IR-transparent MgO–Gd₂O₃ composite ceramics produced by self-propagating high-temperature synthesis and spark plasma sintering

Dmitry A. PERMIN^{a,b,*}, Maksim S. BOLDIN^b, Alexander V. BELYAEV^a,
Stanislav S. BALABANOV^a, Vitaly A. KOSHKIN^{a,b}, Atrem A. MURASHOV^b,
Igor V. LADENKOV^c, Evgeny A. LANTSEV^b, Ksenia E. SMETANINA^b,
Nadia M. KHAMALETDINOVA^d

^aG. G. Devyatikh Institute of Chemistry of High-Purity Substances of the RAS, Nizhny Novgorod 603137, Russia

^bLobachevsky State University of Nizhny Novgorod, Nizhny Novgorod 603950, Russia

^c“Joint-stock company” Research and Production Enterprise “Salut”, Nizhny Novgorod 603950, Russia

^dG.A. Razuvaev Institute of Organometallic Chemistry of the RAS, Nizhny Novgorod 603137, Russia

Received: July 3, 2020; Revised: October 5, 2020; Accepted: October 30, 2020

© The Author(s) 2020.

Abstract: A glycine–nitrate self-propagating high-temperature synthesis (SHS) was developed to produce composite MgO–Gd₂O₃ nanopowders. The X-ray powder diffraction (XRD) analysis confirmed the SHS-product consists of cubic MgO and Gd₂O₃ phases with nanometer crystallite size and retains this structure after annealing at temperatures up to 1200 °C. Near full dense high IR-transparent composite ceramics were fabricated by spark plasma sintering (SPS) at 1140 °C and 60 MPa. The in-line transmittance of 1 mm thick MgO–Gd₂O₃ ceramics exceeded 70% in the range of 4–5 mm and reached a maximum of 77% at a wavelength of 5.3 mm. The measured microhardness HV0.5 of the MgO–Gd₂O₃ ceramics is 9.5±0.4 GPa, while the fracture toughness (K_{IC}) amounted to 2.0±0.5 MPa·m^{1/2}. These characteristics demonstrate that obtained composite MgO–Gd₂O₃ ceramic is a promising material for protective infra-red (IR) windows.

Keywords: MgO–Gd₂O₃; self-propagating high-temperature synthesis (SHS); spark plasma sintering (SPS); optical properties; infra-red (IR) ceramics

1 Introduction

Recently, nanocomposite materials that are transparent in the infra-red (IR) range have attracted a steady interest for use as infrared windows and domes with enhanced mechanical strength, thermal shock resistance,

and lower emissivity. These characteristics are crucial to develop new advanced units for aerospace applications [1]. Normally, opaque or translucent ceramics can be made transparent if the grain size is smaller than the wavelength of interest. Both the preparation methods and properties of IR-transparent composite ceramics are most widely studied for MgO–Y₂O₃ material [1–6]. It was shown that this material is able to compete with the best single-phase

* Corresponding author.

E-mail: Permin@ihps.nnov.ru

infrared materials in terms of its thermal and mechanical characteristics [2]. Moreover, ceramic technology for manufacturing such composites allows for control of the shape and size of the resulting parts, which determines the significant economic benefits of this approach compared, for example, with the production of optical elements from sapphire single-crystals.

However, attempts are still being made to improve methods for obtaining composite IR ceramics, as well as to search for new materials that provide higher performance characteristics. In particular, it was shown that the values of microhardness of the Y_2O_3 – MgO – ZrO_2 ceramics increase proportionally to the square root of the ZrO_2 concentration [7]. Good mid-infrared transmittance was maintained over the 3–7 μm wavelength range with ZrO_2 addition up to 8.8 mol%. It is also known that even a small substitution in any one of the components could lead to a reduction in the thermal conductivity of a material, worsening the thermal shock performance [8]. Both Y_2O_3 – ZrO_2 and MgO – ZrO_2 systems have areas of homogeneity, so more characteristics should be considered to determine the benefits of increasing the microhardness of composite MgO – Y_2O_3 ceramics by a ZrO_2 additive.

Another option for improving the properties of composite IR ceramics is to replace yttrium oxide with gadolinium oxide. In Ref. [9], the MgO – Gd_2O_3 composite was produced by hot pressing of powders obtained by a Pechini method. Wu *et al.* [9] revealed that increasing the sintering temperature from 1200 to 1350 °C leads to the conversion of Gd_2O_3 from a cubic to a monoclinic phase, which increases the microhardness of the material from 8.4 to 14.1 GPa. This value is sufficiently higher compared to 10–10.5 GPa for MgO – Y_2O_3 [4,10–12].

