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Evolution of Spinel Magnesium Aluminate by Combustion Route Using Glycine as Fuel and Its Characterization

Soumya Mukherjee
Department of Metallurgical Engineering, Kazi Nazrul University, Asansol, Burdwan,
West Bengal, India.
Email: smmukherjee3@gmail.com, smmukherjee4a@gmail.com

Abstract: Magnesium aluminate spinel was synthesized by solution combustion route in place of industrial practised solid-state process. To maintain the proper stoichiometric ratio, nitrate salt precursors were used in 2:1 molar ratio while glycine was used as a fuel and reducing agent for preparation. After annealing the prepared solution at 700 °C for 5 hours with variation in glycine as 1.25, 1.50 and 1.75 molar ratio phases were developed. XRD analysis confirmed the phases developed after proper annealing in an oxidizing atmosphere. FTIR analysis yields the M-O coordinations and the bonding information of the synthesized compound. SEM analysis exhibits irregular polygon particulates having agglomerated chunk morphology with negligible porosity while EDX analysis confirmed the elements required for phase formation.

Keywords: EDX analysis, M-O coordinations, Phase analysis, Spinel.

I. Introduction

Magnesium aluminate is a spinel based compound having formula AB_2O_4 where A and B are divalent, trivalent metal ions having tetrahedral, octahedral co-ordinations with oxygen as an anion. Stoichiometric spinel contains 71.8 wt% Alumina and 28.2 wt% MgO. Solid solutions of higher alumina or magnesia content spinel can be prepared at higher temperatures and can be retained by rapid cooling [1]. Spinel magnesium aluminate offers various unique properties like high melting point, excellent resistance against chemical attack, can retain high strength even at elevated temperatures and possess good thermal characteristics. $MgAl_2O_4$ develops high strength at both normal and elevated temperature and it has no phase transition up to a melting point (2135 ºC) [2]. Variation in synthesis condition leads to changes in morphological features and variation in particle sizes. Moreover, final properties of the products based on spinel magnesium aluminate are found to be dependent on texture analysis which is controlled by nature, amount of additive solvents, calcination temperature and presence of atmosphere control during synthesis [3]. Excellent performance and affordability of $MgAl_2O_4$ yield the material as superior armor materials in compare to sapphire, AlON, soda-lime silicate glass, and MgF_2 [4]. Among chemical routes, the sol-gel technique is an extensive popular one and it provides the advantage of pure, ultrafine powders, uniform distribution with high surface area and porosity distribution at a lower temperature than solid-state calcination [5]. Till date, several other chemical routes are adopted for the synthesis of spinel magnesium aluminate. Some of the commonly adopted routes as reported in previous research articles are citrate-nitrate route [6], a sol-gel technique [7], Pechini [8] and coprecipitation method [9]. Solution combustion route of synthesis has been regarded as the most effective and economic methods among wet processing methods due to its convenient processing, simple experimental setup and significant time-saving and high purity products [10].

In the present article synthesis of spinel, magnesium aluminate is tried using Magnesium nitrate, Al-nitrate precursor solutions and glycine as fuel and reducing agent by solution combustion route.

II. Methods of Preparation

AR grade high purity precursor salts of Magnesium nitrate, Al nitrate were used in 2:1 molar ratio along with glycine as fuel and reducing agent. Glycine was added in 1.25, 1.50 and 1.75 molar ratio with the salt precursors maintaining stoichiometric ratio along with double distilled water for preparing the resultant solution. Proper stirring and heating of mixed solution were ensured at about 80 °C for 3-4 hours. Ensuring proper drying of the solution, the resultant mass was made to undergo annealing at about 700 °C for 5hours for 3 different fuel ratios of 1.25, 1.75 and 1.50 respectively. XRD analysis of the annealed powder evaluates the required phases while M-O coordination bonding of the synthesized powder samples (pelletized form) was executed by FTIR analysis. Morphology was studied by SEM followed by EDX to confirm the elements present in the sample.

