 molar ratios in distilled water for stirring. The solution undergoes stirring by magnetic beads for sufficient time. After proper mixing of nitrates urea, thiourea was added in 1.25, 1.50 and 1.75 molar ratio with respect to nitrate salts and again undergoes stirring for about 1 hour to ensure homogeneity. The resultant solution undergoes drying in an oven (heater) at about 80°C for about 3-4 hours to obtain a dry gel-like mass. The gel was put into DTA-TGA analyzer (Diamond Pyris, Perkin Elmer) in presence of Nitrogen atmosphere at the heating rate of 10°C/min for determining the thermal characteristics of the sample. Crystallization temperature for spinelization was obtained and after that, the gel was put for annealing at 700°C for 5 hours in the case of urea as fuel. The annealing temperature was 700°C for 5 hours, 800°C for 4.5 hours and 900°C for 4.5 hours respectively for thiourea as fuel. Phase analysis was carried by XRD (Rigaku, Ultima III) having Cu $K\alpha$ wavelength of 1.54Å, 40KV with a scan range of 10-80° having a scan rate of 5°/minute. Bonding analysis was carried by FTIR (IR Prestige-21, Shimadzu) to determine M-O coordination of the required phase after preparing pellet samples with KBr. Morphological structures were analyzed by SEM (Jeol, JAX 840A) using carbon conducting tape to stick the powder sample for better resolution and to avoid electrostatic charging.

3. RESULTS AND DISCUSSIONS

DTA-TGA curve exhibits initial weight loss in the temperature range between 100-200°C. From the curve in Fig. 1 two prominent endothermic peaks at about 100°C and 200°C are noted. First one suggests the removal of physically absorbed water and 2nd one suggests removal of structural water.

A large exothermic peak is observed due to burning or oxidation of organic compounds which is mainly a combustion of carbonaceous and sulphur

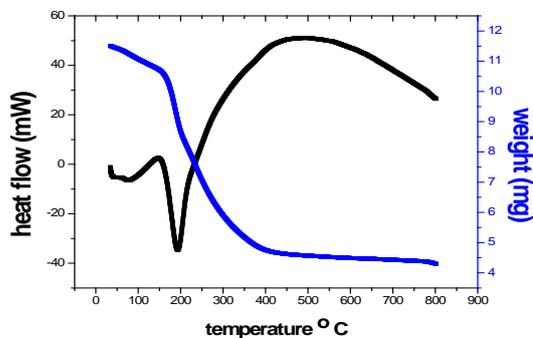


Figure 1. DTA-TGA curve of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with thiourea as fuel and reducing agent having a heating rate of 15°C/min.

elements due to thiourea corresponding to 2nd prominent weight loss. A minor endothermic peak is observed around 350°C due to the initial formation of γ -alumina. (Macêdo Maria laponeide Fernandes *et al.* 2007) The second endothermic peak with minor weight change is noted due to possible dissociation of nitrate precursor salts at about 450°C (Macêdo Maria laponeide Fernandes *et al.* 2007). A broad weak exothermic peak ranging from 500°C to 700°C is noted which corresponds to the initiation of the crystallization process and records the third weight loss. Crystallization of gel from precursors always involves weight loss and undergoes exothermic reaction. Weight loss occurs possibly because of the presence of the multicomponent compound and their interactions. The stability of weight loss indicates full onset of the crystallization process.

Figures 2-7 represent XRD spectra of the synthesized sample using Urea and thiourea respectively as fuel. Three different molar ratios of 1.25, 1.50 and 1.75 are considered for each fuel respectively. It has been noted that for spinel magnesium aluminate synthesized by urea annealing temperature and soaking period are kept fixed. For such conditions, spinel has been noted for all molar ratios of urea as fuel, reducing agent. Peak intensity is optimum for all cases. Slight amorphous nature of spectra is noted for all cases. Lower urea fuel ratio of 1.25 exhibits much better crystalline nature of spectra than higher fuel ratio. It may be possible due to higher reduction tendency and calorific value of fuel with more molar ratio which could also possibly accelerate the reaction and shorten the transformation period to induce the required phase. In contrast with thiourea as fuel, the reducing agent annealing temperature is increased. Annealing temperature and soaking period carried are carried as follows 700°C for 5 hours, 800°C for 4.5 hours and 900°C for 4.5 hours, respectively. The crystallinity of peaks got increased with temperature for thiourea but in the present research the focus is on lower temperature spinelization hence for both fuels 700°C for 5 hours is taken as reference. For both cases, successful spinel phase formation is noted. For urea, spinel formation is verified by comparing the XRD spectra with JCPDS card file #01-077-1193, #01-075-1800, #01-082-2424 and #01-077-0437 respectively. For thiourea based fuel spinel is verified by comparing the XRD spectra with JCPDS card file #01-086-0085, #01-075-1800, #01-082-2424 and #01-077-0437 respectively. Using urea as fuel all peaks are indexed as spinel phase. No intermediates or other phases are noted. Major planes of growth for Spinel is noted along (311), (220), (111), (400), (511) and (440) planes. A similar trend is also noted for thiourea as fuel and reducing agent. For thiourea based fuel no intermediates or presence of other phases are noted except for only spinel phase. Crystallite size is calculated by Scherrers formula $t = 0.9\lambda/\beta\cos\theta$ where t is the crystallite size, λ is the wavelength, $\text{Cu K}\alpha = 1.54\text{\AA}$, β is the full width of

