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Densification Peculiarities of Transparent $MgAl_2O_4$ Ceramics—Effect of LiF Sintering Additive[1]

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Abstract—A new method of doping of spinel nanopowders with LiF sintering additive has been proposed, consisting in its introduction via solution technology, which leads to improved sinterability of the ceramic. The effect of LiF doping on densification behavior, microstructure, and optical and mechanical properties of hot-pressed $MgAl_2O_4$ ceramics has been studied. Samples of $MgAl_2O_4$ optical ceramics with density close to that theoretically achievable have been produced by hot pressing of 0.5 wt % LiF-doped nanopowders at 1600°C for 1 h. It has been shown that addition of LiF changes crack propagation in spinel ceramic from transgranular to intergranular.

Keywords: transparent ceramics, $MgAl_2O_4$, LiF doping, optical properties, electron microscopy
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INTRODUCTION

Transparent polycrystalline $MgAl_2O_4$ ceramics are promising material for optical, electronic, structural, and other applications (high pressure arc lamps, optical heat exchangers, transparent armor, etc.). $MgAl_2O_4$ ceramics have excellent mechanical properties comparable to those of sapphire and high optical transmittance within the ultraviolet, visible, and near-infrared ranges [1]. The conventional approaches to produce $MgAl_2O_4$ transparent ceramics are based on hot pressing (HP) of nanopowders [2, 3] or its combination with hot isostatic pressing (HIP) methods [4]. Mass transport during sintering of $MgAl_2O_4$ can be accelerated by using sintering additives that increase ionic diffusivity by modification of the host defect chemistry or enhancement of diffusion via formation of a liquid phase. $MgAl_2O_4$ optical ceramics were synthesized using Sc_2O_3 [5], B_2O_3 [6], CaO [7], TiO_2 [8], LiF [2, 3, 9, 10], $AlCl_3$, $CaCl_2$, BaF_2 [11] as a sintering additive. Lithium fluoride is one of the most effective sintering additives, which promotes densification of powders into transparent ceramics via hot pressing. According to Reimanis and Kleebe [12], the densification mechanism of LiF-doped $MgAl_2O_4$ involves formation of the LiF liquid phase at the intermediate sintering stage and dissolving of LiF into the spinel matrix at the final sintering stage. Moreover, the residual LiF reacts with impurities, thereby acting as a cleanser. The thermal removal of excess LiF or of any fluoride gas before pore closure is an important prerequisite for obtaining high transparency.

The effect of LiF on densification of $MgAl_2O_4$ powders depends on the particle size distribution, the doping method, the distribution uniformity of lithium fluoride, its concentration, etc. According to different authors, the optimal concentration of LiF in doping of $MgAl_2O_4$ ceramics varies within wide concentration range from 0.07 to 5–10 wt % [2, 9, 13–15]. The effect of LiF on the densification of $MgAl_2O_4$ ceramics and their properties was investigated for both stoichiometric spinel $MgO \cdot Al_2O_3$ [10, 15] and nonstoichiometric spinel ($MgO \cdot nAl_2O_3$ with $n = 1–3.5$) [16]. It was shown that $MgAl_2O_4$ ceramics possess excellent optical transparency when the concentration of LiF ranges from 1.0 to 1.5 wt %. The highest transmission reported for $MgO \cdot 1.5Al_2O_3$ ceramics sintered with 0.25 wt % LiF exceeds 80% for the wavelength range of 380–1100 nm [16]. For hot-pressed samples, the transmittance in the infrared range of 3–5 μm reaches approximately 80% when the concentration of LiF is 2.5 wt % [17]. However, high doping concentrations reduce the mechanical properties (hardness) of $MgAl_2O_4$ ceramics by 20% or more.

Recently, we obtained highly transparent $MgAl_2O_4$ ceramics by hot pressing of LiF-doped powders synthesized by using double magnesium aluminum iso-

[1] The article was translated by the authors.