III. Results and Discussion

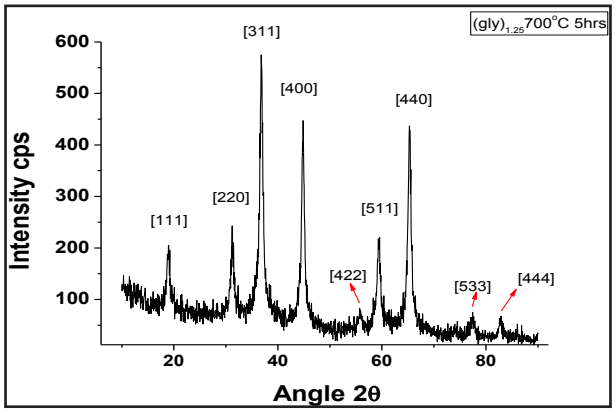

Fig. 1: XRD of Spinel Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.25 Molar Ratio

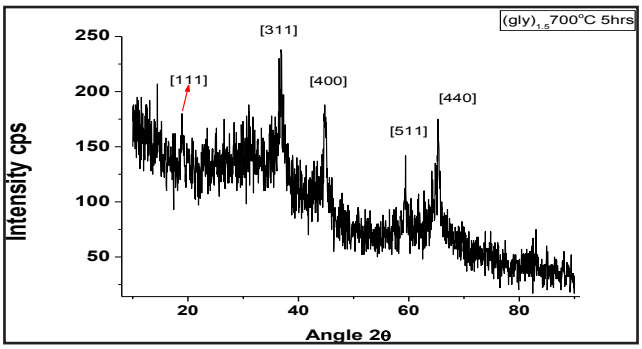

Fig. 2: XRD of Spinel Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.50 Molar Ratio

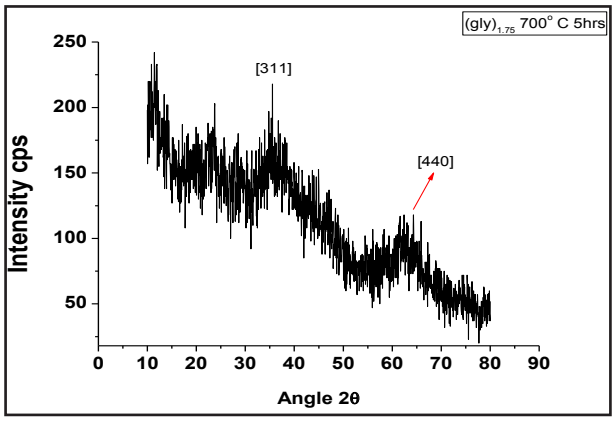

Fig. 3: XRD of Spinel Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.75 Molar Ratio

Fig. 1 corresponds to XRD spectra which have been indexed with the help of the standard JCPDS library (#01-082-2424, #01-077-1193, #01-075-1800) and all the peaks are of $MgAl_2O_4$ spinel. Prominent 6 planes of orientation (111), (220), (311), (400), (511) and (440) were noted for glycine of 1.25 molar ratio, after annealing at 700 °C followed by 5 hours of soaking period. All the major and minor planes were indexed with the spinel phase while no intermediates or presence of precursor oxides were noted. Using Scherrer's formula crystallite size was estimated to be about 17.81 nm. For 1.50 molar ratio of glycine, (Fig. 2) spinel magnesium aluminate crystallite size was noted to be 48.63 nm (JCPDS #01-082-2424, #01-075-1800) and this change was quite drastic even though the annealing condition maintained was similar. For this molar ratio of glycine 5 major indexed planes were noted instead of previously mentioned 6 major planes. Plane of (220) was found to be disappeared with higher glycine content which was present in the previous case. Interestingly, crystalline peaks noted were slight with amorphous wide peaks and planes were not sharply defined as in the previous case of spinel developed using 1.25 molar ratio of glycine (Fig. 3, JCPDS #1-077-0437). It was noted from the experiments using a still higher molar ratio of glycine 1.75 molar ratio amorphous peaks were noted with poor rate of crystallization. Only 2 prominent intermediate sharp peaks of (311) and (440) planes were noted. Both peaks were noted in all three molar ratio of glycine content at fixed annealing conditions. Crystallite size was estimated to be about 44.11 nm. Intermediate oxides or precursor oxides were not noted in these cases indicating successful phase evolution of spinel magnesium aluminate for all conditions. Crystallite size was noted to be least for lower glycine content as fuel and reducing agent while crystallite size was observed to increase with higher glycine content. The entire phase evolution of spinel was carried at a fixed annealing temperature and soaking period.

