A review on magnesium aluminate ($MgAl_2O_4$) spinel: synthesis, processing and applications

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Magnesium aluminate ($MgAl_2O_4$) spinel (MAS) is a synthetic material with cubic crystal structure and excellent chemical, thermal, dielectric, mechanical and optical properties. These properties made MAS an indispensable material for optically transparent windows, domes and armours, and for certain refractory applications. High processing cost of dense MAS ceramics is in the main responsible for its limited usage in certain important applications despite its excellent performance in them. The volume expansion (~8%) associated with MAS phase formation from alumina and magnesia does not allow obtaining dense MAS bodies in a single-stage reaction sintering process. Therefore, dense MAS bodies are made by following a double stage firing process, which is expensive. The existing literature suggests that the processing cost of dense MAS ceramics could be reduced to a great extent by decisive selection of starting raw materials, powder processing and densification conditions, and by understanding the underlying mechanisms of MAS formation and densification. Since there is no review article covering the complete comprehensive information of MAS, an attempt is made to write this review article with a main perspective of synthesis, processing and important applications of MAS and its utility for certain future emerging novel and innovative applications.

Keywords: Magnesium aluminate spinel, Optically transparent ceramics, Infrared domes/windows, Hot pressing, Hot isostatic pressing, LiF, Y_2O_3, Net shape consolidation, Humidity sensors, Refractory material, Catalyst, Catalyst support

List of symbols

a_0	lattice parameter
$Al_{Al}^{\times}$	aluminium ion sitting on aluminium site with neutral charge
$Al_i^{\bullet\bullet\bullet}$	aluminium interstitial ion with triple positive charge
$Al_{Mg}^{\bullet}$	aluminium ion sitting on magnesium lattice site with single positive charge
i	antisite defect
$Mg_{Al}^{'}$	magnesium ion sitting on aluminium site with single negative charge
$Mg_i^{\bullet\bullet}$	magnesium interstitial ion with double positive charge
$Mg_{Mg}^{\times}$	magnesium ion sitting on magnesium site with neutral charge
$O_i^{''}$	oxygen interstitial ion with double negative charge
$O_O^{\times}$	oxygen ion sitting on oxygen site with neutral charge
R_a	roughness
tan δ	dielectric loss
$V_{Al}^{'''}$	aluminium vacancy with triple negative charge
$V_{Mg}^{''}$	magnesium vacancy with double negative charge
$V_O^{\bullet\bullet}$	oxygen vacancy with double positive charge
ε'	dielectric constant
ζ	zeta potential
Φ	Schottky defect
Γ	centre of Brilliun zone
ΔG_f^o	standard molar Gibbs energy of formation
ΔG_r	Gibbs energy of reaction
ΔH_f	enthalpy of formation
ΔS_f	entropy of formation

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Introduction

Recently, magnesium aluminate ($MgAl_2O_4$) spinel (MAS) has received a great deal of attention from academia and the industry sector on account of its best combination of several important properties, such as high melting point (2135°C), high hardness (16 GPa), relatively low density (3·58 g cm^{-3}), high mechanical strength both at room (135–216 MPa) and elevated temperatures (120–205 MPa at 1300°C), high resistance against chemical attack, wide energy band gap, high electrical resistivity, relatively low thermal expansion coefficient (9×10^{-6}°C^{-1} between 30 and 1400°C), high thermal shock resistance, etc.[1–6] Furthermore, MAS does not react with SiO_2 until 1735°C, with MgO or CaO until 2000°C, with Al_2O_3 until 1925°C and, excepting alkaline earth metals, it can be in contact

