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Exploring the Properties, Synthesis, and Applications of Magnesium Aluminate Nanoparticles

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Abstract

Magnesium aluminate ($MgAl_2O_4$) is a synthetic ceramic compound, characterized by a spinel structure and comprised of magnesium oxide (MgO) and aluminum oxide (Al_2O_3). Magnesium aluminate is esteemed for its distinctive combination of thermal, mechanical, and optical characteristics, making its role remarkable for various applications. Hence this review, focuses mainly on magnesium aluminate nanoparticles, a subject that is gaining prominent attention in the current research scenario. There are several methods available for the synthesis of $MgAl_2O_4$ nanoparticles (MANPs), including sol-gel and co-precipitation techniques, along with those that incorporate green methodologies. The high melting point, substantial hardness, and excellent thermal shock resistance of the host material suggest that MANPs could hold a significant place in the field of nanotechnology. Numerous studies have demonstrated that the introduction of different ions into MANPs through doping effectively altered their characteristics, thereby improving their functional capabilities. Thus, this review gives a comprehensive examination of the properties of magnesium aluminate, the synthesis methods utilized, impacts of doping, and various applications of magnesium aluminate nanoparticles.

Keywords: Magnesium Aluminate Nanoparticles, Spinel, Synthesis, Sol-gel, Precipitation, Doping, Refractory

Introduction

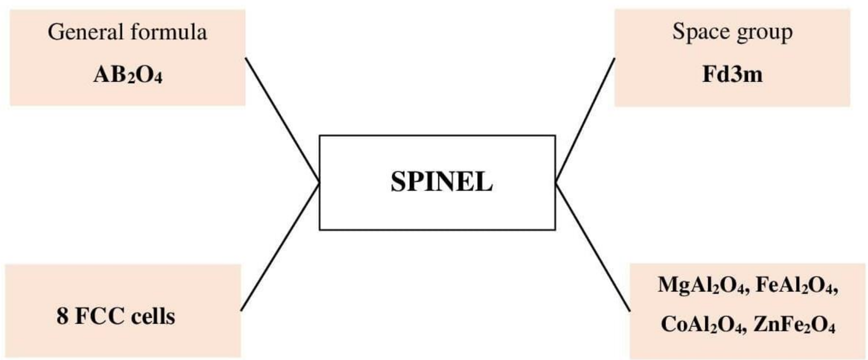
Magnesium Aluminate ($MgAl_2O_4$) is an artificially synthesized compound, having outstanding chemical, optical and electric properties. These exceptional properties contribute to its uniqueness and have attracted considerable interest worldwide. Since its natural occurrence is mere, the synthesis of $MgAl_2O_4$ is commonly achieved through a direct solid-state reaction between MgO and Al_2O_3 (Ganesh, 2013). The thermal characteristics of magnesium aluminate have been thoroughly examined, with findings indicating its ability to operate at high temperatures reaching 2000°C, substantial strength at elevated temperatures, and notable corrosion resistance (Khan et al., 2024). Owing to the remarkable properties exhibited by magnesium aluminate, the properties and applications of magnesium aluminate nanoparticles are currently under investigation. The effective functioning of some nanoparticles requires adjustment of their attributes. Doping is a process characterized by the integration of individual ions into nanostructures, has been acknowledged as a significant and innovative approach for property enhancement (Sharma et al., 2022). $MgAl_2O_4$, doped with various ions resulted in relevant conclusions.

Magnesium aluminate nanoparticles find usefulness in a range of industrial applications, including water purification, production of ceramics, removal of dyes etc. (Tun & Naing, 2019).
This review aims to provide an in-depth perspective on magnesium aluminate and $MgAl_2O_4$ nanoparticles, highlighting the synthesis methods, effect of doping and applications of MANPs.
Magnesium aluminate spinel (MAS) is a notable ceramic material, esteemed for its distinctive array of advantageous characteristics (Baruah et al., 2023). These properties include high melting point (2135ºC), low density (3.58 g/cm^3), a non-reactive nature towards chemicals, thermal stability at elevated temperatures and a surface that is capable of adsorption (Khan et al., 2024). Magnesium aluminate spinel, is a durable cubic single crystal material with desirable and unique qualities such as durability, chemical resistance, high hardness, high strength, and good shock resistance. Polycrystalline magnesium aluminate spinel serves as a budget-friendly alternative to sapphire crystals in the realm of optical applications due to its large band gap and isotropic reflection index (Talimian et al., 2019). Magnesium aluminate spinel in its natural state exhibits the regular spinel structure, but, synthetic spinels manufactured at high temperatures adopt an inverse structure (Tropf & Thomas, 1997). The general properties of Magnesium Aluminate Spinel are represented in Table 1 and Figure 1.