half mean, θ is the angle corresponding to the spectra. For 1.25, 1.75 molar ratio of urea, crystallite size is found to be about 36.52nm, while for 1.50 molar ratio it is noted to be about 48.69nm. In the case of thiourea, crystallite size is calculated and noted to be about 42.96nm, 48.69nm and 73.02 nm respectively. Such variation in crystallite size is noted since annealing temperature varies. In the present context, the focus is on lower temperature synthesis henceforth, further analyses will be carried for samples synthesized at 700°C for 5 hours for both urea, thiourea as fuel where full phase development is noted from XRD analysis.

Figures 8-9 represent FTIR spectra of spinel synthesized using urea and thiourea as fuel. For both cases, scanning range is within 450-4500 cm^{-1} while major M-O coordinations are noted within 1000 cm^{-1} . It has been noted for the urea-based synthesis of spinel, M-O coordinations are noted mostly within 1000 cm^{-1} . Al-O stretching is noted at about 539 cm^{-1} while Mg-O-Al vibration is observed at 677 cm^{-1} approximately. The FTIR analysis is noted to be in correspondence with research findings by (S.R. Ghosh *et al.* 2018; Mukherjee 2020). For thiourea, M-O coordinations are noted for Al-O stretching, Al-Mg-O stretching at about 609 cm^{-1} and 1100 cm^{-1} respectively. Spectral peaks at about 1655 cm^{-1} , 2356 cm^{-1} and 3311 cm^{-1} are noted for H-O-H stretching, $\text{CH}_3\text{-CH}_2$ vibration, and O-H bonding vibration. The presence of H-O-H stretching, O-H vibration is possibly due to some physically absorbed moisture on the surface of the sample since FTIR analysis is carried in a normal atmosphere without any purging of gas. Figures 10 and 11 represent morphology obtained by SEM analysis of spinel after annealing at 700°C for 5 hours using thiourea and urea of 1.25 molar ratios as fuel. For both fuels, agglomeration tendency is observed with the irregular polygonal shape of the agglomerated chunk. Figs. 10 A and B represent morphology for thiourea based spinel samples with minor porosity on the surface and negligible interconnected porosity. Figure 10 B exhibits agglomerated chunk for spinel by thiourea as fuel having irregular step around the periphery of agglomerate with some convex fracture at some portion of the chunk morphology. Figures 10 A-D execute individual particulates to be spherical or bean shape to irregular polygonal shape for thiourea based fuel for spinel formation. Figure 10 D represents a bit flaky structure for some portion. Figure 11 B represents an agglomerate chunk with a polygonal shape having sharp edges while the size of the agglomerated chunk is noted to be about 4 μm while individual particulates are about 0.2 μm . Figures 11 A-C execute dense compact formation of spinel using urea as fuel in compare to a bit porous structure noted using thiourea as fuel. Individual particulates are spherical with agglomerate having dimensions close to 2.5 μm to 5 μm . Individual particulates are noted to be about 0.3 μm to 0.4 μm in range.

