

# Synthesis of $\text{MgAl}_2\text{O}_4$ Spinel in $\text{MgO-Al}_2\text{O}_3$ and $\text{MgO-Al}_2\text{O}_3\text{-Al}$ Systems via HPHT Sintering

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Received: 28.02.2025 & Accepted: 29.05.2025

Doi: [10.12693/APhysPolA.147.456](https://doi.org/10.12693/APhysPolA.147.456)

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The synthesis of magnesium–aluminum spinel ( $\text{MgAl}_2\text{O}_4$ ) by high-pressure–high-temperature sintering within the  $\text{MgO-Al}_2\text{O}_3$  and  $\text{MgO-Al}_2\text{O}_3\text{-Al}$  systems has been investigated. The experiments were carried out at a pressure of 2 GPa and temperatures ranging from 400 to 1600°C. Increasing the sintering temperature resulted in a higher  $\text{MgAl}_2\text{O}_4$  content in both  $\text{MgO-Al}_2\text{O}_3$  and  $\text{MgO-Al}_2\text{O}_3\text{-Al}$  systems. This, in turn, led to an increase in the hardness of the synthesized samples. The results suggest that high-pressure–high-temperature synthesis requires a sintering temperature of at least 1000°C in a pressure range of 2.0–5.0 GPa to achieve optimal physical properties.

topics: magnesium–aluminum spinel, high-pressure–high-temperature (HPHT) sintering, chemical interaction, liquid phase sintering

## 1. Introduction

Magnesium–aluminum spinel ( $\text{MgAl}_2\text{O}_4$ , MAS) has been identified as the sole stable compound that is formed within the  $\text{MgO-Al}_2\text{O}_3$  system. The use of MAS in a variety of fields, including refractories, optical materials, electronics, and catalysis, is largely attributable to its exceptional properties. These include high chemical resistance (7.5–8 Mohs) and the ability to retain strength at elevated temperatures [1, 2].

There are various ways to make  $\text{MgAl}_2\text{O}_4$ , such as chemical methods, mechanochemical processes, plasma-chemical synthesis, melting in electric arc furnaces, firing in high-temperature furnaces, and sol–gel techniques [3–5]. Table I presents the results of an analysis of primary technologies. However, many of these methods are energy- and time-intensive and often require specialized equipment, increasing production costs, while

high-pressure–high-temperature (HPHT) sintering allows to obtain bulk samples with sufficient level of properties in a short time.

It is well established that high-pressure conditions can alter phase stability and reaction pathways, thereby enabling spinel formation at reduced temperature or over a shorter time [6, 7]. Furthermore, high-pressure applications have been demonstrated to induce alterations in the stoichiometries of sintered spinel and other materials [8]. Despite the extensive research conducted on spinel synthesis under atmospheric and high-pressure conditions (e.g., HP-SPS at 50–500 MPa [2, 3]; HP-SPS — high-pressure–spark plasma sintering), there remains a paucity of research on reaction sintering at elevated temperatures and pressures exceeding 1 GPa. The behavior of high-temperature-calcined  $\text{MgAl}_2\text{O}_4$  nanopowders under high-pressure conditions (2–5 GPa) at lower temperatures of 500–700°C has been described in the work [9]. The authors have shown that such nanoceramics should be highly

Comprehensive analysis of the  $MgAl_2O_4$  spinel synthesis methods.

TABLE I

Parameter	Spark plasma sintering (SPS) [2, 3, 5]	Sol-gel methods [3]	Conventional solid-state [4]	HPHT sintering (this work)
pressure	50–500 MPa	atmospheric	atmospheric	2–6 GPa
temperature range	1300–1600°C	600–1550°C (multi-step)	1400–1650°C	300–2000°C
hold time	20 min	hours to days	2–8 h	1–5 min
spinel content	> 98% (optimized)	phase-pure (post-calcination)	> 95% (prolonged sintering)	up to ~ 90% ( $MgO-Al_2O_3$ )
hardness [GPa]	15–20	12–18 (after densification)	16–22	7–9, but should be improved
key advantages	high density, transparency	low-temperature initiation	industrial scalability	rapid synthesis [min]
limitations	specialized equipment required	multi-step processing	energy, time-intensive	microcracks, residual stress
additions and their effects	often used for rapid densification and transparency (e.g., $TiO_2$ , $ZnO$ , $B_2O_3$ )	rarely used, but possible for microstructure control	sometimes used (e.g., $TiO_2$ , $ZnO$ , $ZrO_2$ , $B_2O_3$ , $Y_2O_3$ , $SiO_2$ , $LiF$ , $CaO$ )	aluminum