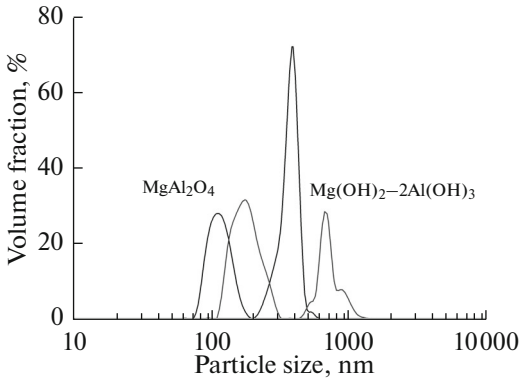

Fig. 1. Particle size distribution of magnesium-aluminum hydroxides and $MgAl_2O_4$ powders calcined at 750°C.

propoxide as a precursor [3]. It is supposed that doping of spinel powders with lithium fluoride during the nanopowder synthesis stage will increase the homogeneity of the sintering additive distribution and decrease the concentration required to obtain dense ceramics.

The aim of this work was to study the effect of LiF on the densification, microstructure, and optical and mechanical properties of hot-pressed $MgAl_2O_4$ ceramics. The utilization of nanosized powder with a highly homogeneous distribution of the sintering additive was assumed to have a positive impact on the microstructure and optical properties of sintered ceramics.

EXPERIMENTAL

Double aluminum magnesium isopropoxide was obtained according to the procedure described in [18]. The addition of LiF was carried out as follows. The suspension prepared by interaction of $LiNO_3$ and NH_4F aqueous solutions was added to 1200 mL of i-C_3H_7OH–H_2O azeotrope and further added to 1 mol of $MgAl_2(i\text{-}OC_3H_7)_8$ under stirring. The amount of added LiF varied between 0 and 1 wt % (0, 0.3, 0.5, 0.7, 1 wt %). After hydrolysis, the suspensions were cooled to room temperature in air. The obtained suspensions were dried at 100–150°C under pressure of ~1 kPa, followed by calcination in air at 750°C for 3 h. The impurity loadings in the resulting powders were checked by the inductively coupled plasma atomic emission spectrometry (ICP-AES) method. The total concentration of impurities in the synthesized $MgAl_2O_4$ powders was well below 100 ppm, which is comparable to that of commercially available spinel nanopowders [14].

To obtain $MgAl_2O_4$ optical ceramics, the synthesized powders were preshaped, loaded into the graphite mold, and heated from room temperature to 1600°C at the rate of ~7.5°C/min and held for 1 h before cooling down. The load was applied at the temperature of 800°C and then was increased to ~35 MPa for 30 min. The pressure was released before free cooling of the furnace.

The particle size of the magnesium-aluminum hydroxide and $MgAl_2O_4$ powders was determined by laser diffraction (dynamic light scattering, DLS) on a NanoBrook 90 PlusZeta device. X-ray diffraction analysis was conducted on a XRD-6000 Shimadzu X-ray diffractometer (CuK_α radiation, $\lambda = 1.5406$ Å) equipped with a graphite monochromator. The thermal analysis was assessed by the thermogravimetry (TG) and differential scanning calorimetry (DSC) methods using a Netzsch STA 409 PC/PG thermal analyzer (Germany). The samples were enclosed in platinum crucibles, and the measurements were conducted in flowing argon at a heating rate of 5°C/min up to 1200°C. The morphology of powders and ceramics was investigated using an Ultra 55 field emission scanning electron microscope (SEM) (Carl Zeiss, Germany) operating at the accelerating voltage of 5 kV using secondary electron imaging. The density of the samples was determined by hydrostatic weighing with an accuracy of 0.01 g/cm^3.

The kinetics of densification for the spinel ceramics (shrinkage/expansion behavior) was examined by a NETZSCHDIL 402C dilatometer (Netzsch) operating at a heating rate of 5°C/min to 1570°C under high vacuum. The optical properties were studied on polished $MgAl_2O_4$ ceramic samples 1 mm thick. The optical transmission spectrum was recorded using an SF-2000 UV/VIS spectrophotometer (LOMO, Russia) in the wavelength range of 0.18–1.1 μm (transmission given without correction for reflection). Vickers hardness (H_V) and Palmquist fracture toughness (K_{IC}) of the samples were measured using a Struers Duramin-5 microhardness tester with a load of 0.5 kg.

RESULTS AND DISCUSSION

Structural and Morphological Characteristics of $MgAl_2O_4$ Nanopowders

The DLS results of a mixture of magnesium and aluminum hydroxides and LiF-doped $MgAl_2O_4$ nanopowders calcined at 750°C are shown in Fig. 1. After 10 min of ultrasound processing of the suspension, three modes of particle size distribution with maxima of 200 nm, 700 nm (largest in volume), and 950 nm are observed in the initial hydroxides. In the calcined $MgAl_2O_4$ powders, only two modes of particle size distribution with maxima of 120 and 430 nm are observed. Thus, the degree of agglomeration of the powders is determined at the stage of hydrolysis of double magnesium aluminum isopropoxide.