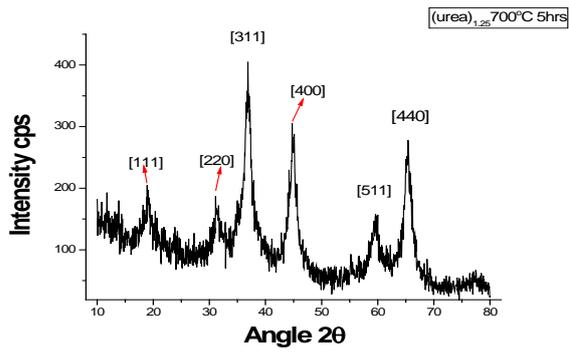


Figure 2. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with urea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

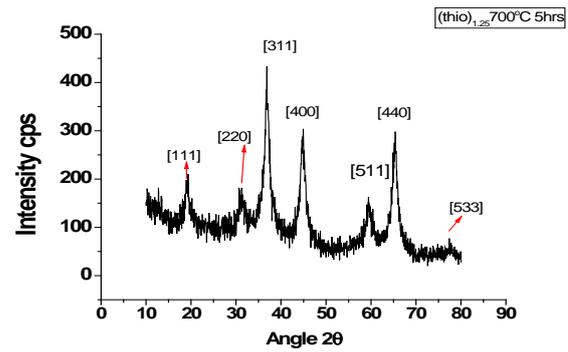


Figure 5. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with thiourea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

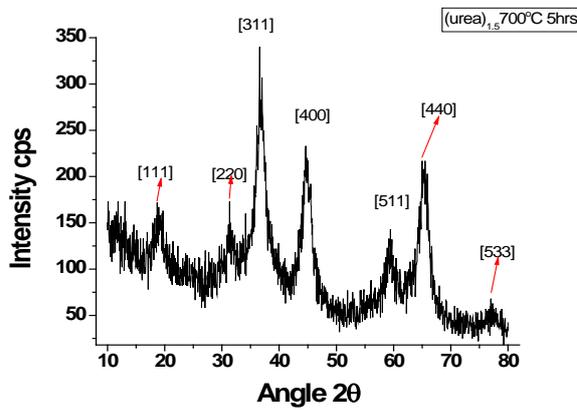


Figure 3. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with urea as fuel and reducing agent having 1.50 molar ratio after annealing at 700°C for 5 hours.

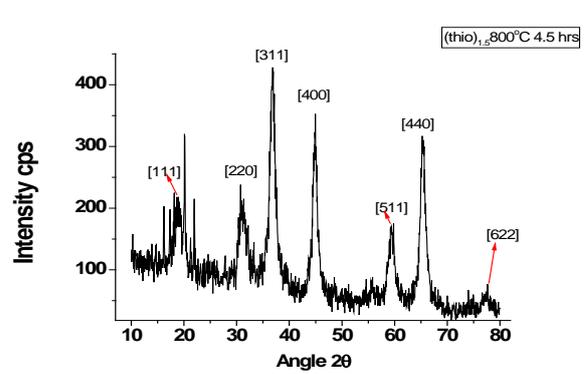


Figure 6. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with thiourea as fuel and reducing agent having 1.25 molar ratio after annealing at 800°C for 4.5 hours.

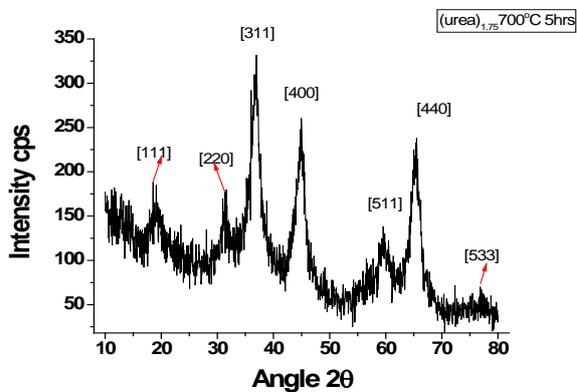


Figure 4. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with urea as fuel and reducing agent having 1.50 molar ratio after annealing at 700°C for 5 hours.

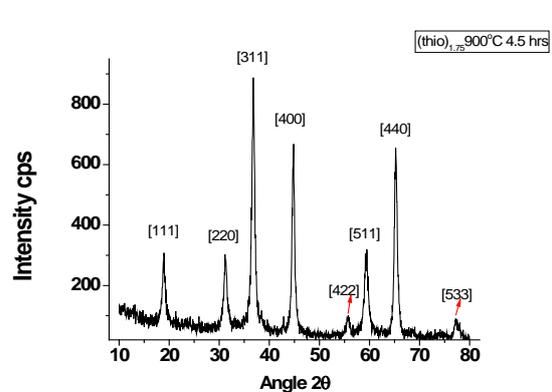


Figure 7. XRD spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with thiourea as fuel and reducing agent having 1.25 molar ratio after annealing at 900°C for 4.5 hours.

