

SPARK PLASMA SINTERING OF MAGNESIUM-ALUMINATE SPINEL WITH SINTERING ADDITIVES *

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Magnesium-aluminate spinel (MgAl_2O_4 , MAS) is a compound of $\text{MgO-Al}_2\text{O}_3$ system. It has cubic crystal lattice and is considered as perspective ceramics material. MAS combines a set of unique properties: high hardness, high melting point, low dielectric constant and transmittance in visible light [1]. It is widely used as arming, protective windows for sensors in infrared, alternative materials to replace the conventional carbon anode in aluminum electrolytic cells, humidity sensors and refractory materials for cement rotary kilns and steel ladles [1].

The properties of transparent ceramics depend on the composition, powders' properties, impurities or additives, and fabrication methods [2]. Transparent ceramics is fabricated by several technologies: cold pressing with subsequent thermal treatment, hot pressing and spark plasma sintering (SPS). The SPS method is the most promising among listed. It allows to reduce the time required for the manufacture of ceramics and enables to achieve nearly full densification by limiting grain growth and by obtaining uniform grain-size distribution [3].

One of the main problems encountered in the manufacture of transparent ceramics by SPS is darkening of the material and decrease in its optical characteristics. It can be explained by formation of oxygen vacancies or contamination of the sintered material with graphite upon contact with molds. There are several methods to solve this problem. One of them is annealing in the air atmosphere. It allows to reduce oxygen vacancies and to increase optical characteristics, but thermal threaten at high temperatures can led to grain growth [4]. Another way to prevent darkening of ceramics is usage of inert foils such as Mo and Ta foils during SPS [5]. These elements form stable carbide phases at high temperatures in the presence of carbon, preventing further carbon penetration into the sintered material. Present of sintering additives in sintering material allows to both reduce oxygen vacancies and to prevent carbon contamination [6].

There are two most popular types of sintering additives in MAS-ceramics manufacturing: additives that form a solid solution: Ga_2O_3 , B_2O_3 , CaO and others and additives that melt during the sintering process: LiF , MgF_2 , CaF_2 and others. The first type of compounds can cause changes in crystal lattice and the phase composition of ceramics, thereby having a negative impact on optical and mechanical characteristics. The second type of additives is more promising [7]. It does not change the crystal lattice and has a relatively low melting point (870-1255 °C) and the sintering process proceed with the participation of the liquid phase [7].

In this work spark plasma sintering of a mixture of commercial powders of magnesium-aluminate spinel and sintering additives of lithium fluoride and magnesium fluoride with different concentrations was carried out. The effect of the additive composition on the process of spark plasma sintering, as well as its content in the initial powder mixture on the characteristics of manufactured MAS-ceramics, has been studied.

REFERENCES

- [1] A. Zegadi, M. Kolli, M. Hamidouche, G. Fantozzi, "Transparent MgAl_2O_4 spinel fabricated by spark plasma sintering from commercial powders," *Ceramics International*, vol. 44, pp. 18828–18835, Oct. 2018, doi: 10.1016/j.ceramint.2018.07.117.
- [2] . Zegadi, M. Kolli, M. Hamidouche, G. Fantozzi, "Transparent MgAl_2O_4 spinel fabricated by spark plasma sintering from commercial powders," *Ceramics International*, vol. 44, pp. 18828–18835, Oct 2018, doi: 10.1016/j.ceramint.2018.07.117.
- [3] S.F. Wang, J. Zhang, D.W. Luo, F. Gu, D.Y. Tang, Z.L. Dong, G.E.B. Tan, W.X. Que, T.S. Zhang, S. Li, L.B. Kong, "Transparent ceramics: processing, materials and applications," *Progress in Solid State Chemistry*, vol. 41, pp. 20-54, May 2013, doi: 10.1016/j.progsolidstchem.2012.12.002.
- [4] P. Fu, Y. Xu, H. Shi, B. Zhang, X. Ruan, W. Lu, "The effect of annealing process on the optical and microwave dielectric properties of transparent MgAl_2O_4 ceramics by spark plasma sintering," *Optical Materials*, vol. 36, pp. 1232-1237, May 2014, doi: 10.1016/j.optmat.2014.02.035.
- [5] M. Sakajio, G. E. Shter, M. Mann-Lahav, V. Beilin, S. Zamir, G. S. Grader, "Carbon Contamination Prevention during Spark Plasma Sintering," *ACS Applied Materials & Interfaces*, vol. 15, pp. 38080–38089, Jul. 2023, doi: 10.1021/acsami.3c07265.
- [6] P. Cui, B. Qin, G. M. Haarberg, "The Behavior of Additives LiF , MgF_2 and KF on Current Efficiency in Aluminium Electrolysis", *Journal of The Electrochemical Society*, vol. 166, pp. D559-D563, Aug. 2019, doi: 10.1149/2.0431913jes.
- [7] V. Nečina, J. Hostaša, W. Pabst, M. Veselý "Magnesium fluoride (MgF_2) – A novel sintering additive for the preparation of transparent YAG ceramics via SPS", *Journal of the European Ceramic Society*, vol. 42, pp. 3290-3296, Jul. 2022, doi: 10.1016/j.jeurceramsoc.2022.02.003.

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