Transparent ceramic based on magnesium aluminate spinel for armor

D O Lemeshev, M O Senina, M S Pedchenko and A V Boyko

Dmitry Mendeleev University of Chemical Technology of Russia, Miusskaya sq. 9, 125047 Moscow, Russia
E-mail: diolem@muctr.ru

Abstract. Prospects of appliance of transparent ceramic based on magnesium aluminate spinel are considered. Sintering additive that makes it possible to synthesise transparent ceramic material from spinel was selected. Boron oxide was selected as such compound. The influence of concentration of this additive component as well as the influence of the method of its injection into the load on the properties of products based on magnesium aluminate spinel are considered.

1. Introduction
Optically transparent ceramic is the ceramic that is transparent to electromagnetic waves. This material is distinguished by fine optical transmission, density, durability, corrosion stability which make possible its usage in many fields [1]. Thus, transparent ceramic is popular in metallurgy, radioengineering, chemical industry, protection and armor system and nuclear power industry being a prospective raw material for it. That is why optically transparent ceramic property investigation and synthetic methods from spinel is a highly topical issue of the research.

Scientists develop new processes which allow to enter manufacturing of products based on different forms of optical ceramic including details that may be used in airplane wings in future.

Global study report of world market in the field of polycrystalline transparent ceramic is serially made. It comprehends historical sources as well as the prognosis before 2025. The report contains information about leading global producers of this ceramic type, main types of products, tendencies and the field way forward. Thus, main companies which are producing optical ceramic were indicated: CoorsTek Inc. (USA), Surmet Corporation (USA), Schott AG (Germany), II-VI Optical Systems (USA), CILAS (France), Brightcrystals Technology Inc. (China), CeramTec-ETEC GmbH (Germany) [2].

Asian-Pacific Region is a large market of transparent ceramic due to its high demand in many technical fields. The growth of demand for electronics and arms industry products in major countries such as China and India stimulates development of markets in this part of the world. As estimated Asian-Pacific Region is the fastest growing market for transparent ceramic production. The region offers potential opportunity of development due to strong production basis and administrative norms which promote foreign investments receipt resulting in market growth in developing countries.

In North America the USA is the primary customer for transparent ceramic. It is associated with increase of transparent ceramic usage in the military field.

In Russia transparent ceramic production has worse development rates than in European, American and Asian countries.
One of the non-conventional materials for transparent ceramic production is magnesium aluminate spinel which is not studied enough in that field. Spinel may be used in the capacity of armour-coated glass which has the advantage by weight in comparison with sorts of glasses which are used nowadays, protecting masks for soldiers, laser optics and multispectral sensory glasses.

Magnesium aluminate spinel (MgAl2O4) is a synthetic material which crystallizes as cubes. The crystalline order of MgAl2O4 is characterized by tetrahedral coordinated magnesium ions and octahedral coordinated aluminum. Elementary cell contains 32 oxygen ions, 16 octahedral cations and 8 tetrahedral tetrahedral. Due to lack of polymorphic transformations spinel does not undergo thermic phase change. Spinel is distinguished by high hardness (13,5 hPa), thermal shock resistance, resistance to mineral acids, alkali melts, carbon and various metals, fine optical transmission in UV- (180-400 nm), visible (180-400 nm) and IR- (740-5000 nm) spectral band. This is attributable to cubic lattice structure which allows to avoid light scattering due to different refraction indexes along the axis of the crystal, and, therefore, permanent optical transmission till 92% in visible spectral band. Magnesium aluminate spinel melting point is high accounting for 2135°C [3].

Production of transparent ceramic from magnesium aluminate spinel comes amid some difficulties. Getting close texture material with a porosity slim to none is near-impossible without the use of special additives. The additive when interacting with powdery ceramic material under sintering may form interstitial solid solution or substitutional solid solution or a novel compound either fully from its own components or from a new blend composition which appears when interacting with a basic material. The additives that are forming liquid phase and are not interacting with spinel and thus, not forming second phase presence of which resulting lack of transparency in obtainable ceramic. Additives of such sort intensify the process of liquid-phase sintering and then vaporize due to temperature increase. Particularly, such additives are B2O3, LiF, CaF2 etc.