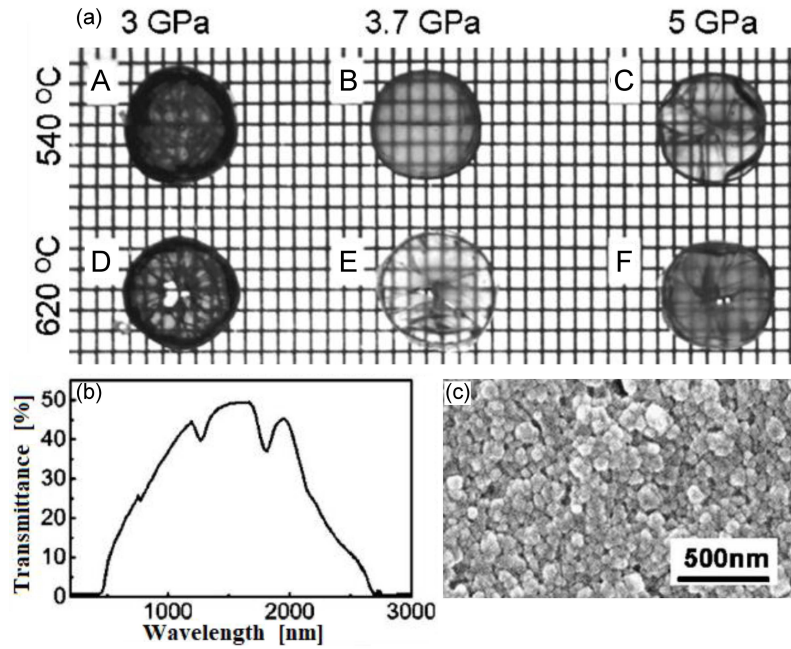


Fig. 1. (a)  $MgAl_2O_4$  nanoceramics prepared at 540°C/3 GPa (sample A), 540°C/3.7 GPa (sample B), 540°C/5 GPa (sample C), 620°C/3 GPa (sample D), 620°C/3.7 GPa (sample E), and 620°C/5 GPa (sample F), respectively; (b) transmission spectrum of sample B; and (c) SEM image of sample E.

transparent despite having relative densities of less than 99%, due to the low or negligible light scattering from the nanosized grains and pores (see Fig. 1).

Sreekumar et al. [10] demonstrated the effect of temperature and Mg content on the phase equilibrium of  $Al_2O_3/MgAl_2O_4/MgO$ , emphasizing

the significance of regulating magnesium content and thermodynamic parameters. The study conducted in [11] examined the kinetics of magnesium–aluminum spinel formation at elevated temperatures (1200–1600°C) and pressures (1.0–4.0 GPa), along with the interdiffusion mechanisms of  $Mg^{2+}$

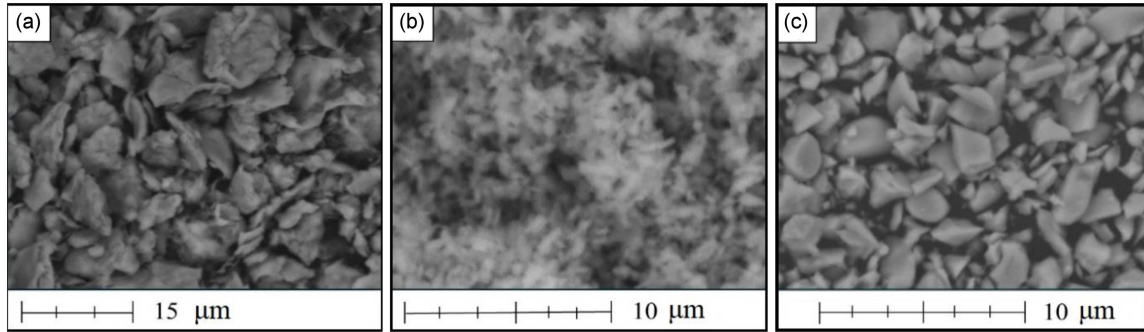


Fig. 2. Morphology of aluminum micropowders (a), magnesium oxide nanopowder (b), and aluminum oxide micropowders (c).