Since the IR-transmittance of composite ceramics depends significantly on the grain size and the presence of pores, it is necessary to use methods and approaches that ensure the production of a high-density fine-grained ceramic structure. One of the most effective methods for obtaining a fine-grained structure in ceramics is the method of spark plasma sintering (SPS) [3,6,10–16]. This method is based on the controlled heating of the powder material in a graphite mold via a sequence of direct current pulses with simultaneous application of uniaxial mechanical pressure.

The choice of the initial powder synthesis approach is an equally important task for the preparation of non-porous ceramics. As shown in Ref. [16], for the

MgO – Y_2O_3 composite, it is possible to obtain IR-transparent ceramics through colloidal grinding of MgO and Y_2O_3 powders with the subsequent high-temperature treatment. This requires the use of nanosized initial powders of Y_2O_3 and MgO and careful selection of conditions for colloidal grinding of components to achieve homogeneity. In the overwhelming number of publications devoted to the preparation of composite MgO – RE_2O_3 ceramics, the uniformity of the distribution of the components is achieved by the use of special methods for obtaining powders, such as flame spray pyrolysis [2] and Pechini method [9]. Previously, it was shown that the self-propagating high-temperature synthesis (SHS, combustion synthesis, and sol–gel combustion) method can be successfully applied to the synthesis of individual magnesium oxide [17,18] and rare earth element oxides [19–21], as well as mixed MgO – Y_2O_3 oxides [4,10,11]. SHS is characterized by high productivity and rapidity and since the components in the precursors are mixed at a molecular level, this approach makes it possible to obtain composite nanopowders with uniform volume distribution of components. However, the synthesis and structure of MgO – Gd_2O_3 SHS powders are not described in the literature.

The aim of this study was to investigate the possibility of obtaining an IR-transparent composite MgO – Gd_2O_3 ceramics by a combination of SHS and SPS methods, as well as to study its main properties.

2 Experimental

The starting materials for the synthesis of SHS precursors were gadolinium oxide Gd_2O_3 (99.99% Polirite, Russia), magnesium oxide MgO (99.99% Unikhim, Russia), nitric acid HNO_3 (99.9999% Khimreaktiv, Russia), and glycine NH_2CH_2COOH (99.9% Vitareaktiv, Russia).

For the SHS of highly dispersed MgO – Gd_2O_3 powders, metal nitrates were used as an oxidant and glycine as a fuel (reducing agent). At first, the weighted amounts of gadolinium and magnesium oxides were dissolved in nitric acid under heating and constant stirring. A concentration of the prepared $Mg(NO_3)_2$ and $Gd(NO_3)_3$ solutions was determined gravimetrically after calcination of the dry residue at 1200 °C. Then the nitrate solutions were mixed in a proportion according to the oxide volume ratio of 50:50 (corresponding to 68:32 weight ratio). After that,

glycine was added to the solution in a quantity of 95% of the stoichiometric value, assuming the chemical interaction can be expressed by the following chemical reactions:

Such conditions (lack of fuel) were applied to minimize the possibility of product contamination with carbon-containing substances [11].

Then the solution was evaporated at 110 °C to remove the excess water. To initiate the SHS process, the precursor in a quartz flask was placed in a furnace preheated to 500 °C. As a result of the combustion, fine powders were formed.

The content of trace impurities in the synthesized powders was determined by the inductively coupled plasma atomic emission spectrometry (ICP-AES) on iCAP 6300 spectrometer (Thermo Electron Corp., UK).

The XRD patterns of the prepared powders and ceramics were recorded at room temperature in the range from 20° to 70° (2θ) with a step of 0.04° and counting time of 1 s on a XRD-7000 powder diffractometer (Shimadzu, Japan) using filtered Cu Kα radiation. Quantitative phase analysis was carried out according to the Rietveld method using the TOPAS-Academic software [22], and the measurement inaccuracy was 1%. Original PDF-cards and CIF-files of identified phases were taken from the PDF-2 and the ICSD database. The crystallite size (d_{XRD}) was calculated by Bruker Diffrac EVA software using the full width at half maxima of diffraction peaks and Scherrer equation. The powders were calcined at a temperature of 800–1300 °C in air in a muffle furnace SNOL 12/16 (Nakal, Russia) with a heating rate of 5 °C/min, holding at a maximum temperature of 60 min and cooling at a speed of 10 °C/min to room temperature to determine the effect of additional heat treatment on the material's crystal structure.

The powders were annealed at a temperature of 800 °C for 60 min prior to sintering and compacted in a stainless steel mold at a pressure of ~10 MPa to cylinders of 15 mm diameter and 10 mm height. The conditions for calcining the powders were selected based on earlier studies on the SPS of MgO–Y₂O₃ composites [11].