Table 1: General properties of Magnesium Aluminate Spinel

Chemical formula	$MgAl_2O_4$	
Appearance	White colour	
Molecular weight	142.27 g/mol	
Structure	Cubic crystal structure (spinel)	(Ganesh, 2013)
Melting point	2135ºC	(Rooi Ping et al., 2001)
Density	3.58 g/cm^3	(Talimian et al., 2019)
Specific gravity	3.3	(Tun & Naing, 2019)
Thermal expansion coefficient	9 x 10^{-6} °C at a temperature between 30 and 1400ºC	(Ganesh, 2013)
Solubility	Insoluble	(Tun & Naing, 2019)

Figure 1. An overview of Spinel materials



Methods of synthesis of Magnesium Aluminate Nanoparticles

Numerous methods have been developed for the synthesis of Magnesium aluminate nanoparticles. Sol-gel auto combustion method, an innovative and economical method, was utilized in certain studies to synthesis magnesium aluminate nanoparticles, where oxalic acid, urea, and citric acid fuels were bound to play the role of chelating agents (Nassar et al., 2014). In a recent study aimed at detecting the concentrations of Ni(II) ions in products commonly consumed by children, a modified co-precipitation technique was performed to develop MANPs (Mostafa et al., 2024). Magnesium aluminate is recognised as a part of the ceramic family, and MANPs were found useful in developing refractory crucibles. To achieve this, MANPs were synthesised via the molten salt method, where powders of MgO and Al_2O_3 were employed as the raw materials (Khan et al., 2024). Ghodrati et al. (2023) developed MANPs by combustion synthesis to make PLA/$MgAl_2O_4$ scaffolds (Ghodrati et al., 2023). The co-precipitation method was utilised in several studies with 5% NH4OH (Madduluri et al., 2020), liqour ammonia (Viswanathan et al., 2020), urea, and ammonium bicarbonate (Serivalsatit et al., 2012) as precipitating agents for various purposes. The sol-gel method serves as a prominent method for the synthesis of MANPs. Investigations had featured stearic acid as a capping agent (Eslami et al., 2024), while EDTA, salicylic acid, and oxalic acid had also been used as chelating agents (Liu et al., 2023). Earlier, magnesium aluminate nanoparticles were synthesized by hydrothermal-assisted sol-gel method using aluminium nitrate, magnesium chloride and urea (Tun & Naing, 2019). In a recent study, Santos and Ribeiro (2024) employed a polyol-mediated process for the synthesis of magnesium aluminate nanoparticles, with diethylene glycol serving as the solvent (Lopes Nunes Abreu Dos Santos & Ribeiro, 2024). Another study reported that MgCl 2 addition increased the amount of spinel phase in $MgAl_2O_4$ spinel synthesized by the oxide mixing method (Mohammadi et al., 2014). In order to investigate their role as an adsorbent, $MgAl_2O_4$ nanoparticles were produced through a hydrolysis reaction utilizing aluminum isopropoxide and magnesium ethoxide as the precursor materials (Rao et al., 2020). Magnesium aluminate spinel ($MgAl_2O_4$) synthesized by a self-propagating high-temperature synthesis method using Mg–Al alloy were reported to be of high purity and excellent crystallinity (Wang et al., 2022). Citrate–nitrate sol–gel route was employed once to develop $MgAl_2O_4$ nanoparticles with varying concentration of Chromium for assessing the effect of doping with Cr (Saha et al., 2012). Photocatalytic studies of $MgAl_2O_4$ nanoparticles with different concentrations of Alumina were carried out (Rahman & Jayaganthan, 2015). A green methodology utilizing starch was performed to fabricate pure magnesium aluminate nanoparticles (Talebi et al., 2016). The production of magnesium aluminate spinels using aloe vera as a chelating agent worked well with reasonable indications in the field of green synthesis of nanoparticles (Ferreira et al., 2022). A surfactant-assisted precipitation method was employed to synthesize nanocrystalline $MgAl_2O_4$ spinel, with N-Cetyl-N,N,N-trimethylammonium bromide (CTAB) serving as the surfactant. Addition of the surfactant has positively influenced the structural properties of the material (Alvar et al., 2010). A solution combustion reaction, combined with the use of a domestic microwave oven, has accomplished the successful synthesis of nanocrystalline $MgAl_2O_4$ spinel. The resultant material was found to have better phase purity and compositional stability than those synthesised through conventional technique (Ganesh et al., 2005). A simple and affordable method was employed to produce MgO/$MgAl_2O_4$ nanopowder, where they used scrap wastes of magnesium and aluminium. The synthesised powder was also ideal for many applications (Ewais et al., 2017). Pechini method, also known as polymeric precursor method was employed to produce ultrafine magnesium aluminate nanoparticles. This method is known for many advantages like ability to synthesise large quantity from one batch, production of stable complexes over varying pH (Rufner et al., 2013).