and  $\text{Al}^{3+}$  ions at the interface. The findings indicate that the interaction between  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  with  $\text{MgAl}_2\text{O}_4$  spinel formation is most active at elevated temperatures ( $\approx 2000^\circ\text{C}$ ) and pressures (4.0 GPa), with temperature having a more significant impact on reaction kinetics than sintering pressure.

However, there is little research on the preparation of bulk magnesium–aluminum spinel samples by direct reaction of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  powders. Therefore, the investigation into the synthesis of spinel under high pressure via HPHT sintering in different systems, such as  $\text{MgO}$ – $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ – $\text{Al}_2\text{O}_3$ – $\text{Al}$ , is of great scientific and practical interest. This method will help us learn more about the formation of spinel structures under extreme conditions. It is expected that the use of metallic aluminum as a precursor will influence its in situ oxidation during synthesis. In addition, the presence of aluminum will affect the reaction kinetics by activating liquid phase sintering due to the low melting point of aluminum. This, in turn, will allow us to obtain MAS with a more ordered structure at a lower temperature in a shorter time (potentially, it should be helpful for the obtaining of optically transparent MAS samples).

## 2. Methods and materials

Aluminum,  $\text{Al}_2\text{O}_3$ , and  $\text{MgO}$  nanopowder (12N-0801) were used as raw materials. The morphology of the powders was examined utilizing a Hitachi SU8010 scanning electron microscope in a cold field (Fig. 2). The scanning electron microscopy (SEM) analysis showed that Al powder has a flat, plate-like shape with particle sizes between 5 and 15  $\mu\text{m}$ ,  $\text{MgO}$  nanopowders have a nearly shapeless form, and  $\text{Al}_2\text{O}_3$  powder has grain sizes of about 2 to 3  $\mu\text{m}$ .

The sintering was carried out in a toroidal-type high-pressure apparatus (HPA) at a pressure of 2 GPa and temperatures (400–1600 $^\circ\text{C}$ ). This pressure was chosen because a previous study showed that the highest spinel phase content was observed

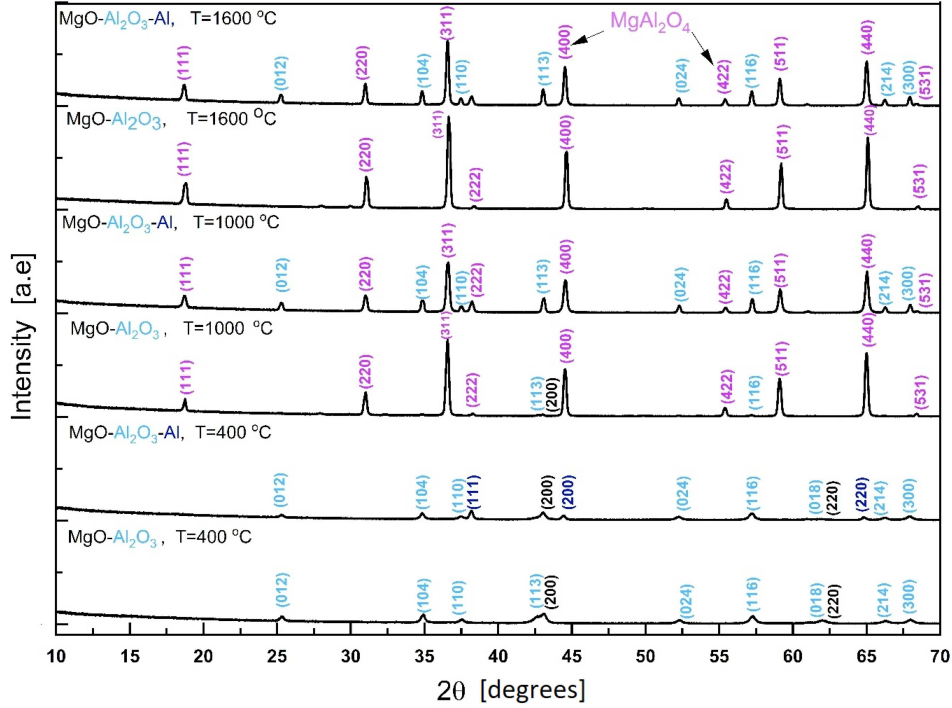
in samples pressed at 2 GPa [12]. The samples were heated from room temperature to the specified sintering temperature for 5 s; the temperature hold time was 1 min, followed by a temperature drop to room temperature for 5 s. The samples had a diameter of 9.2 mm and a height of 3.2 to 3.5 mm. The diameter was specified by the graphite container, whereas the height was determined by the powder filling level within the graphite container and the subsequent surface treatment. Before the microstructural studies, the surface of the samples was ground and polished with diamond paste. This treatment was carried out to remove the surface layer contaminated with graphite due to the contact of the filled powder with the heated graphite container.