Sintering of the samples was carried out by SPS method in a graphite mold using a DR. SINTER model

SPS-625 SPS system (SPS SYNTEX INC. Ltd., Japan) at a temperature of 1140 °C and holding time of 10 min. The heating rate up to 600 °C was 100 °C/min, further heating to the sintering temperature was carried out at the heating rate of 50 °C/min with an intermediate dwelling at 780 °C for 10 min. Uniaxial pressure of 30 MPa was applied in the first minute of the sintering process and was kept constant until the end of isothermal dwelling at 780 °C. Afterward, the pressure was raised up to 60 MPa and was kept constant throughout the sintering process. Sintering was carried out in a vacuum ~10 Pa. After completion of the sintering process, the samples were cooled in the off mode. The sintering temperature was measured using a Chino IR-AHS2 pyrometer focused on the outer surface of a graphite mold with an outer diameter of 30 mm. The actual temperature of the sample was determined by a calibration curve obtained using a K-type thermocouple [23]. After that, the composite ceramics were additionally annealed at 1000 °C for 5 h in a muffle furnace. Then the ceramic samples were mirror-polished to the thickness of 1 mm with diamond pastes and slurries from 50 down to 0.5 μm.

The density (ρ) of the sintered samples was measured using the Archimedes principle in distilled water using a Sartorius CPA scales (Sartorius, Germany) with an accuracy of 0.005 g/cm³.

Vickers hardness (HV) was determined using a Qness Q60 microhardness tester (Qness, Austria) by measuring the lengths of the diagonal prints of a diamond pyramid (indenter) on the polished surface of a sample. The influence of the applied load on hardness was investigated in the range from 0.1 to 5 kg. A diamond pyramid with an apex angle of 136° and a diagonal length of 500 μm was chosen as an indenter. The loading time was 30 s.

Fracture toughness (K_{IC}) was calculated using the Palmqvist method [24]:

$$K_{\text{IC}} = 0.016 \left(\frac{P}{\sqrt{c^3}} \right) \cdot \left(\frac{E}{\sqrt{HV}} \right) \quad (3)$$

where P is the diamond pyramid load, c is the distance from the center of the print to the tip of the crack, and E is the Young's modulus.

The E of the MgO–Gd₂O₃ ($E = 217$ GPa) was chosen as a rough estimate of average values of $E(\text{MgO}) = 310$ GPa [2] and $E(\text{Gd}_2\text{O}_3) = 124$ GPa [25].

Fourier-transform infrared (FT-IR) spectra of the composite ceramics were recorded with a FT-IR

Spectrometer FSM 1201 (Infraspek, Russia).

The powder morphology and microstructure of the sintered ceramics were studied using an Auriga CrossBeam (Carl Zeiss, Germany) scanning electron microscope (SEM) at an accelerating beam voltage of 3 keV with a secondary electron detector. The average grain size was estimated by measurement of at least 200 grains.

3 Results and discussion

Figure 1 presents the results of the XRD analysis of the SHS MgO–Gd₂O₃ powders calcined at different temperatures and XRD-data for MgO (PDF 00-004-0829) cubic Gd₂O₃ (PDF 00-012-0797) and monoclinic Gd₂O₃ (PDF 00-042-1465). Table 1 shows the mass fractions, unit cell parameters a , theoretical densities ρ_{XRD} , and average crystallite sizes d_{XRD} of the gadolinium and magnesium oxides in the prepared

Table 1 Phase composition, unit cell parameter a , theoretical density ρ_{XRD} , and equivalent diameter d_{XRD} of the Gd₂O₃ and MgO phases in the prepared powders annealed at different temperatures

T (°C)	Phase composition (wt%)	d_{XRD} (nm)	a (Å)	ρ_{XRD} (g/cm ³)
800	(C) Gd ₂ O ₃	71	12	10.819
	MgO	29	14	4.218
900	(C) Gd ₂ O ₃	70	13	10.830
	MgO	30	16	4.220
1000	(C) Gd ₂ O ₃	66	16	10.831
	MgO	34	23	4.221
1100	(C) Gd ₂ O ₃	67	18	10.813
	MgO	33	27	4.215
1200	(C) Gd ₂ O ₃	67	19	10.814
	MgO	33	29	4.215
1300	(C) Gd ₂ O ₃	65	19	10.806
	(B) Gd ₂ O ₃	~2.5	—	—
	MgO	35	25	4.214

Fig. 1 XRD patterns of SHS-derived MgO–Gd₂O₃ powders (a) annealed at temperatures of 800–1300 °C and (b) enlarged 27°–33° diffraction angle region for the sample annealed at 1300 °C.

powders depending on the annealing temperature. After annealing at a temperature of 800 °C, the XRD shows the presence of only two cubic phases—magnesium oxide and gadolinium oxide. Broad diffraction peaks indicate a small crystallite size for these phases—12 and 14 nm, respectively. Diffraction peaks of cubic Gd₂O₃ and MgO become sharper with an increase in the calcination temperature up to 1200 °C, indicating an increase in the crystallinity of the powders. Also, at low calcination temperatures, distortion in the crystal lattices caused by the composite structure and high powder dispersity led to deviation of the calculated phase composition compared to a preset value. Calcination at 1100 and 1200 °C causes crystal structure ordering, and the calculated mass fractions of Gd₂O₃ and MgO within measurement inaccuracy are complementary to 68 wt%:32 wt%.