Addition of CaO observably increased the sintering rate and had an effect on MgAl2O4 grain growth. Addition of just 0,1 wt % of CaO allows to densify severely, maximum values of density became available at 0,5-1,0 wt %. In contrast the amount of additive which is more than 1,5 wt % had a negative effect on the process. When optimum quantity of CaO was used and temperature ranged from 1800 to 1900°C vacuum sintering allowed to get material with density value from 99,7 to ~ 100 % of theoretic density value. Porosity of material was almost reduced while CaO concentrations were of 0,5 and 1,0 wt % and the samples were semitransparent [4].

LiF also is very common additive for spinel ceramic sintering. It is possible to synthesize transparent ceramic based on magnesium aluminate spinel using 1 wt % LiF via pressure sintering at a temperature up to 1550°C during 2 hours. The samples are characterized with fine visible transmission coefficient ~ 85 % [5].

It was found [6, 7] that addition of a small amount of boron oxide B2O3 (0,05-0,5 wt %) promoted much more effective MgAl2O4 powder sintering which was exposed to hot isostatic pressing method. Experimental results made it clear that presence of boron oxide not only allows to decrease precursor-powder sintering temperature but inhibits ceramic grains growth as well that is very important to provide fine transparence. The 1 mm thick samples may have fine optical transmission of 80 % when the concentration of B2O3 was optimal: 0,15 wt %.

Though LiF is necessary for spinel packing to be transparent it may react with aluminum in spinel matrix producing regions enriched with magnesium. These regions decrease transparency in consolidated material due to poor sintering. Also it is possible that LiAlO2 crusts during the reaction that causes nontransparent regions formation [8].

2. Results and discussion
This work is focused on investigation of the influence of vaporized boron oxide sintering additive concentration as well as injection method of this additive on properties of ceramic based on magnesium aluminate spinel.
Aluminium hydroxide (R) and magnesium hydrocarbonate (R) were used as input materials for production of ceramic based on magnesium aluminate spinel. Aluminum oxide and magnesium oxide ratio was 50:50 mol. %. As temporary technological bond paraffin (P-2) was used.

Powder fusion temperature is an important technological parameter while producing spinel. With a rise of temperature higher than 1000°C the composition of spinel changes greatly. So called γ-nonstoichiometry appears: magnesium aluminate spinel enriches with quite large excessive mass of Al₂O₃. Any stoichiometry change comes with an appearance of disorder in crystal – appearance of vacancies in sites of the lattice or voids colonization [9], that may affect material transparence and structural characteristics in a negative way. It is found that spinel formation process is reliant on many factors such as dispersiveness of primary components, their nature and impurity types, special additives, annealing conditions etc.

A large body of research of powder structure influence on sintering, microstructure and properties of ceramic allows to choose necessary requirements to initial powder:
- lack of aggregates with a size of more than 1 micron;
- controllable phase composition and chemical purity;
- high dispersion ability;
- powder sintering activity [10].

Magnesium aluminate spinel powder was synthesized via thermic method as it is the easiest and the most cost-efficient method in comparison with other techniques in operation.

To investigate the influence of sintering additive on the product properties 1,5; 3; 5; 7; 10 % wt of boron oxide were added into synthesized spinel.

For workpiece formation semidry molding was used. Molding pressure was equal to 100 MPa.

Sintering was carried out in two stages. At the first stage temporary technological bond was removed from the workpiece at a temperature of 800°C in air. At the second stage sintering was carried out at a temperature of 1650°C under vacuum. For the achievement of high-density state of the samples the second stage was carried out at exposures at a maximum temperature within 3 hours.

In this work the following research methods were used:
- Determination ignition loss (DIL) was determined in accordance with Russian government technical requirements 3594.15 – 93.
- Differential thermal analysis (DTA) was carried out per unit Q-1500D of Paulig-Paulig-Erdey system. Quantitive evaluation was carried out via programme “ECOKHROM”.
- Scanning electron microscopy (SEM) investigation was carried out on Tescan MIRA III XMU scanning electron microscope.
- X-ray phase analysis was carried out on DRON-3M apparatus. Results evaluation was carried out via programme Crystallographica.

In order to determine magnesium aluminate spinel fusion temperature differential thermal analysis of aluminium hydroxide and magnesium hydrocarbonate mixture was carried out. The results are presented on figure 1.
Figure 1. The results of differential thermal analysis of aluminium hydroxide and magnesium hydrocarbonate mixture

The synthesis of magnesium aluminate spinel started at a temperature of 550°C, active crystallization occurred at a temperature of 1350°C. To complete the process of spinel phase formation the mixture was calcinated at a temperature of 1350°C during 1 hour. The results of X-ray phase analysis are presented on figure 2 below.