Scanning electron microscopy (SEM) studies of the ceramic samples were performed using a Hitachi SU-70 scanning electron microscope. The studied materials were characterized using X-ray diffraction (XRD), which was done using a PANalytical X'Pert PRO MRD diffractometer equipped with a hybrid two-bounce Ge (220) monochromator and triple-bounce Ge (220) analyzer in front of the detector. Vickers hardness (HV) was measured using an ARS900 Japan microhardness tester. Values of HV were calculated according to the standard method [13] using the formula  $\text{HV} = 1.854P/D^2$ , where  $P$  represents the indenter load (9.8 H), and  $D$  is the length of the diagonal of the Vickers pyramid indentation. The dwell time of each indentation was 15 s.

## 3. Results and discussion

### 3.1. The influence of sintering temperature and pressure on the phase composition of the obtained samples

The X-ray diffraction (XRD) patterns of samples sintered at low temperatures (400 $^\circ\text{C}$ ) exhibit a pronounced background intensity at small angles (see Fig. 3).


 Fig. 3. XRD patterns of  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Al}$  and  $\text{MgO}-\text{Al}_2\text{O}_3$  samples sintered at different temperatures.

Samples sintered at higher temperatures (1000–1600°C) exhibit reduced background intensity, which is attributed to the growth of crystalline grains with increasing sintering temperature. Increasing sintering temperature leads to a higher presence of  $\text{MgAl}_2\text{O}_4$  in the  $\text{MgO}-\text{Al}_2\text{O}_3$  and  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Al}$  systems. The  $\text{MgO}-\text{Al}_2\text{O}_3$  samples sintered at 1600°C showed the highest  $\text{MgAl}_2\text{O}_4$  peaks, while a sintering temperature of 400°C did not result in the formation of  $\text{MgAl}_2\text{O}_4$  in either system (Fig. 3).

This study found that magnesium oxide ( $\text{MgO}$ ) and alumina ( $\text{Al}_2\text{O}_3$ ) interact over a wider temperature range compared to the previous study [12]. In our work, spinel phase formation was identified at both 1000°C and 1600°C. In comparison,  $\text{MgO}-\text{Al}_2\text{O}_3$  samples sintered at pressures ranging from 5.0 to 7.5 GPa and a temperature of 1900°C, as detailed in [12], demonstrated that the spinel content was less than 1.7%. It can be concluded that pressure influences the interaction between  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  in a complex way. Increasing the pressure to 2.0 GPa expands the temperature range for their interaction, allowing spinel formation between 1000–1600°C, compared to 2135°C at atmospheric pressure. However, increasing the pressure further to 5.0–7.5 GPa prevents spinel formation from the initial components, even at 1900°C, unless a liquid phase component, such as aluminum, is added.