The calculated values of the unit cell parameter and the phase density of the cubic (C) Gd₂O₃ and MgO within the measurement inaccuracy (~1%) correspond to Refs. [26,27], indicating an extremely low mutual solubility of ceramic components.

It is known that at temperatures of 1200–1250 °C, gadolinium oxide has a phase transition with the formation of a monoclinic (B) modification [28]. According to the Rietveld refinement, the powders calcined at 1300 °C contain a monoclinic Gd₂O₃ at the level of detection limit (< 2.5 wt%). The reflexes of the (B)Gd₂O₃ phase can be seen in the 2θ degree

region of 27° – 33° in Fig. 1(b). The mass fraction of the (C) Gd_2O_3 phase decreases with respect to magnesium oxide approximately by the same value, which confirms monoclinic phase formation. Low intensity, as well as the absence of certain reflexes, makes it difficult to calculate the parameters of this phase. A possible reason for the low content of the monoclinic phase (instead of full conversion) is the relatively slow cooling of the powders after calcination. It is highly likely that the reverse $\text{B} \rightarrow \text{C}$ Gd_2O_3 phase transition occurs at this time. This means that it will be technologically difficult to obtain a large window from composite ceramics containing gadolinium oxide in the monoclinic phase. A large ceramic sample, especially in a massive graphite mold, cools slowly under normal conditions. Also, as will be shown below, ceramics require annealing at a high temperature (about 1000°C) after sintering when there is also the possibility of the $\text{B} \rightarrow \text{C}$ phase transition.

SEM images of the synthesized MgO – Gd_2O_3 powders are shown in Fig. 2. The morphology of the powders is characterized by the presence of flakes with a porous structure, which is probably associated with the release of a large amount of gaseous products at the synthesis process. The characteristic size of agglomerates is

more than $10\text{ }\mu\text{m}$, as shown in Fig. 2(a). At higher magnification (Fig. 2(b)), a fine structure of flakes is discernible. These are fragile hollow spheres, the walls of which are easily destroyed with little impact and the primary particles are the walls of spheres, with a thickness of a few nanometers and a size of up to hundreds of nanometers. This structure is very typical for powders obtained by glycine–nitrate SHS and caused by the synthesis mechanism. The propagation of the reaction front causes foaming of the precursor, followed by the onset of the combustion reaction. The release of a large amount of gaseous products during the reaction prevents the collapse of these pores and hard agglomeration of the primary particles. For example, powders of rare earth element oxides [19–21] with a similar structure were obtained earlier.

Fabrication of optical ceramics requires controlling the purity of the materials. Often the impurity composition of powders is overlooked, despite the fact that impurities can inhibit (or improve) sintering of ceramics with a dense structure, cause optical losses due to absorption and scattering, impair mechanical strength and thermal conductivity, etc. Table 2 shows the impurity composition of the synthesized MgO – Gd_2O_3 powders according to ICP-AES. The powders

Fig. 2 SEM images of as-synthesized MgO – Gd_2O_3 powders.

Table 2 Trace elemental impurity analysis results by the inductively coupled plasma atomic emission spectrometry (ICP-AES) of the MgO – Gd_2O_3 powders

Element	SHS MgO – Gd_2O_3 (ppm)	Element	SHS MgO – Gd_2O_3 (ppm)	Element	SHS MgO – Gd_2O_3 (ppm)	Element	SHS MgO – Gd_2O_3 (ppm)
Al	70	Ni	< 0.2	Hf	< 5	W	< 1
Ca	22	Pb	< 2	K	0.3	Zn	6
Co	< 0.5	Si	7	Mn	1.8	Zr	< 1
Cr	0.17	Sn	< 2	Mo	< 0.5	—	—
Cu	< 0.8	Ta	< 1	Na	20		
Fe	2.3	Ti	< 0.2	V	< 0.3		

have an acceptable level of purity for the production of IR-transparent ceramics. The highest content was observed for Al (70 ppm), Ca (22 ppm), Na (20 ppm), Si (7 ppm), Fe (2.3 ppm), and Zn (6 ppm). The content of other impurities does not exceed 2 ppm. Obviously, the source of contamination is the impurities contained in the starting powders, primarily magnesium oxide.