Figure 2 shows the X-ray diffraction pattern of the $MgAl_2O_4$ powder (with addition of 0.5 wt % LiF) calcined at 750°C. The X-ray diffraction patterns of powders with different LiF concentration have a similar appearance. The position of the peaks corresponds to

the $MgAl_2O_4$ spinel phase; no other phases were detected. The average crystallite size of synthesized powders was shown to be ~80 nm. The amount of LiF (0.3–1 wt %) does not have a significant effect on the crystallite size of the samples since the peaks corresponding to the spinel phase have almost identical intensities and half-widths.

Figure 3 shows the SEM image of the $MgAl_2O_4$ nanopowders doped with 0.5 wt % LiF and calcined at 750°C for 3 h. The SEM images of powders with different LiF concentration (up to 1 wt %) are almost the same under the identical measurements conditions. The SEM results indicate that primary particles of doped spinel powders (0.3–1 wt % LiF) having a diameter of 50–100 nm are combined into weakly agglomerated secondary particles reaching several microns in size. The comparison of particle size of powders performed by DLS (120 and 430 nm), SEM (50–100 nm), and XRD (crystallite size ~80 nm) indicates agglomeration of particles. Therefore, calcination was carried out at the lowest temperature (750°C) required for the formation of the spinel phase and removal of the hydroxyl groups.

Densification Peculiarities of LiF-Doped $MgAl_2O_4$ Ceramics

Figure 4 displays the shrinkage curves of $MgAl_2O_4$ nanopowders containing different amounts of LiF. The sintering process begins and the material starts to shrink for any studied LiF concentrations when a temperature of 950°C is reached. As shown in Fig. 4, the maximum sintering rate (given by the differential curves) of undoped powders is achieved at 1230°C. Increase in the sintering additive concentration shifts the maximum of the sintering rate to lower temperatures, which reaches 1070°C for $MgAl_2O_4$ nanopowder with 1 wt % LiF.

The peak of the maximum shrinkage rate is divided into two for a sample of $MgAl_2O_4$ nanopowder doped with 0.3 wt % LiF, which we attribute to the rapid evaporation of lithium fluoride at the initial sintering stage. Further shrinkage behavior is the same as for the undoped sample. As the LiF concentration increases, a second maximum appears on the differential shrinkage curve, which shifts from 1450 to 1240°C with an increase in the sintering additive concentration from 0.5 to 1%. The appearance of an additional peak is also associated with the dynamics of evaporation of the sintering additive. Densification of $MgAl_2O_4$ powder doped with LiF can be realized at lower temperatures at a higher rate compared to the undoped powder, and even a small amount of LiF improves the sinterability of spinel nanopowders.

Since the dilatometric curves are recorded without applying pressure to the sample, the observed shrinkage curves allow only a qualitative judgement of the processes that occur during hot pressing. To estimate the sinterability behavior of synthesized alkoxy-derived powders, nanocrystalline spinel doped with lithium fluoride was subjected to hot pressing under pressure of 35 MPa at $T = 1600$°C for 1 h. The density of $MgAl_2O_4$ ceramics after hot pressing was 3.58 g/cm^3, which corresponds to the theoretical density.

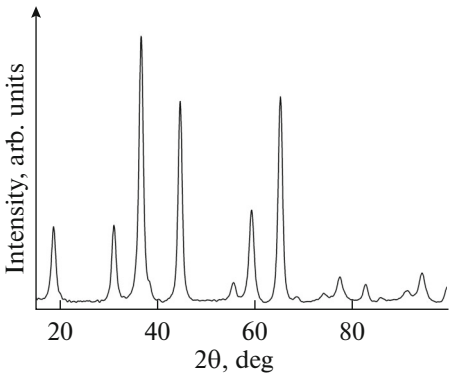

Fig. 2. X-ray powder diffraction pattern of $MgAl_2O_4$ powder doped with 0.5 wt % LiF calcined at 750°C.