Previous studies [12] showed that the addition of aluminum significantly increased the  $\text{MgAl}_2\text{O}_4$  phase content from 1.7% (in samples without aluminum) to 80–90% (in  $\text{MgO}-\text{Al}_2\text{O}_3$  samples). As

TABLE II

Parameters of the crystal lattice [ $\text{\AA}$ ] of magnesium-aluminum spinel formed during sintering.

$T$ sintering [ $^{\circ}\text{C}$ ]	Powder mix	
	$\text{MgO}-\text{Al}_2\text{O}_3$	$\text{MgO}-\text{Al}_2\text{O}_3-\text{Al}$
400		
1000	8.079(9)	8.078(15)
1600	8.076(2)	8.05(8)

the melting point of aluminum increases with pressure [14, 15], it was expected that reducing the pressure to 2.0 GPa would enhance the diffusion and liquid-phase sintering processes [16]. However, in the samples analyzed in this study, the most intense peaks of the spinel phase, and consequently, its highest content, were observed in samples without the addition of aluminum, regardless of the sintering temperature. Analysis of the lattice parameters of the spinel formed during sintering (Table II) shows that the addition of aluminum results in a decrease in the unit cell parameter of  $\text{MgAl}_2\text{O}_4$ . This suggests a reduction in the amount of impurities absorbed by the spinel from the melt, leading to an increase in the purity and structural perfection of the crystallites formed by  $\text{MgAl}_2\text{O}_4$ , particularly in the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Al}$  system. In the  $\text{MgO}-\text{Al}_2\text{O}_3-\text{Al}$  samples sintered at 1000°C and 1600°C, aluminum peaks were not detected due to their overlap with aluminum oxide and magnesium-aluminum spinel peaks (at 37–39° and 65°  $2\theta$  angles, respectively).

### 3.2. The influence of sintering temperature on the structure and properties of MgO–Al<sub>2</sub>O<sub>3</sub> and MgO–Al<sub>2</sub>O<sub>3</sub>–Al composites

Increasing the sintering temperature leads to the intensification of the reaction between MgO and Al<sub>2</sub>O<sub>3</sub> with the formation of MgAl<sub>2</sub>O<sub>4</sub> for both systems (i.e., MgO–Al<sub>2</sub>O<sub>3</sub> and MgO–Al<sub>2</sub>O<sub>3</sub>–Al). The presence of spinel is confirmed by both X-ray diffraction and electron microscopy. Microstructural analysis of MgO–Al<sub>2</sub>O<sub>3</sub> samples sintered within the temperature range of 1000–1600°C revealed the existence of a needle-like, randomly oriented MgAl<sub>2</sub>O<sub>4</sub> phase throughout the sample volume, with crystals measuring less than 1  $\mu$ m in diameter and exceeding 10  $\mu$ m in length (Fig. 4). The character of the crystallites suggests an active process of heat and mass transfer during their formation, indicating non-equilibrium conditions during the sintering [17, 18]. The microstructure of the MgO–Al<sub>2</sub>O<sub>3</sub> sample sintered at 1000°C has small alumina particles between needle-shaped spinel crystals (Fig. 4a). At 1600°C, the microstructure of the sample contains no residual Al<sub>2</sub>O<sub>3</sub> crystals and features needle-shaped MgAl<sub>2</sub>O<sub>4</sub> spinel crystals across the surface (Fig. 4b).

The evidence of residual Al<sub>2</sub>O<sub>3</sub> phase was also confirmed by the energy-dispersive X-ray (EDX) analysis (Fig. 5).