Figure 3 shows the SPS mode of MgO–Gd₂O₃ SHS powders and the shrinkage rate curve. Highly dispersed powders of magnesium and rare earth oxides easily absorb gases from the air. An intermediate dwelling at a temperature of 780 °C for 10 min was used during the sintering process to remove moisture and carbon dioxide from the surface of the powder particles. The powder densification occurs at temperatures of 780–1140 °C and coincides in time with the moment of pressure application to the sample. Sintering at a temperature of 1140 °C provides complete shrinkage of the compact. As can be seen from Fig. 3, the temperature line does not flat at dwell time at the intermediate step (at a temperature of 780 °C) and the final step (at a temperature of 1140 °C). This is a consequence of the pyrometer feedback delay. The value of this overrun does not exceed 10°–15° compared to the set temperature, and it takes no more than 2 min to eliminate this mismatch.

The applied pressure also deviates from the setting. After the intermediate, dwelling the pressure starts raising (up to 60 MPa), but at this very moment, the intensive powder shrinkage weakening the pressure under the graphite punch and leading to a local minimum appears on the pressure line at about 1200 s. We also can observe the peak at about 1600 s where the pressure had already reached the maximum. This peak on the pressure line shows the completion of the shrinkage. At this moment, the powder shrinkage rate

Fig. 3 Time profiles of temperature, pressure, and shrinkage rate at SPS of MgO–Gd₂O₃ SHS powders.

becomes equal to zero, and the ongoing thermal expansion of the graphite die due to the dwelling under a high temperature leads to further increasing of the linear sizes of the graphite units of the press (spacers, punches, etc.).

The SPS temperature for MgO–Gd₂O₃ is lower compared to the similar yttria–magnesia composite. The reported optimal sintering temperature of glycine–nitrate-derived MgO–Y₂O₃ powders is 1350 [10] and 1300 °C [4]. In Ref. [11], the best transmission of MgO–Y₂O₃ composite was achieved at 1150 °C, while the temperature was measured by pyrometer on the outside of the graphite mold without correction and the reliable value for the sample was about 200° higher. The decrease in sintering temperature of MgO–Gd₂O₃ powders in comparison with MgO–Y₂O₃ is probably due to the intensification of mass transfer processes in materials at temperatures of phase transitions [29]. Although the sintering temperature of MgO–Gd₂O₃ composite ceramics is slightly lower (by 60 °C) than that required for the C→B Gd₂O₃ phase transition, applied pressure could provide a decrease in the temperature of this transition [30].

According to the results of the XRD analysis, the composite ceramic sample after SPS (Fig. 4) is a mixture of (C) Gd₂O₃, (B) Gd₂O₃, and MgO phases with average crystallite sizes of 35, 44, and 32 nm, respectively.

Table 3 presents Rietveld refined mass fractions, measured values of the density, and hardness of the MgO–Gd₂O₃ composite ceramics in comparison with the literature data on MgO–Gd₂O₃. The total content of gadolinium oxide is at the level of 61 wt%, which is 5% lower than in the powder. Based on the fact that

Fig. 4 XRD patterns of the MgO–Gd₂O₃ ceramics prepared by SPS at 1140 °C and additionally annealed at 1000 °C in air.

Table 3 Comparison of the prepared MgO–Gd₂O₃ composite characteristics with some literature data

Source	Sintering temperature (°C)	Phase composition (wt%)			Relative density (%)	HV0.5 (GPa)
		(C) Gd ₂ O ₃	(B) Gd ₂ O ₃	MgO		
This work	1140	52	9	39	98.5	9.5±0.4
Ref. [9]	1200	70.3	0	29.7	96.1	8.4±0.4
Ref. [9]	1250	51.9	20.5	27.6	98.4	10.5±0.5
Ref. [9]	1350	0	70.3	29.7	99.8	14.1±0.2

processes leading to a decrease in the actual gadolinium content (evaporation, etc.) are unlikely, we can assume the presence of an amorphous or deformed monoclinic phase of Gd₂O₃ in the amount of 5%. Annealing the ceramics at 1000 °C does not notably affect the phase composition, and the mass fractions of the components calculated from Fig. 4(b) correspond within the measurement error to the values for ceramics after SPS. The obtained material has a density of 5.52 g/cm³. Calculation of the theoretical density of the prepared MgO–Gd₂O₃ material is complicated because it is impossible to estimate the density of the amorphous Gd₂O₃ phase. Compared to MgO–(C) Gd₂O₃, the relative density of the prepared ceramics is 98.5%. The proposed SPS/SHS approach allows one to obtain a material with the same density as for hot-pressed samples at a lower temperature and a significant reduction in the heat treatment time.

