Influence of gallium oxide concentration on the properties of transparent ceramics based on magnesium aluminate spinel

A V Ulyanova, M O Senina and D O Lemeshev

D Mendeleev University of Chemical Technology of Russia, Moscow, Russia
alenkachim@mail.ru

Annotation. The article deals with the preparation precursor of magnesium aluminate spinel by the method of inverse co-precipitation, as well as the study of effect of firing temperature and the concentration of the gallium oxide addition on the optical and ceramic properties of the products is shown.

1. Introduction
To date, the production of optically transparent ceramics is being actively developed. This involves the use of ceramic products in the defense industry as helmet visors and armor windows of civil military equipment, as well as it is used to make lenses for lasers, night vision devices.

Currently, technologies for producing transparent armor based on aluminum oxynitride (AlON) and aluminum oxide, also known as sapphire, which have excellent functional properties, are being actively used. But this fabrication process of products from these materials requires large financial and energy costs due to the use of expensive equipment and high temperatures in the production process [1, 2].

In the second half of the last century, magnesium aluminate spinel MgAl$_2$O$_4$ (AMS) was synthesized, which in its properties is not inferior to AlON and sapphire, which are analogues. At the moment, transparent polycrystalline ceramics based on magnesium aluminate spinel are one of the most profitable materials for the production of transparent armor, due to the isotropic structure, which allows to achieve a high degree of light transmission up to 95 % in the visible area of the spectrum; low density (3.58 g/cm$^3$) compared to metals, while having excellent mechanical characteristics; also, production of the material is marked by simplicity in comparison with production by growing single crystals from a melt [3].

The purpose of the work was to study the influence of concentration and method of introduction of gallium oxide sintering additive, as well as the temperature of roasting on the properties of ceramics based on the magnesium aluminate spinel, obtained by the method of reverse heterophase co-precipitation.

2. Materials and Methods
The process diagram includes:
1. Synthesis of powder AMS.
2. Introduction of a sintering additive.
3. Introduction of temporary technological binder.
4. Dry pressing at 100 MPa.
5. Burning in the air at 1100 °C.
6. Burning in a vacuum at 1700 and 1750 °C.
Highly dispersive powder of double magnesian-aluminum hydroxide of strictly stoichiometric composition, \( \text{MgAl}_2\text{(OH)}_8 \), which are precursors of the magnesium aluminate spinel, is synthesized by reverse heterophase co-precipitation, since this method does not require the use of special equipment and high temperatures, and is characterized by relatively short reaction time. Water nitrates of aluminum and magnesium (\( \text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O} \) and \( \text{Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \)), taken in a ratio of 50:50 mol % in terms of oxides, were used as the initial components for synthesis.

In order to determine the temperature of the precursor heat treatment, a differential-thermal analysis (DTA) was carried out, the results of which are presented in Figure 1.

![Figure 1. DTA of the spinel precursor obtained by reverse heterophase co-precipitation.](image)

According to this differential-thermal data, we can assume that 1 peak (150 °C) refers to the removal of physically connected water; 2 peak (270 °C) refers to the removal of chemically bound water; 3 peak (610 °C) refers to the beginning of spinel formation; 4 peaks (1150 °C) – completion of spinel formation.

Based on the results of the differential-thermal analysis, the optimal temperature of the synthesis of the precursor powder for the production of the AMS phase equal to 1200 °C was chosen. The choice of the synthesis method and the firing temperature is confirmed by the X-ray phase analysis data.

To reduce porosity, gallium oxide is selected as an additive, since it contributes to the formation of vacancies of solid solutions in both spinel undergrates, which improves sintering. The additive was introduced in the amount of 5 and 7 mol. %, in powder of spinel via wet method, with different methods of introduction: directly in the precursor and in the synthesized spinel. The semi-manufactured materials were formed by dry pressing at a pressing pressure of 100 MPa. The removal of temporary technological binder was carried out at a temperature of 1100 °C, and the burning of samples - at a temperature of 1700 and 1750 °C in a vacuum with a time of exposure of 3 hours. The material light transmission of the samples with different types of additive injection on the SHIMADZU UV-3600 spectrometer was measured.