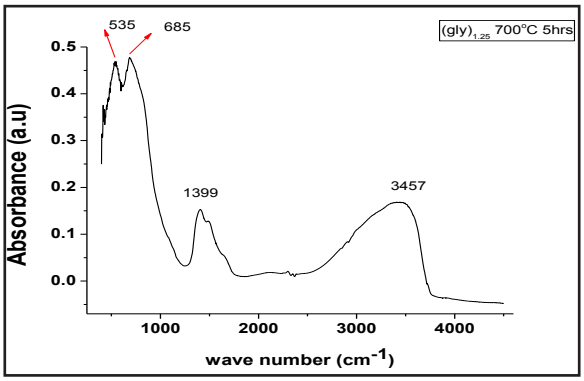

Fig. 4: FTIR Spectra of Spinel Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.25 Molar Ratio

Fig. 4 give IR spectra value for Spinel ($MgAl_2O_4$) synthesized using Glycine as a fuel and reducing agent. Out of 3 different molar ratio of glycine utilized for synthesis lower molar ratio was noted to have better crystalline nature and formation rather than other 2 molar ratios. FTIR analysis gives the bonding information of the synthesized sample in the form of pellet using KBr as a reference. Annealing at 700 °C for 5 hours with 1.25 molar ratio was shown where M-O coordinations of 535 cm and 685 cm^{-1} were the main spectral peaks. Al-O stretching corresponds to 535 cm^{-1} and Mg-O-Al vibration corresponds to 685 cm^{-1} indicating the successful sample synthesis aligning it with XRD phase identification.

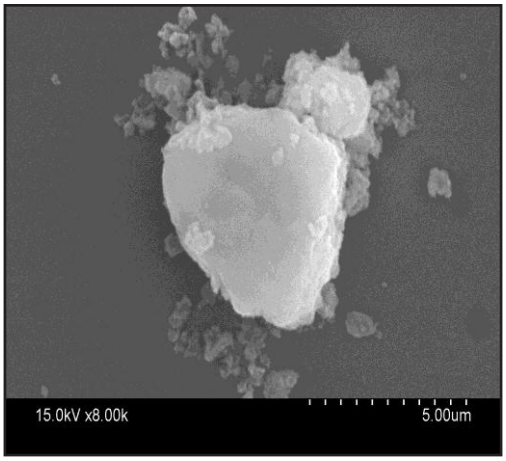

Fig. 5: SEM Morphology of Spinel Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.25 Molar Ratio

Fig. 5 exhibits morphology of spinel magnesium aluminate synthesized after annealing at 700 °C for 5 hours using 1.25 molar ratio of glycine. Morphology of the sample exhibits an agglomeration tendency. The agglomerated chunk was spade shape, flaky layers with negligible porosity on the surface. As a whole, the agglomerated chunk was dense type structure while the individual particles were spherical or polygonal shape in the order of 0.2 μ to 1 μ. Agglomerate was a soft type with weak bondage as observed due to sporaidic arrangement of particulates as noted in the top portion of the morphology of the chunk.

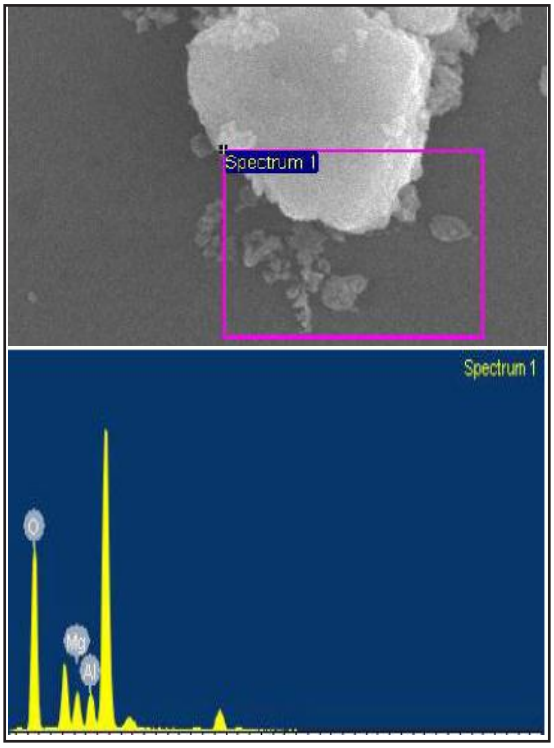

Fig. 6: EDX Analysis of Magnesium Aluminate After Heating at 700 °C for 5 Hours Using Glycine of 1.25 Molar Ratio