Measured HV0.5 microhardness of the MgO–Gd₂O₃ composite ceramics is 9.5 GPa, which is slightly lower than the values for MgO–Y₂O₃ ceramics (10–10.5 GPa [4,10–12]). From the data given in Ref. [9], it can be seen that the microhardness depends linearly on the fraction of the monoclinic Gd₂O₃ phase. The microhardness value of our MgO–Gd₂O₃ composite ceramics, containing 9 wt% monoclinic Gd₂O₃ phase, fits into this dependence.

A 0.5 kg load is often used to determine the Vickers microhardness of various materials. However, for ceramics, such a low load may give an overestimated value of their microhardness. At low loads, the size of the indenter print is comparable to both the size of the microstructure flaws and the size of the macrostructure defects (surface polishing defects). Increasing the load leads to an expansion of the print size, i.e., an increase in the volume of the material to be examined. Figure 5 shows the dependence of the microhardness of MgO–Gd₂O₃ composite ceramics on the load value. As seen in Fig. 5, the measured values of HV decrease with increasing load and reach saturation at a pressure of more than 2 kg. The reliable value of the microhardness

Fig. 5 Dependence of the microhardness of the MgO–Gd₂O₃ composite ceramics on the applied load.

for the MgO–Gd₂O₃ ceramics can be considered the value of HV = 9 GPa.

Fracture toughness $K_{IC} = 2.0 \pm 0.5 \text{ MPa} \cdot \text{m}^{1/2}$ was calculated at load $P = 2 \text{ kg}$. No reference data was found on the toughness of MgO–Gd₂O₃ composites. The MgO–Y₂O₃ K_{IC} values are determined by hot pressing conditions and lie in the range of 1.6–2.5 MPa·m^{1/2} [4], which is close to that obtained for MgO–Gd₂O₃. Comparison with single-phase materials shows that the prepared material has the same toughness as aluminum–magnesium spinel MgAl₂O₄ ceramics [31].

Figure 6 shows the SEM micrographs of the fabricated MgO–Gd₂O₃ composite ceramics. The bright grains are the Gd₂O₃ phase, and the dark grains are the MgO phase. As can be seen, the Gd₂O₃ and MgO grains are fine and uniformly distributed in the sample volume, which is favorable for the ceramics' mechanical and optical properties. The average grain sizes are about 150 nm for both gadolinia and magnesia, which is 3–5 times larger than those measured on XRD. This could mean that the observed grains are polycrystalline. Also, there are still a few pores between the Gd₂O₃ and the MgO grains. Intergranular fracture is observed on fractograms of MgO–Gd₂O₃ ceramics. Magnesia has significantly higher mechanical characteristics compared

Fig. 6 SEM micrographs of the MgO-Gd₂O₃ ceramics fractured surface after SPS and calcination in air.

with gadolinium oxide. This explains the absence of MgO grain destruction. However, the absence of Gd₂O₃ grain destruction indicates lower Mg–O–Gd bond energy compared to bonds in individual oxides and/or the presence of impurities at the grain boundaries that weaken them. Such impurities, as will be shown below, can be carbon and residual carbonate and hydroxyl groups. Additional annealing at 1000 °C for 5 h did not affect the ceramic density and average grain size.

Figure 7 shows the appearance and transmission spectra of MgO-Gd₂O₃ composite ceramics after sintering and after additional annealing in air at 1000 °C for 5 h. The transmission of the ceramics after SPS is below 60%. Apparently, this is due to significant contamination of the ceramics with carbon, partial reduction of metal oxides, and the emergence of a significant amount of oxygen vacancies, which appears in the slightly gray color of the sample. After annealing in air at a temperature of 1000 °C, MgO-Gd₂O₃ composite ceramics become almost white, and the transmission increases significantly. The transmission spectra of MgO-Gd₂O₃ composite ceramics exhibit an

intense absorption band at wavelengths of about 7 μm due to the content of residual carbonate groups and in the range of 2.7–4 μm, associated with residual hydroxyl groups [6,10–12]. Annealing reduces the content of hydroxyl groups but has little effect on the content of residual carbonate groups. It is assumed that the operating range of IR ceramics is 4–5 μm and the residual absorption at wavelengths of 3 and 7 μm, where the atmosphere is almost opaque, does not directly affect the performance of the protective window. However, in some cases, the absence of absorption at 3 and 7 μm may be important. However, these bands are characteristics for MgO-Y₂O₃ and MgO-Gd₂O₃ composite ceramics obtained by SPS and hot pressing methods, because of the graphite mold and the residual pressure of carbon monoxide. As far as we know, it was only the authors of Ref. [32] who managed to overcome this effect for MgO-Y₂O₃ by introducing an additive of lithium fluoride. However, LiF also increased the average grain size of the ceramic, resulting in a decrease in overall transmission.