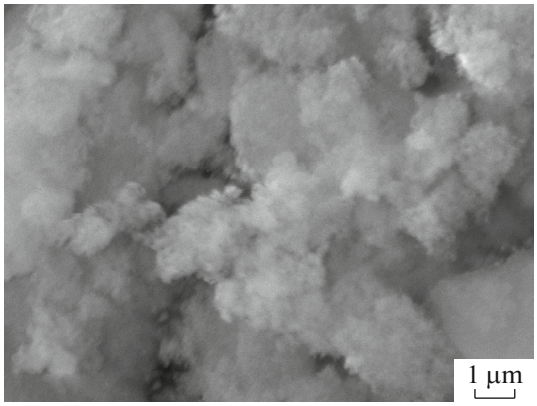

Fig. 3. SEM micrograph of $MgAl_2O_4$ spinel powder doped with 0.5 wt % LiF calcined at 750°C for 3 h.

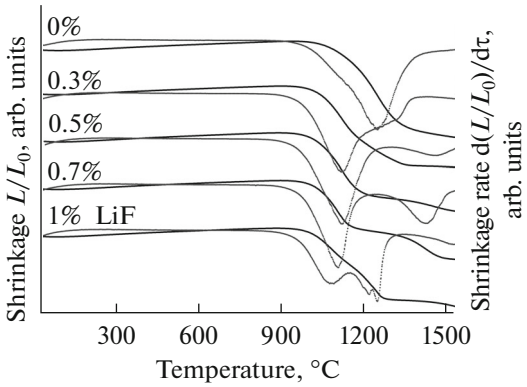

Fig. 4. Shrinkage curves (solid lines) and shrinkage rate (dotted lines) of $MgAl_2O_4$ powders doped with different LiF concentration.