Effect of Doping

Doping is an innovative technique for the modification of nanoparticles, affecting their physical, chemical, electrical, optical and other properties to enhance their applications in various fields (Shenoy et al., 2022). Upon doping magnesium aluminate nanoparticles with sodium (Na), an improvement in their optical properties was observed, with transmittance values greater than those of the undoped $MgAl_2O_4$ nanoparticles (Abdullah Al Mahmood et al., 2016). Similarly, thermoluminiscence and Optically Stimulated Luminescence were investigated in Carbon doped $MgAl_2O_4$ nanoparticles that were synthesized by two different methods by electron gun and vacuum assisted melting of $MgAl_2O_4$ in presence of graphite (Raj et al., 2016). Rare-earth dopants can be used to modify the microstructure of Magnesium Aluminate Spinel leading to significant enhancement of their mechanical and sintering characteristics.

Dysprosium (Dy3+) doped $MgAl_2O_4$ nanoparticles were successfully produced through the wet chemical sol-gel method, and their luminescent properties were investigated. The result showed a transition in emission from yellow-green to nearly white light, highlighting their suitability as energy efficient materials for white light applications (Kaur et al., 2023). An examination of the effects of doping concentration on both structural and luminescent characteristics was done on Eu^{3+}-doped $MgAl_2O_4$ nanopowders (Kolesnikov et al., 2016). Another group of investigators have studied the photoluminescence of Magnesium aluminate doped with Ce3+, prepared by combustion synthesis (Singh et al., 2019). Utilizing coprecipitation method, $MgAl_2O_4$ nanoparticles doped with silver (Ag) were synthesised. Under sunlight, they exhibited efficient degradation of crystal violet and phenol, thereby showing its photocatalytic activity (Farooq et al., 2023). Sol-gel combustion method was used to synthesise Cerium doped $MgAl_2O_4$ nanocrystallites and their structural and dielectric properties were studied (Rahim et al., 2024). The doping of magnesium aluminate NPs with chromium (Cr) revealed a strong relationship between the electrical and the nanostructural properties, with their continuous variation when the doping concentration was rised (Saha et al., 2012). Magnesium aluminate ($MgAl_2O_4$) nanoparticles doped with varying amounts of iron were createdand their structural and electrical characteristics were examined (Sharma & Arora, 2015). The thermodynamic and kinetic properties of $MgAl_2O_4$ nanoparticles were observed to improve upon doping with manganese (Mn) (Nakajima et al., 2020).In another study, investigations were carried out on transparent LiOH doped MANPs produced by spark plasma sintering (Pouchlý et al., 2023). Using citrate based combustion method, Copper (Cu) doped $MgAl_2O_4$ nanoparticles were produced. This doping remarkably altered its structural and photocatalytical activity, moulding it into an efficient material for many applications (Javed et al., 2024).

Applications

Magnesium Aluminate is a significant refractory material that has gained prominent interest due to their distinctive attributes. Consequently, magnesium aluminate nanoparticles are also studied to have refractory applications. Owing to their excellent thermal stability, MANPs are ideal for making melting crucibles. Cracking was found to be a serious issue in transparent magnesium aluminate spinel ceramics manufactured by a laser direct deposition method. Doping with silica was reported to have significantly addressed the cracking issues. (Khan et al., 2024). Magnesium aluminate spinel ceramics containing aluminum titanate were synthesised in two different ways; with the addition of pre-synthesized Al 2TiO

