Investigation of the influence LiF sintering additive on the properties of magnesium aluminate spinel ceramics

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Annotation. The relevance of developing a technology for creating transparent ceramics based on magnesium aluminate spinel is considered. The spinel precursor was obtained by the reverse coprecipitation method. The effect of the phase composition of spinel powder and sintering additive on the properties of ceramics is shown.

1. Introduction
More attention is focused on the issue of creating materials that have a whole range of functional properties. Polycrystalline materials with special properties, which have, for example, transparency in a certain spectral range are of interest. Such products should also have high mechanical properties in addition to transparency.

The technologies for creating optically transparent ceramics from aluminum oxynitride and polycrystalline aluminum oxide have been studied quite well.

Aforecited ceramic has high operational characteristics (Table 1), but its manufacturing technology is energy-consuming and expensive, because it requires the use of hot pressing processes (HP) and hot isostatic pressing (HIP) at high temperatures.

Table 1. Physical properties of certain ceramic materials [1].

| Material | Strength, MPa | Elastic modulus, GPa | Density, g/cm³ | Melting temperature, K |
|----------|---------------|----------------------|----------------|----------------------|
| AlON     | 300           | 323                  | 3.68           | 2425                 |
| Sapphire | 700           | 345-386              | 3.98           | 2300                 |

Today, transparent polycrystalline ceramics based on magnesium aluminate spinel (AMS) is one of the most promising materials for the manufacture of transparent armor.

Magnesium aluminate spinel is a binary thermodynamically stable compound with a cubic crystalline structure.

It has a high level of light transmission in a wide range of radiation with a wavelength of 180 to 5000 nm, which includes 3 areas: ultraviolet (180-400 nm); visible (400-700 nm) and infrared (740-5000 nm). Spinel has a distinct transmission advantage over sapphire and AlON in the range of 4500–5500 nm, a region of particular importance for seeker and electro-optic imaging systems. Spinel also has high heat resistance, chemical resistance to aggressive environments, melting point above 2100 °C [2, 3]. In addition, spinel ceramics have a significant advantage over AlON due to the greater availability of the starting components and lower temperature of hot isostatic pressing [4].
In the synthesis of spinel with increasing temperature above 1000 °C, the composition of the spinel changes significantly. The so-called γ - non-stoichiometry arises: magnesium aluminate spinel is enriched with a rather significant excess of Al₂O₃ [5]. Aluminium oxide has good solubility in spinel with formation of a wide range of solid solutions from MgO·Al₂O₃ to MgO·5Al₂O₃ [6].

Obtaining transparent ceramics is impossible if many factors are not observed. One of the requirements for creating a transparent ceramic material is its monophase, the second phase leads to the absence of a high level of light transmission due to the difference in the refractive indices of different phases and light scattering. However, the authors [7] showed the preparation of transparent ceramics from magnesium aluminate spinel with an excess of aluminium oxide (MgO·nAl₂O₃, n = 1.05–2.50). Its light transmission amounted to 84 %. It should be noted that in this work, hot isostatic pressing was used.

An alternative to HP and HIP processes is sintering in vacuum without applying of pressure, which is more energy efficient.

In this work, sintering of spinel ceramics in vacuum was studied. Sintering ceramics of magnesium aluminate spinel to an almost non-porous state is also necessary to obtain a transparent material. And it’s impossible without using of sintering additivites.

Lithium fluoride was chosen as such additive. At the initial stages of the process, it forms a melt and thereby intensifies liquid phase sintering, and when the temperature rises, it evaporates and enters into a defect formation reaction with magnesium aluminate spinel according to the following scheme:

\[
3\text{LiF} \xrightarrow{MgAl}_2\text{O}_4 \rightarrow \text{Li}_{M\beta} + 2\text{Li}_{Al}'' + 3\text{F}_O + \text{V}_O
\]  

As a result, oxygen vacancies are formed. It helps to intensify diffusion mass transfer in the volume of material and therefore, accelerates sintering and allows to obtain a higher density of the product [8-11]. Also, the activation energy of the process is lowering, which leads to a decrease of sintering temperature.

The positive effect of LiF also lies in the fact that this additive does not allow volatilization of a large amount of magnesium oxide and violation of stoichiometry in spinel. According to the authors [12] slight heat evaporation of MgO is possible during the heat treatment of ceramics made of magnesium aluminate spinel. Magnesium oxide leaves the crystal lattice and this also leads to the formation of micropores, which are not completely healed during sintering, which leads to residual porosity and non-transparency of the ceramic [13]. The addition of LiF in this case makes it possible to “capture” magnesium oxide and return spinel to the crystal lattice, thereby preserving the stoichiometric composition of the compound.