The maximum transmission of 77% is observed at a wavelength of 5.3 μm; however, this is still less than

Fig. 7 (a) Appearance and (b) IR Fourier transmission spectra of MgO-Gd₂O₃ composite ceramics after SPS and additional annealing at 1000 °C for 5 h.

the transmittance of 80.4%–84.8% over 3–6 μm reported in Ref. [9]. In addition to the absorption of OH and CO_3 groups, the transmission of the ceramics is limited by scattering both on residual pores and on the MgO and Gd_2O_3 grains. The significant reduction in sintering temperature (less than 1200 $^\circ\text{C}$) demonstrated in this study, compared to processes for other known MgO – Gd_2O_3 or MgO – Y_2O_3 composites, means that the range of possible materials for mold manufacturing is expanded. Thus, the process can be carried out in a completely graphite-free or bonded graphite environment like WC/Co or SiC.

It is worth mentioning that to the best of our knowledge, this article presents the results of the first attempt of the SPS of the MgO – Gd_2O_3 composite. We are sure that applying well-known approaches like a two-step SPS mode [33,34] or using high-pressure during SPS [15,35] could improve density and, as a result, transmittance of MgO – Gd_2O_3 ceramics.

4 Conclusions

Nanocomposite MgO – Gd_2O_3 powders were successfully obtained by glycine–nitrate self-propagating high-temperature synthesis. According to SEM and XRD methods, the powders are highly dispersed cubic phases of gadolinium and magnesium oxides. Composite IR-transparent MgO – Gd_2O_3 ceramics were successfully produced by the SPS method for the first time. The highest linear transmittance, 77%, was observed at 5.3 μm for MgO – Gd_2O_3 ceramic samples obtained at a temperature of 1140 $^\circ\text{C}$. Comparison of mechanical and structural characteristics shows a substantial potential of the chosen SHS/SPS approach for fabrication of IR-transparent MgO – Gd_2O_3 ceramics.

Acknowledgements

The study was funded by the Russian Science Foundation (Research Project No. 19-73-10127). The IR spectral studies were performed on the equipment of the Analytical Centre of the G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences.

References

- [1] Xie JX, Mao XJ, Zhu QQ, *et al.* Influence of synthesis conditions on the properties of Y_2O_3 – MgO nanopowders

- and sintered nanocomposites. *J Eur Ceram Soc* 2017, **37**: 4095–4101.
- [2] Harris DC, Cambrea LR, Johnson LF, *et al.* Properties of an infrared-transparent MgO – Y_2O_3 nanocomposite. *J Am Ceram Soc* 2013, **96**: 3828–3835.
- [3] Jiang DT, Mukherjee AK. Spark plasma sintering of an infrared-transparent Y_2O_3 – MgO nanocomposite. *J Am Ceram Soc* 2010, **93**: 769–773.
- [4] Ma HJ, Jung WK, Baek C, *et al.* Influence of microstructure control on optical and mechanical properties of infrared transparent Y_2O_3 – MgO nanocomposite. *J Eur Ceram Soc* 2017, **37**: 4902–4911.
- [5] Stefanik T, Gentilman R, Hogan P. Nano-composite optical ceramics for infrared windows and domes. *Proc SPIE* 2007, **6545**: 65450A.
- [6] Yong SM, Choi DH, Lee K, *et al.* Study on carbon contamination and carboxylate group formation in Y_2O_3 – MgO nanocomposites fabricated by spark plasma sintering. *J Eur Ceram Soc* 2020, **40**: 847–851.
- [7] Wang JW, Zhang LC, Chen DY, *et al.* Y_2O_3 – MgO – ZrO_2 infrared transparent ceramic nanocomposites. *J Am Ceram Soc* 2012, **95**: 1033–1037.
- [8] Information on <http://www.dtic.mil/dtic/tr/fulltext/u2/a460289.pdf>.
- [9] Wu N, Li XD, Li JG, *et al.* Fabrication of Gd_2O_3 – MgO nanocomposite optical ceramics with varied crystallographic modifications of Gd_2O_3 constituent. *J Am Ceram Soc* 2018, **101**: 4887–4891.
- [10] Safronova NA, Kryzhanovska OS, Dobrotvorska MV, *et al.* Influence of sintering temperature on structural and optical properties of Y_2O_3 – MgO composite SPS ceramics. *Ceram Int* 2020, **46**: 6537–6543.
- [11] Permin DA, Boldin MS, Belyaev AV, *et al.* IR-transparent MgO – Y_2O_3 ceramics by self-propagating high-temperature synthesis and spark plasma sintering. *Ceram Int* 2020, **46**: 15786–15792.
- [12] Kryzhanovska OS, Safronova NA, Balabanov AE, *et al.* Y_2O_3 – MgO highly-sinterable nanopowders for transparent composite ceramics. *Funct Mater* 2019, **26**: 829–837.
- [13] Xie JX, Mao XJ, Li XK, *et al.* Influence of moisture absorption on the synthesis and properties of Y_2O_3 – MgO nanocomposites. *Ceram Int* 2017, **43**: 40–44.
- [14] Yong SM, Choi DH, Lee K, *et al.* Influence of the calcination temperature on the optical and mechanical properties of Y_2O_3 – MgO nanocomposite. *Arch Metall Mater* 2018, **63**: 1481–1484.
- [15] Liu LH, Morita K, Suzuki TS, *et al.* Evolution of microstructure, mechanical, and optical properties of Y_2O_3 – MgO nanocomposites fabricated by high pressure spark plasma sintering. *J Eur Ceram Soc* 2020, **40**: 4547–4555.
- [16] Liu LH, Morita K, Suzuki TS, *et al.* Synthesis of highly-infrared transparent Y_2O_3 – MgO nanocomposites by colloidal technique and SPS. *Ceram Int* 2020, **46**: 13669–13676.
- [17] Özdemir H, Faruk Öksüzömer MA. Synthesis of Al_2O_3 ,