5 to the spinel powder or the additionof Al_2O_3 and TiO_2 powder. Such ceramics were shown to have an improved thermal shock resistance (K. Moritz, 2014). Addition of MANPs into a flame retardant coating formulation made by mixing Ethylenediamine modified ammonium polyphosphate (EDA-MAPP) and charring-foaming agents (CFA) was found to increase flame retardancy (Abuhimd et al., 2020).
The release of specific dyes into water bodies by manufacturing units can result in critical health issues. Various studies have demonstrated that MANPs can photolytically degrade certain dyes, including Congo Red (Al-Farraj & Abdelrahman, 2024) and Reactive Red 195 (Mohammad Reza Mohammad Shafiee et al., 2016), implying that MANPs could aid in pollution control. The results of a study revealed that MANPs could detoxify about 99% of the most toxic warfare agents Soman and Sarin in a duration of 8 to 10 minutes (Prasad et al., 2020). Nano-porous magnesium aluminate spinel synthesized by self-combustion route was explored for the photocatalytic removal of methylene blue in the wastewater and the suitability of synthesized spinel for the removal of cationic dye was demonstrated (Salem et al., 2020).
Utilizing 3D printing, scaffolds incorporated with Polylactic acid (PLA) and magnesium nanoparticles were developed. The findings indicated that the inclusion of MANPs to PLA contributed to an increase in biodegradability and effectively decreased thermal degradation upto to a limit (Ghodrati et al., 2023). MANPs serve as efficient adsorbents. They were studied for their effectiveness in the extraction and purification of Dimethomorph pesticide from pipe water, with a recovery rate of 90 to 94% (Rao et al., 2020). Magnesium aluminate nanoparticles are regarded as a noteworthy option for hydrogen energy storage, with a max. capacity of 4000 mAh/g (Eslami et al., 2024). The doping of Cr3+ ions with $MgAl_2O_4$ led to a unique electrochemical response, rendering it an appropriate candidate for use as an anodic electrode in supercapacitors (Pratapkumar et al., 2021). Ceramic magnesium aluminum spinel nanoparticles based on carbon paste electrode synthesised using a modified co-precipitation method were found to be effective in monitoring Nickel ion assessment in children's daily consumption of samples including cocaine, candy, coca, chocolate, and fizzy drinks (Mostafa et al., 2024). Recently, a group of investigators could successfully synthesise cordierite single-phase powders with high purity through heat treatment of combustion synthesized magnesium aluminate spinel and silica nanoparticles (Shafiee Afarani et al., 2023). In epoxy/IFR coating systems, $MgAl_2O_4$ nanoparticles act as a highly efficient promotional agent, produce a rigid layer that obstruct the transfer of oxygen and heat (Abuhimd et al., 2020). An analysis of $MgAl_2O_4$ nanocomposites revealed their notable antibacterial applications, effectively suppressing the growth of both gram-negative and gram-positive bacteria (Bhargavi & Bose, 2023). Nanocomposites of SnO_2 doped with $MgAl_2O_4$ were synthesized and assessed for their applicability in gas sensing technologies. The results indicated that these nanocomposites exhibited a quick and improved response to gases such as O_2, CO_2, and C_2H_5OH at different working temperatures (Nithyavathy et al., 2016). The application of nanocrystalline $MgAl_2O_4$ as a novel efficient catalytic system was shown to advance the synthesis of 1,2,4,5-tetrasubstituted imidazole derivatives through ultrasonic irradiation (Safari et al., 2013). The incorporation of copper into $MgAl_2O_4$ nanoparticles resulted in significant photodegradation activity, suggesting their suitability for applications in the pharmaceutical industry and wastewater treatment (Javed et al., 2024).

Conclusion

Magnesium Aluminate ($MgAl_2O_4$) has received prominent interest due to their extraordinary mechanical, thermal and optical propeties. The spinel structure of $MgAl_2O_4$ confers its notable stability and versatility, making it an ideal candidate for various applications. Similarly, magnesium aluminate nanoparticles are also emerging as a irreplaceable aspect in nanotechnology. The advancement in synthesis methods has enabled the development of MANPs with tailored characteristics, further elaborating their potential uses. Furthermore, the process of doping can improve the efficiency of these nanoparticles. In this review, we have discussed the features of magnesium aluminate, the various synthesis approaches, studies associated with doping, and the relevant applications of magnesium aluminate nanoparticles (MANPs). However, reports on magnesium aluminate nanoparticles are currently limited. A comprehensive evaluation of their toxicity and biocompatibility is crucial for their utilization across various sectors. The progressive development of magnesium aluminate nanoparticles hold strong promise for the future of nanotechnology. Hence, this review intends to inspire innovative research, guiding future researchers to foster further exploration of magnesium aluminate nanoparticles.

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