3. Results and discussion
The stoichiometric composition of the magnesium aluminate spinel has the only crystal phase (Figure 2).
Figure 2. The MgAl₂O₄ diffractogram obtained at 1200 °C.

Figure 3 (a, b) shows scanning electron microscopy (SEM) images of the precursor and spinel powder microstructures.

As can be seen in the figures, the precursor and spinel have a polyfraction composition with particles of different shape and size. As a result of this composition, pores can form in the material. The X-ray phase analysis data (Figure 4) confirms the formation of a composition of gallium oxide and magnesium aluminate spinel of variable composition.
Figure 4. Diffractogram of Ga$_2$O$_3$ solid solutions in MgAl$_2$O$_4$.

The alloying addition introduced is not released in the form of an independant phase, which suggests the formation of a solid replacement solution in the lattice of the magnesium aluminate spinel.

The high dispersion of the produced powders provides their activity to sintering, which can lead to the pecking of particles and contribute to the process of aggregation already at the initial stages of pressing firing. It appears advisable to synthesizing of solid solutions at higher temperatures.

The following information about the properties of burned samples at 1700 °C was obtained during the studies.

Analysis of the graphs makes it possible to distinguish the best indicators of average density, open porosity at introduction of 7 mol. % of gallium oxide (Figure 5.)

Figure 5. Properties of samples at a firing temperature of 1700 °C.

Than the properties of the samples produced by different methods of additive introducing with a concentration of 7 mol. % - into the precursor and into the synthesized spinel at a temperature of 1700 and 1750 °C were investigated. According to the results of the tests, it was revealed that the increase in temperature of firing leads to a significant improvement in the properties of ceramics. Thus, the best properties of the products were confirmed with temperature of firing (Figure 6).
Figure 6. Comparison of the properties of samples with temperatures of firing of 1700 and 1750 °C.

Figure 7 shows the microstructure of the sample of 7 mol % of gallium oxide burned at a temperature of 1750 °C. As a result of the sintering temperature increase, samples with a homogeneous structure were obtained, including a small number of intercrystalline and intra-crystalline pores.

Figure 7. Microstructure of ceramics from AMS with additive Ga₂O₃, T<sub>firing</sub> = 1750 °C.

In Figure 8 a photograph of 7 mol % gallium oxide doped magnesium aluminate spinel ceramics is shown.

The light transmission graphs of ceramics are shown in Figure 9 (a, b).
Figure 8. Photograph of a ceramic sample of gallium oxide doped magnesium aluminate spinel.

The graphs show that the sample, obtained by the method of 7 mol. % additive introducing into the spinel has a higher degree of light transmission then 7 mol. % additive introduction into the precursor, temperature of firing is up to 1750 °C.

Figure 9. Dependence of light transmission on wavelength, sample 7 mol. % of gallium oxide added in a) precursor, b) spinel.

4. Conclusion
Thus, according to the experimental results, the following conclusions can be drawn:

1. The aluminum spinel is a promising material for the creation of optically transparent ceramics, since it has high optical, mechanical and inert properties with respect to aggressive environment, as well as it characterized by the isotropic structure, in which it is possible to achieve high light transmission, and the availability of raw materials.

2. One of the most relevant methods of obtaining spinels should be coprecipitation from aqueous solutions, since it does not require the use of special equipment and high temperatures, and also is characterized by a relatively short reaction time.

3. The best parameters of open porosity and average density are observed when adding 7 mol. % of gallium oxide after spinel synthesis. When adding an additive to the precursor, the quality of the sample is worse.

4. With the increase temperature of firing from 1700 to 1750 °C, the values of open porosity decrease, which indicates the beneficial effect of the firing temperature increase on the properties of ceramics from the aluminum magnesium spinel with the addition of gallium oxide to when it is inserted into the synthesized spinel.

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