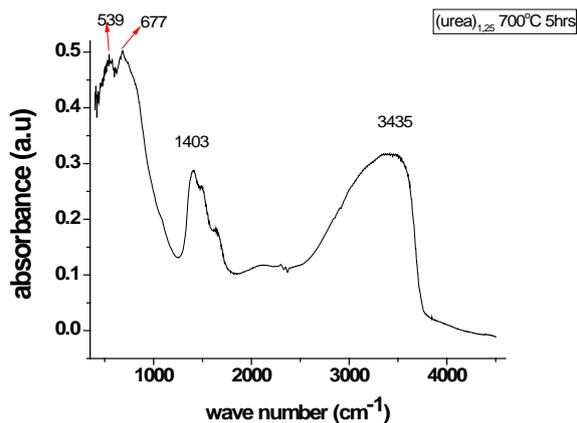


Figure 8. FTIR spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with urea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

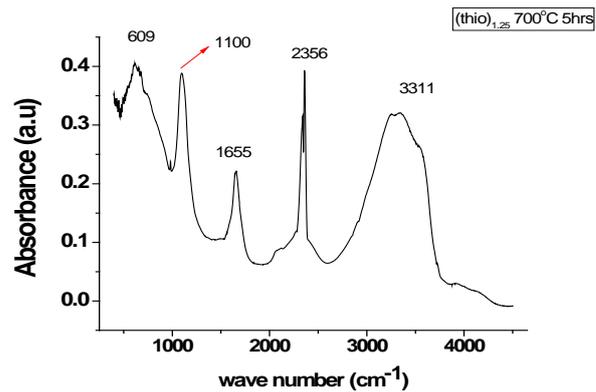


Figure 9. FTIR spectra of Magnesium nitrate: Al-nitrate precursors in 1:2 molar ratio with thio urea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

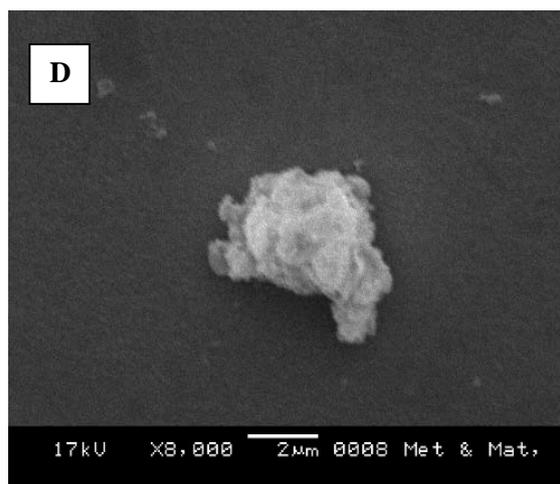
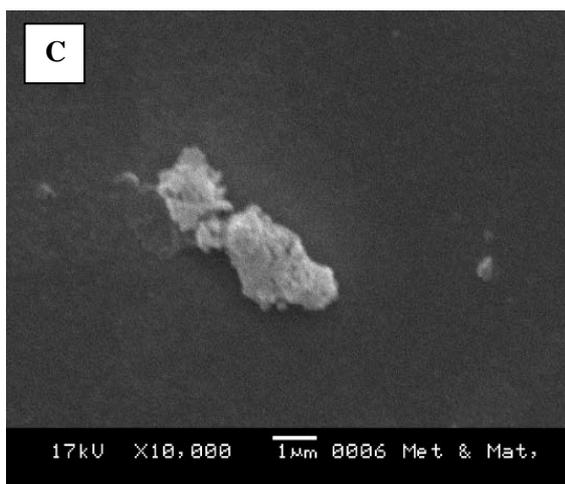
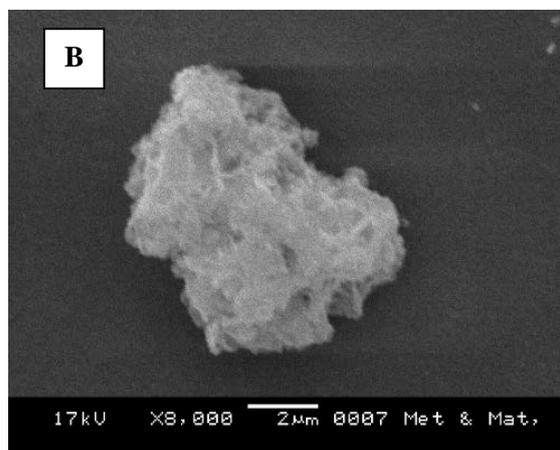
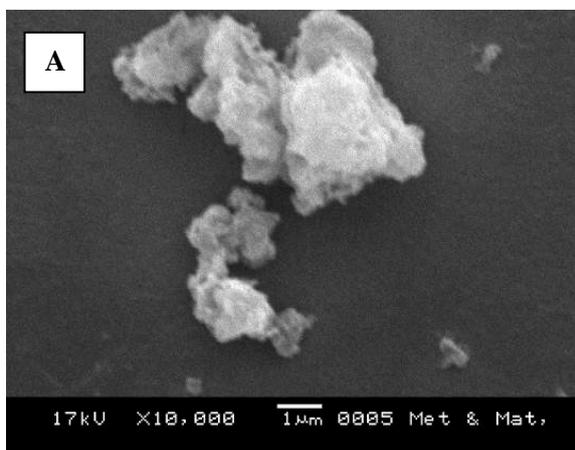