- MgO and MgAl_2O_4 by solution combustion method and investigation of performances in partial oxidation of methane. *Powder Technol* 2020, **359**: 107–117.
- [18] Orante-Barrón VR, Oliveira LC, Kelly JB, *et al.* Luminescence properties of MgO produced by solution combustion synthesis and doped with lanthanides and Li. *J Lumin* 2011, **131**: 1058–1065.
- [19] Permin DA, Balabanov SS, Snetkov IL, *et al.* Hot pressing of Yb: Sc_2O_3 laser ceramics with LiF sintering aid. *Opt Mater* 2020, **100**: 109701.
- [20] Balabanov SS, Permin DA, Rostokina EY, *et al.* Sinterability of nanopowders of terbium solid solutions with scandia, yttria, and lutetia. *J Adv Ceram* 2018, **7**: 362–369.
- [21] Permin DA, Kurashkin SV, Novikova AV, *et al.* Synthesis and luminescence properties of Yb-doped Y_2O_3 , Sc_2O_3 and Lu_2O_3 solid solutions nanopowders. *Opt Mater* 2018, **77**: 240–245.
- [22] Coelho AA. Whole-profile structure solution from powder diffraction data using simulated annealing. *J Appl Cryst* 2000, **33**: 899–908.
- [23] Chuvil'deev VN, Boldin MS, Dyatlova YG, *et al.* Comparative study of hot pressing and high-speed electropulse plasma sintering of $\text{Al}_2\text{O}_3/\text{ZrO}_2/\text{Ti}(\text{C},\text{N})$ powders. *Russ J Inorg Chem* 2015, **60**: 987–993.
- [24] Lawn B. *Fracture of Brittle Solids*. 2nd edn. Cambridge: Cambridge University press, 1993.
- [25] Warlimont H. Ceramics. In *Springer Handbook of Condensed Matter and Materials Data*. Martienssen W, Warlimont H, Eds. Berlin, Heidelberg: Springer Berlin Heidelberg, 2005: 431–476.
- [26] Information on https://materials.springer.com/isp/crystallographic/docs/sd_0547532
- [27] Information on https://materials.springer.com/isp/crystallographic/docs/sd_0561181.
- [28] Zinkevich M. Thermodynamics of rare earth sesquioxides. *Prog Mater Sci* 2007, **52**: 597–647.
- [29] Rhodes WH. Controlled transient solid second-phase sintering of yttria. *J Am Ceram Soc* 1981, **64**: 13–19.
- [30] Zhang FX, Lang M, Wang JW, *et al.* Structural phase transitions of cubic Gd_2O_3 at high pressures. *Phys Rev B* 2008, **78**: 064114.
- [31] Aksel C, Riley FL. Magnesia–spinel (MgAl_2O_4) refractory ceramic composites. In *Ceramic-Matrix Composites. Microstructure, Properties and Applications*. Cambridge: Woodhead Publishing Limited, 2006: 359–399.
- [32] Ma HJ, Kong JH, Kim DK. Insight into the scavenger effect of LiF on extinction of a carboxylate group for mid-infrared transparent Y_2O_3 –MgO nanocomposite. *Scripta Mater* 2020, **187**: 37–42.
- [33] Wang CJ, Huang CY, Wu YC. Two-step sintering of fine alumina–zirconia ceramics. *Ceram Int* 2009, **35**: 1467–1472.
- [34] Madhav Reddy K, Kumar N, Basu B. Innovative multi-stage spark plasma sintering to obtain strong and tough ultrafine-grained ceramics. *Scripta Mater* 2010, **62**: 435–438.
- [35] Kim BN, Hiraga K, Grasso S, *et al.* High-pressure spark plasma sintering of MgO-doped transparent alumina. *J Ceram Soc Japan* 2012, **120**: 116–118.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made.

The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder.

To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.