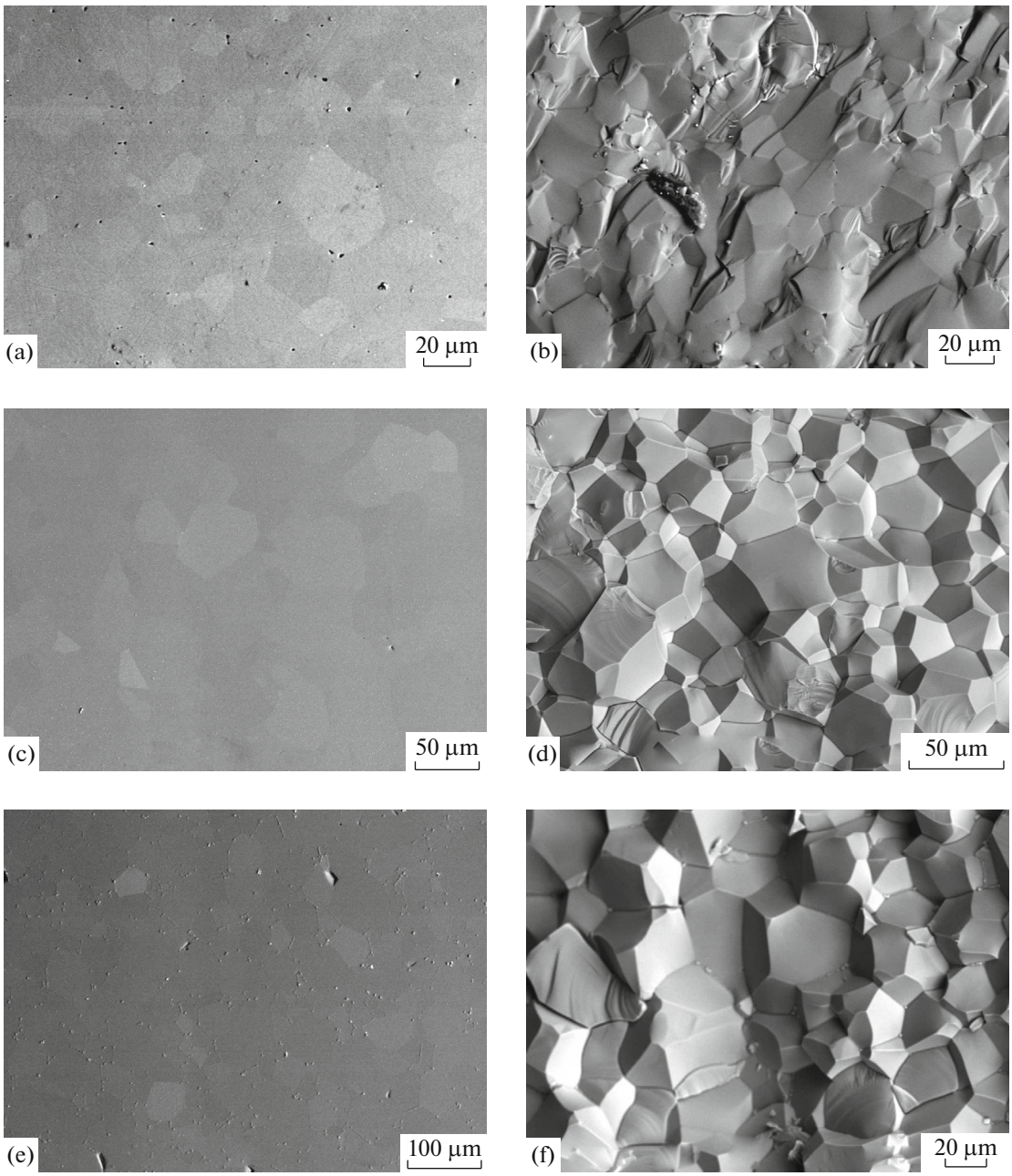

Fig. 5. SEM microstructure of $MgAl_2O_4$ ceramics undoped (a, b) and doped with (c, d) 0.5 wt % and (e, f) 1 wt % LiF hot-pressed under 35 MPa at 1600°C for 60 min. The thermally etched surfaces (a, c, e) and fracture surface (b, d, f) are shown.

SEM images of $MgAl_2O_4$ ceramics undoped and doped with 0.5 and 1 wt % LiF are shown in Fig. 5. As one can see, the sample without LiF (Figs. 5a, 5b) exhibits a bimodal grain size distribution; the average grain sizes are 20–40 and 7–10 μm. Some intra- and intergranular pores with characteristic diameter of about 2 μm were revealed inside the ceramics. The pore entrapment occurs when the grain boundary mobility rate becomes superior to the pore one, though the mechanism of the pore–grain boundary separation requires additional study.

Doping with LiF results in more homogeneous microstructure, while grain size of ceramics increases (Fig. 5). The average grain size of $MgAl_2O_4$ ceramics doped with 0.5 wt % LiF is about 30 μm. The volume fraction of residual porosity is much lower in comparison with the sample without LiF (Figs. 5c, 5d); only separate individual pores are observed. We relate the more uniform grain size distribution to the homogeneous doping of the starting powders with lithium fluoride. As a rule, lithium fluoride is introduced during ball milling of spinel powders. However, anomalous grain growth occurs in the regions with excess of fluo-

rine ions. Reimanis and Kleebe [19] revealed a bimodal grain size distribution of spinel ceramics subjected to fast-cooling studies. In those studies, the large spinel grains, as opposed to small grains, contained F^- ions inside, suggesting that LiF dissolves in the spinel lattice, thus enhancing grain growth via formation of oxygen vacancies. Other reports on transparent spinel doped with LiF as a sintering additive indicate that a bimodal grain-size distribution is a common feature [20]. When the amount of LiF is 1 wt % (Figs. 5e, 5f), the average grain size increases to about 37 μm. A secondary phase of unidentified composition is visible along the grain boundaries, which could be attributed to the entrapment of a residual fluoride phase (Fig. 5e).

Fracture surfaces of hot-pressed $MgAl_2O_4$ ceramics without LiF were predominantly transgranular (Fig. 5b). Doping with LiF changed crack propagation from transgranular to intergranular fracture, as shown in Figs. 5d and 5f. Similar change in destruction mechanism was also observed for MgO and $MgAl_2O_4$ ceramics undoped and doped with LiF [14, 21]. The authors explain the intergranular fracture by the segregation of impurity anions/cations (F^- and/or Li^+ ions) at grain boundaries, which weakens interface bonding.

Figure 6 shows the transmission spectra and photo of $MgAl_2O_4$ ceramics doped with different concentrations of LiF sintering additive. The samples were mirror polished on both surfaces using a diamond slurry to form disks 13 mm in diameter and 3 mm in thickness. The highest in-line optical transmission (80% at $\lambda = 1000$ nm) was obtained for ceramics sintered with 0.5 wt % LiF. Without lithium fluoride, $MgAl_2O_4$ ceramics exhibit transmittance of only 38%. For LiF concentrations greater than 0.5 wt %, the transparency decreases with increasing amount of sintering additive. Optical losses in the visible and ultraviolet wavelength ranges may be related to the presence of residual porosity and/or secondary phases in ceramics. The difference in refractive indexes of the matrix phase and precipitated phases (gas-filled pores) will cause scattering of the incident light. It should be noted that undoped samples have gray color because of carbon contamination (Fig. 6). Even doping with LiF at low concentration (0.3 wt %) is enough to prevent diffusion of carbon from tooling into the ceramics.