Fig. 6 exhibits the EDX spectra of magnesium aluminate after annealing at 700 °C for 5 hours using glycine of 1.25 molar ratio. The sharp spectral peaks of O, Mg and Al respectively were noted which satisfies the successful synthesis of spinel ($MgAl_2O_4$) phase. The portion of image analysed for elemental analysis was marked in the figure. Other peaks of K, Si were noted since drop cast of sample solution was made on a glass slide which contains oxides of Si and K causing the presence of some peak of those elements.

IV. Conclusion

Magnesium aluminate was obtained using Magnesium nitrate, Al-nitrate precursors of 2:1 molar ratio with glycine as a fuel having 1.25 molar ratios were utilized. XRD confirms the proper spinel phase as per JCPDS #01-077-1193, #01-082-2424, #01-075-1800 after annealing at 700 °C for 5 hours. It was noted that with increasing glycine molar ratio as fuel crystallization of peaks becomes less intense while crystallite size also increases. M-O co-ordinations confirm the bonding analysis of compound while morphology having agglomerated chunk, with negligible porosity and spherical to polygonal shape particulate was noted. From the above, a simple low-cost combustion route was carried to synthesize Spinel which can withstand high temperature and corrosion in adverse conditions.

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References

[1] N. M. Khalil, M. B. Hassan, F. S. Ali, and M. M. E. Shakdofa, "Preparation and characterization of nano spinel powder via co-precipitation and sol gel techniques," *Main Group Chemistry*, vol. 12, no. 4, pp. 331-347, 2013.

[2] S. R. Ghosh, S. Mukherjee, and S. Banerjee, "Solution combustion synthesis of alumina spinel and its characterization," *Interceram - International Ceramic Review*, vol. 67, pp. 34-41, 2018.

[3] D. Mohapatra, and D. Sarkar, "Effect of in situ spinel seeding on synthesis of MgO-rich $MgAl_2O_4$ composite," *Journal of Materials Science*, vol. 42, pp. 7286-7293, 2007.

[4] N. Habibi, Y. Wang, H. Arandiyan, and M. Rezaei, "Low-temperature synthesis of mesoporous nanocrystalline magnesium aluminate ($MgAl_2O_4$) spinel with high surface area using a novel modified sol-gel method," *Advanced Powder Technology,* vol. 28, no. 4, pp. 1249-1257, 2017.

[5] E. M. M. Ewais, D. H. A. Besisa, A. A. M. El-Amir, S. M. El-Sheikh, and D. E. Rayan, "Optical properties of nanocrystalline magnesium aluminate spinel synthesized from industrial wastes," *Journal of Alloys and Compounds*, vol. 649, pp. 159-166, 2015.

[6] H. J. Zhang, X. L. Jia, Z. J. Liu, and Z. Z. Li, "The low temperature preparation of nanocrystalline $MgAl_2O_4$ spinel by citrate sol–gel process," *Materials Letters*, vol. 58, no. 10, pp. 1625-1628, 2004.

[7] R. K. Pati, and P. Pramanik, "Low-temperature chemical synthesis of nanocrystalline $MgAl_2O_4$ spinel powder," *Journal of the American Ceramic Society*, vol. 83, no. 7, pp. 1822-1824, July 2000.

[8] V. Montouillout, D. Massiot, A. Douy, and J. P. Coutures, "Characterization of $MgAl_2O_4$ precursor powders prepared by aqueous route," *Journal of the American Ceramic Society*, vol. 82, no. 12, pp. 3299-3304, 1999.

[9] G. Ye, G. Oprea, and T. Troczynski, "Synthesis of $MgAl_2O_4$ spinel powder by combination of sol–gel and precipitation processes," *Journal of the American Ceramic Society*, vol. 88, no. 11, pp. 3241-3244, 2005.

[10] S. T. Aruna, and A. S. Mukasyan, "Combustion synthesis and nanomaterials," *Current Opinion in Solid State and Materials Science*, vol. 12, no. 3-4, pp. 44-50, 2008.