2. Materials and Methods
The starting components were magnesium nitrate hexahydrate GOST 11088-75, aluminium nitrate nonahydrate GOST 3757-75, lithium fluoride TU 6-09-3529-78, ammonia aqueous solution GOST 24147-80.

Preliminary synthesis of MgAl₂O₄ powder was carried out by the method of reverse co-precipitation of magnesium and aluminum nitrates into a precipitator solution, followed by heat treatment. The LiF additive in an amount of from 0.5 to 4.5 wt. % was doped into the charge by wet method in a planetary mill for 15 minutes. Ceramic preforms were molded by semi-dry pressing at a pressure of 100 MPa. Firing was carried out in vacuum at a temperature of 1700 °C with exposure at a maximum temperature of 3 hours.

3. Results and discussion
The main phase of the powder obtained after calcination of the precursor is magnesium aluminate spinel (Figure 1).
The structure of the spinel powder is shown in Figure 2. The powder contains plate aggregates ranging in size from 1 to 10 μm. A powder with such particle size distribution can be used in synthesis of transparent ceramics.

Figure 1. X-ray phase analysis of the obtained powder.

Figure 2. Microstructure photo of the obtained powder.

Figure 3 (a, b) shows the results of measuring the properties of ceramics.

According to the obtained data we can conclude that the optimal concentration of lithium fluoride at which the maximum compaction is achieved (open porosity - 4.9%, average density – 3.32 g/cm³) is 2.5 wt. %. The similar nature of the curves can be explained by the fact that when the LiF content is less than 2.5 wt. % there is no significant compaction at the stage of sintering, and at the final stage of sintering, the remaining pores are not healed.
The introduction of additives in excess of 2.5 wt. % promotes the formation of a large amount of melt. As a result, the melt during evaporation leaves a large number of pores, and the material does not sinter to a fully dense microstructure. Figure 4 shows the microstructure of a sample containing 2.5 wt. % LiF.

After sintering, the material is formed by grains with a structure close to cubic, up to 5 μm in size. Material does not sinter to a fully dense microstructure, the presence of pores is noticeable in the scanning electron microscopy image. It may adversely affecting the transparency of the product.

The resulting samples have high values of open porosity, which does not allow to achieve transparency of the product. In the future, it is advisable to control the synthesis parameters of the spinel precursor powder, as well as change the concentration of the sintering additive.

4. Conclusions
The method of heterophase coprecipitation is promising for obtaining a dispersed powder of magnesium aluminate spinel, suitable for creating transparent ceramics.

The effect of the evaporated lithium fluoride additive on the properties of ceramics based on magnesium aluminate spinel was studied. The optimal concentration of the evaporating lithium fluoride additive was determined at a firing temperature of 1750 ºС without applying pressure with a holding time of 3 hours, it amounted to 2.5 wt. %. However, the obtained ceramic has a high value of open porosity (4.9 %) and a low value of average density (3.32 g/cm³). To create a transparent ceramic, it is advisable to consider various modes of heat treatment of the material.

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References
[1] Suárez M, Fernández-Camacho A, Torrecillas R, Menéndez J L 2012 New Emerging Techniques p 527
[2] Pavlyukova L T, Lukin E S, Popova N A 2013 Proceedings of “The VII project contest of young scientists” p 28
[3] Vydrik G A, Solov’eva T V, Kharitinov F Y 1980 Transparent ceramic (Moskva: Energiya) p 97
[4] Bhatngara A 2011 Light ballistic materials: Front page from English (Moscow: Technospher) p 392
[5] Kovtunenko P V 1997 Glass and ceramic 8 p 12
[6] Panda P C, Raj R 1986 Journal of the American Ceramic Society 69 p 365
[7] Hana D, Zhanga J, Liud P, Lia G, Ane L, Wanga S 2018 Ceramics International 44 p 3189
[8] Esposito L, Piancastelli A, Martelli S 2012 J Eur Ceram Soc p 1
[9] Rubat du Merac M. 2012 Ph.D. Thesis Colorado School of Mines Golden, CO and the Technical University Darmstadt Darmstadt Germany to be submitted December
[10] Johnson W C, Stein D, Rice R W 1974 Journal of the American Ceramic Society 57 p 342
[11] Reimanis I E, Kleebe H J 2007 Int J Mater Res 98 p 1273
[12] Esposito L, Piancastelli A, Miceli P, Martelli S 2015 Journal of the European Ceramic Society 35 p 651
[13] Mazzonia A D, Sainzb M A, Caballerob A, Aglietti E F 2002 Materials Chemistry and Physics 78 p 30