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with all other metals.[1] The typical properties of polycrystalline MAS are presented in Table 1.[1–7] Fully dense, polycrystalline MAS is transparent optically, as well as in the 3–5 μm IR regions, given the grain size is much less than the wavelength of incident light.[2–5] As it allows larger wall thickness than alumina without loosing its transparent properties, it has been used for optical engineering applications, such as armoured window systems, high energy laser windows and lightweight armour.[7–16] Now, MAS has replaced the traditional alumina, sapphire, AlON, ZnS and lanthanum niobate ceramics in applications requiring light transmission in the wavelength range of 2–5·5 μm. Good resistance to radiation induced swelling and strength degradation made MAS a potential fusion reactor power core insulating material.[6] Because of its basic nature, porous MAS both in bulk and thin film form showed potential as an electronic humidity sensor.[17–22] Its low dielectric constant (ε=7·5) and low loss tangent (tan $\delta=4\times10^{-4}$) properties, as well as the close match of its oxygen ion lattice structure with Si and with a number of other important oxide systems, made MAS an attractive material for integrated electronic devices.[23] Given its high melting point and high chemical inertness, MAS has been employed to replace traditional chromite based refractories in cement rotary kilns and steel ladles, since the latter refractories contain Cr(VI) species, which create both environmental and health hazards.[1,24] Thin films of MAS exhibited potential utility in thermal barrier coatings (TBCs) for the blades and vanes in the hot section components of gas turbines.[25] Furthermore, MAS has also been employed as an alternative material to replace the conventional carbon anode in aluminium electrolytic cells.[26] Its low acidity and good thermal stability made MAS an excellent catalyst for oxidation of SO_2 to SO_3 and in the fields of environmental, petroleum processing and fine chemical production.[27,28] Owing to the above mentioned properties, MAS was also employed as a catalyst support for a great variety of reactions including De–SO_x,[29,30] selective catalytic reduction (SCR) of NO,[31] ammonia synthesis,[32,33] *n*-butane dehydrogenation,[34,35] dry reforming of methane,[36,37] chemical looping combustion (CLC),[38] water–gas shift reaction,[39] catalytic steam reforming of methane[40] and propane dehydrogenation.[41]

Although, a great number of papers deal with MAS in the literature, none of them present together the complete information pertaining to the fundamentals (properties, crystal structure and phase diagram), the problems of volume expansion associated with MAS phase formation from alumina and magnesia, the utility of single or double stage sintering processes, the methods available to reduce the processing cost of MAS products, the various routes employed for the preparation of MAS powders, single crystals, whiskers and thin films, the available powder consolidation (i.e. processing) techniques, the effects of starting raw materials, chemical composition (i.e. non-stoichiometry), defect reactions, impurities/sintering aids, processing routes, etc., on densification behaviour of the powder, the advanced spectral characteristics of the powders, the optical, mechanical, dielectric, thermal and magnetic properties of sintered materials, the applications, etc.[42–47] This review article is an attempt to fill this gap.

Crystal structure and phase diagram

The crystal structure of MAS has been reported by Bragg[48] and Nishikawa[49] independently (Fig. 1). The spinel structure (sometimes called garnet structure) is named after the mineral spinel ($MgAl_2O_4$); the general composition is AB_2O_4. The structure of MAS is based on the structure of diamond. The positions of the A ions are nearly identical to the positions occupied by carbon atoms in the diamond structure. This could explain the relatively high hardness and high density typical of this group. The arrangements of the other ions in the structure conform to the symmetry of the diamond structure. However, they disrupt the cleavage as there are no cleavage directions in any member of this group. The unit cell of the 2–3 MAS can be expressed as $Mg_8Al_{16}O_{32}$, in which 32 oxygen anions are face centred

Table 1 Typical physical properties of polycrystalline MAS[1–7]

Property		Value							
Density/g cm^{-3}		3·58							
Hardness, Knoop (100 gm)/kg mm^{-2}		1398							
Specific heat (at 20°C)/cal g^{-1} K^{-1}		0·21							
Poisson's ration		0·26							
Melting point		2135°C							
Strength at 25°C	4-point bending	Biaxial	Tension	Compression	Elastic modulus	Bulk modulus		Shear modulus	
	103 MPa	172 MPa	110 MPa	2·69 GPa	273 GPa	192 GPa		110 GPa	
Coefficient of thermal			At 25–200°C	At 25–500°C	At 25–1000°C				
expansion/$\times10^{-6}$ K^{-1}			5·6	7·3	7·9				
Dielectric	1·27 mm thick		0·25 mm thick						
strength/kV mm^{-1}	490		580						
Resistivity/Ω cm	At 25°C		At 300°C	At 500°C	At 700°C				
	$>10^{14}$		5×10^{14}	2×10^{14}	4×10^{14}				
Thermal	At 25°C		At 100°C	At 1200°C					
conductivity/W m^{-1} K^{-1}	24·7		14·8	5·4					
Dielectric properties			1 kHz	1 MHz	9·3 GHz				
	Dielectric constant		8·2	8·2	8·3				
	Dielectric loss		0·00025	0·0002	0·0001				
Refractive index at	0·49 μm		0·59 μm	0·66 μm	1·0 μm	2·0 μm	3·0 μm	4·0 μm	5·0 μm
different wavelengths λ	1·736		1·727	1·724	1·704	1·702	1·698	1·685	1·659