Figure 10. SEM morphology of Spinel Magnesium Aluminate using thiourea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

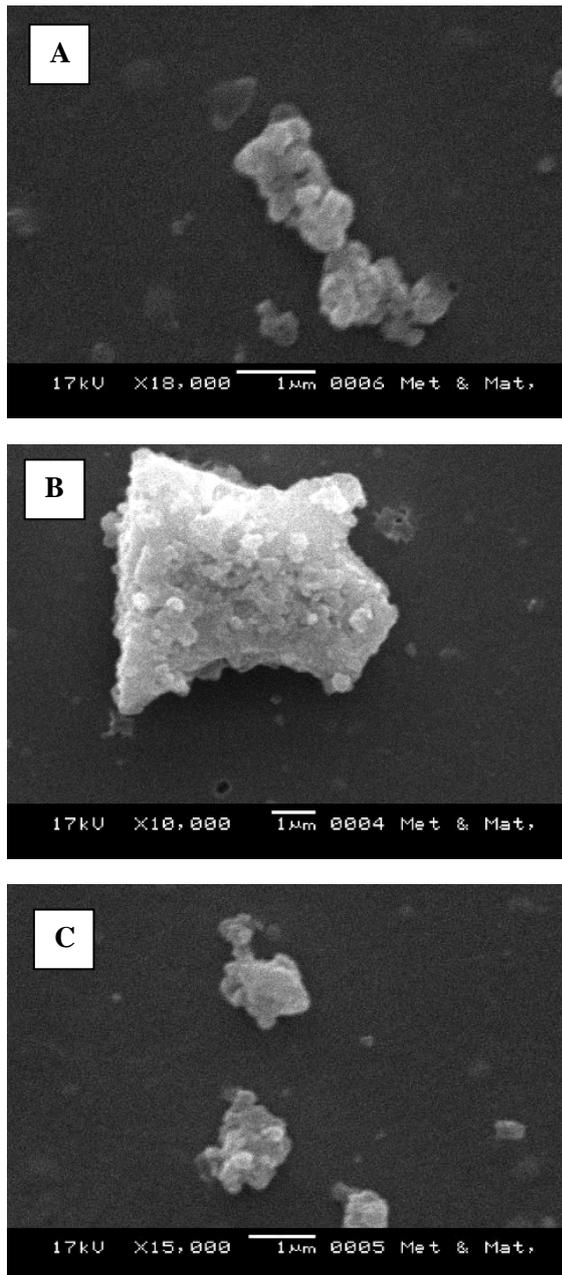


Figure 11. SEM morphology of Spinel Magnesium Aluminate using urea as fuel and reducing agent having 1.25 molar ratio after annealing at 700°C for 5 hours.

CONCLUSION

Spinel magnesium aluminate was prepared using thiourea and urea as a fuel and reducing agent. Thermal analysis of precursors along with fuel indicate the onset of crystallization in the range of 500-700°C. The goal of low-temperature spinelization was achieved for both cases as the temperature was about 700°C with 5 hours soaking period and confirmed from XRD phase analysis. FTIR analysis confirmed the M-O coordinations and it was noted that Al-O coordination was about 539cm⁻¹ while Mg-

O-Al vibration was observed at about 677cm⁻¹. Agglomerated mass with irregular polygon shape was noted as morphological features after using both urea and thiourea as fuel, reducing agent for synthesizing spinel magnesium aluminate. Using thiourea as fuel, the dimension of the agglomerated chunk was about 4μm and for individual particulate, it was about 0.2μm. Similarly, using urea as fuel agglomerate was in the range of 2.5 to 5μm and for individual particulate was about 0.3 to 0.4μm. Thiourea induces a slight porosity in structure while negligible dense mass was noted using urea as fuel.

CONFLICT OF INTEREST

The authors declare that there are no conflicts of interest as regards this article.

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