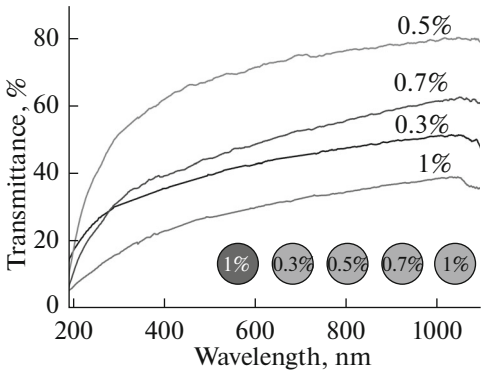

Fig. 6. Optical transmission spectra and appearance of $MgAl_2O_4$ ceramics doped with LiF with thickness of 3 mm obtained by hot pressing of alkoxy-derived nanopowders under 35 MPa at 1600°C for 60 min.

As can be seen from Fig. 6, the optimal concentration of LiF in hot-pressed $MgAl_2O_4$ ceramics is 0.5 wt % for the consolidation conditions studied. Doping with smaller concentrations of LiF is insufficient to produce fully dense $MgAl_2O_4$ ceramics, so the light scattering on residual pores occurs. Introduction of higher LiF concentrations results in rapid sintering of ceramics and precipitation of secondary phases along grain boundaries, which reduces light transmission through the ceramics. The formation of secondary phases could be connected with the interaction of LiF with the $MgAl_2O_4$ matrix phase. It should be noted that amount of LiF required to achieve full density and high transparency of spinel ceramics is much lower in comparison with previously published results [2]. We connect this feature with highly uniform doping of $MgAl_2O_4$ nanopowders with LiF sintering additive.

Microhardness and fracture toughness values of $MgAl_2O_4$ ceramics as a function of the sintering additive concentration are given in Table 1. Addition of even a small amount of sintering additive results in enhancement of microhardness of $MgAl_2O_4$ ceramics, which can be related to a denser microstructure of samples sintered with LiF. On the contrary, the fracture toughness slightly decreases for the doped spinel ceramics, probably because of a small amount of a second phase precipitated along the grain boundaries.

Table 1. Vickers hardness (H_V) and Palmquist fracture toughness (K_{IC}) of $MgAl_2O_4$ ceramics undoped and doped with different concentrations of LiF

Concentration of LiF, wt %	0	0.3	0.5	0.7	1
H_V, GPa	11.9 ± 0.7	13.9 ± 0.8	13.7 ± 0.7	13.8 ± 0.7	14.6 ± 0.4
K_{IC}, MPa $m^{1/2}$	1.2	0.9	1.1	1.0	1.0

Nevertheless, the hardness values of $MgAl_2O_4$ with LiF additive coincide within the measurement error, and the values of fracture toughness of the ceramics studied are very close to each other.

CONCLUSIONS

An original method of doping of spinel nanopowders with LiF via solution technology has been proposed. The effect of LiF sintering additive on densification peculiarities of hot-pressed $MgAl_2O_4$ ceramics has been studied. It has been shown that spinel powders doped with LiF (0.3–1 wt %) consist of primary particles having a diameter of 50–100 nm, which are combined into slightly agglomerated secondary particles reaching several microns in size. Doping with LiF has been shown to have little effect on crystallinity and average particle size of nanopowders obtained by the hydrolysis of double magnesium aluminum isopropoxide, while even small amount of LiF significantly improves the sinterability of spinel nanopowders. It has been determined that $MgAl_2O_4$ ceramics doped with an optimal amount of LiF (0.5 wt %) show the highest transmittance of 80% at $\lambda = 1000$ nm and average grain size of 30 μm among the studied samples. Rather uniform grain size distribution of $MgAl_2O_4$ ceramics hot-pressed at 1600°C for 1 h is related to the homogeneous doping of the starting nanopowders with lithium fluoride.

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