Figure 2. X-ray diagram of powder synthesized at a temperature of 1350°C
The results of X-ray phase analysis suggest that at a temperature of 1350°C pure phase of magnesium aluminate spinel is being formed as is evidenced by lack of extraneous phases. Figure 3 shows microstructure of synthesized magnesium aluminate spinel powder. According to SEM data magnesium aluminate spinel powder is agglomerated. There are agglomerates of spherical shape at rates of 5-15 microns and plate shaped agglomerates at rates of 50-70 microns.

Plate shape of the particles has a fine influence on sintering process helping to achieve condition of densely-sintered material. But the plates form bulky agglomerates that worsen optical indexes because of the structure in which pores are inside the material. Polydisperse structure of powder has a fine influence on sintering.

![Microstructure of thermically synthesized magnesium aluminate spinel powder](image)

**Figure 3.** Microstructure of thermically synthesized magnesium aluminate spinel powder

After calcination middle-density and effective porosity of samples were determined. The results are presented on figure 4 (a, b).

Results of investigation suggest that increase of additive ratios decreases effective porosity and increases middle-density. But at larger concentration ratios (7 and 10 wt %) dramatic effective porosity increase and middle-density decrease occur due to evaporation of a large amount of additive and material cavitation. In this case optimum concentration is 5 wt %.

![Graphs showing middle-density and effective porosity](image)

**Figure 4.** Values of middle-density (a) and effective porosity (b) of samples, calcinated at a temperature of 1650°C.
An important technological stage is sintering additive injection method into a load. Boron oxide in amount of 5 wt % was added to spinel powder in two ways: dry and wet.

Values of ceramic middle-density and effective porosity are almost the same for dry and wet methods. During the experiment sample density values were 3.23 and 3.30 g/cm³ and their porosity values were 2.5 and 2.6 % respectively. Wet method is preferable because in this case the additive dispenses homogeneously by powder volume and the method results higher values of ceramic middle-density. However, these values do not allow to get samples with fine optical transmission due to great number of pores (figure 5). It is possible to solve this problem with heat treatment conditions variation of products under vacuum.

![Figure 5: SEM-picture of ceramic with B₂O₃ additive that was synthesized via wet method Tₛ = 1650°C](image)

According to the analysis data it can be said that sample material structure is nonhomogeneous with grain dimensions of 5-20 microns. Broad range of sizes is accounted for beginning of material recrystallization process. A quantity of pores has been observed as well.

Figure 6 shows synthesized ceramic samples.
3. Conclusion
Thus, basing on the research findings it may be said that B2O3 addition into magnesium aluminate spinel helps to form more dense samples with low-grade of open pores in their structure. Optimum concentration should not be more than 5 wt %, density value was 3.30 g/cm3, porosity value was 2.5%. Larger concentration ratios (7 and 10 wt %) dramatic effective optical properties due to material cavitation.

After calcination material became monophasic and quite dense that allows to draw the conclusion that transparent ceramic production with the help of vaporized additives is possible.

Acknowledgments
The reported study was funded by RFBR according to the research project № 18-33-00507.

References
[1] Vydriv G A, Solov’eva T V, Kharitinov F Y 1980 Transparent ceramic (Moskva: Energiya) p 97
[2] URL: https://www.mordorintelligence.com/industry-reports/transparent-ceramics-market
[3] Streliv K K, Mamykin P S 1978 Refractory engineering (Moskva: Metallurgiya) p 376
[4] Bratton R J 1974 Journal of the American Ceramic Society 57 283
[5] du Merac M R, Reimanis I E, Smith C, Kleebe H- J, Müller M M 2013 International Journal of Applied Ceramic Technology 10 33
[6] Tsukuma K 2006 Journal of the Ceramic Society of Japan 114 802
[7] Misawa T, Moriyoshi Y, Yajima Y, Takenouchi S, Ikegami T 1999 J Ceram Soc Jpn 107 343
[8] Villalobos G R, Sanghera J S, Aggarwal I D 2005 Journal of the American Ceramic Society 88 1321
[9] Kovtunenko P V 1997 Glass and ceramic 8 12
[10] Lukin E S 1996 Refractories and technical ceramic 9 2