The sample sintered at 1000°C (Fig. 5a) demonstrates a substantially higher level of heterogeneity compared to the sample sintered at 1600°C (Fig. 5b). Random point analysis of the 1000°C sample (Fig. 5a) shows that three out of four measurement points (namely points 1, 3, 4) contain low magnesium content (7.5–8.3% atomic). This indicates the dominance of the Al<sub>2</sub>O<sub>3</sub> (corundum) phase with only minor spinel inclusions. Furthermore, significant variations in Mg/Al ratios across different points confirm the non-uniform nature of this sample. In contrast, the sample sintered at 1600°C (Fig. 5b) shows a more improved stoichiometry. Points 2 and 4 show magnesium levels (12.84–13.54% atomic) much closer to the ideal MgAl<sub>2</sub>O<sub>4</sub> composition (theoretical value — 14.3% Mg). In addition, smaller variations in Mg/Al ratios throughout this sample indicate that a more uniform synthesis process occurred at the higher temperature. As a result, it can be concluded that the sample sintered at 1600°C demonstrates significantly better spinel formation, characterized by higher magnesium content and lower residual Al<sub>2</sub>O<sub>3</sub>. This shows that the lower sintering temperature of 1000°C is not sufficient for MgO and Al<sub>2</sub>O<sub>3</sub> to fully react, while 1600°C provides sufficient heat for almost complete spinel formation.

The hardness of all samples increased with an increasing sintering temperature (from 3 to 5 GPa for MgO–Al<sub>2</sub>O<sub>3</sub>–Al samples and from 7 to 9 GPa for MgO–Al<sub>2</sub>O<sub>3</sub> samples), which is also associated with

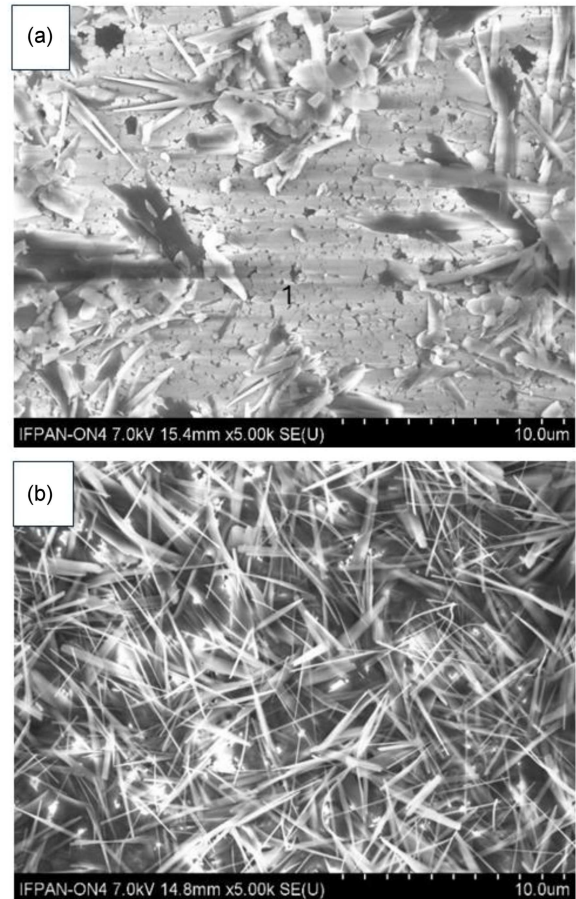


Fig. 4. Microstructure of MgO–Al<sub>2</sub>O<sub>3</sub> samples sintered at 1000°C (a) and 1600°C (b).

an increase in the MgAl<sub>2</sub>O<sub>4</sub> content with increasing sintering temperature (Fig. 6). However, these hardness values are significantly lower than those usually reported in the literature (16–22 GPa) [19], even for samples with the highest content of MgAl<sub>2</sub>O<sub>4</sub> phase with a minimal content of excess alumina (which should not significantly reduce the hardness, since the hardness of Al<sub>2</sub>O<sub>3</sub> is at least 15.6 GPa [20]). The observed lower hardness values result from microstructural heterogeneity visible in SEM and quantified by point EDX measurements and probably from residual porosity (the literature shows that porosity drastically reduces hardness) [21].

The micro- and macrostructure of the samples sintered at the maximum temperature (1600°C) is characterized by the presence of a significant number of cracks over the entire surface. This evidence indicates a high level of microstress resulting from the rapid interaction of the initial components (Al<sub>2</sub>O<sub>3</sub>, MgO) and intensive spinel formation. The limited holding time (1 min) during rapid heating probably does not allow the full implementation of stress relaxation mechanisms, resulting in the formation of micro and macro cracks. Thus, the results indicate the need to optimize the thermobaric



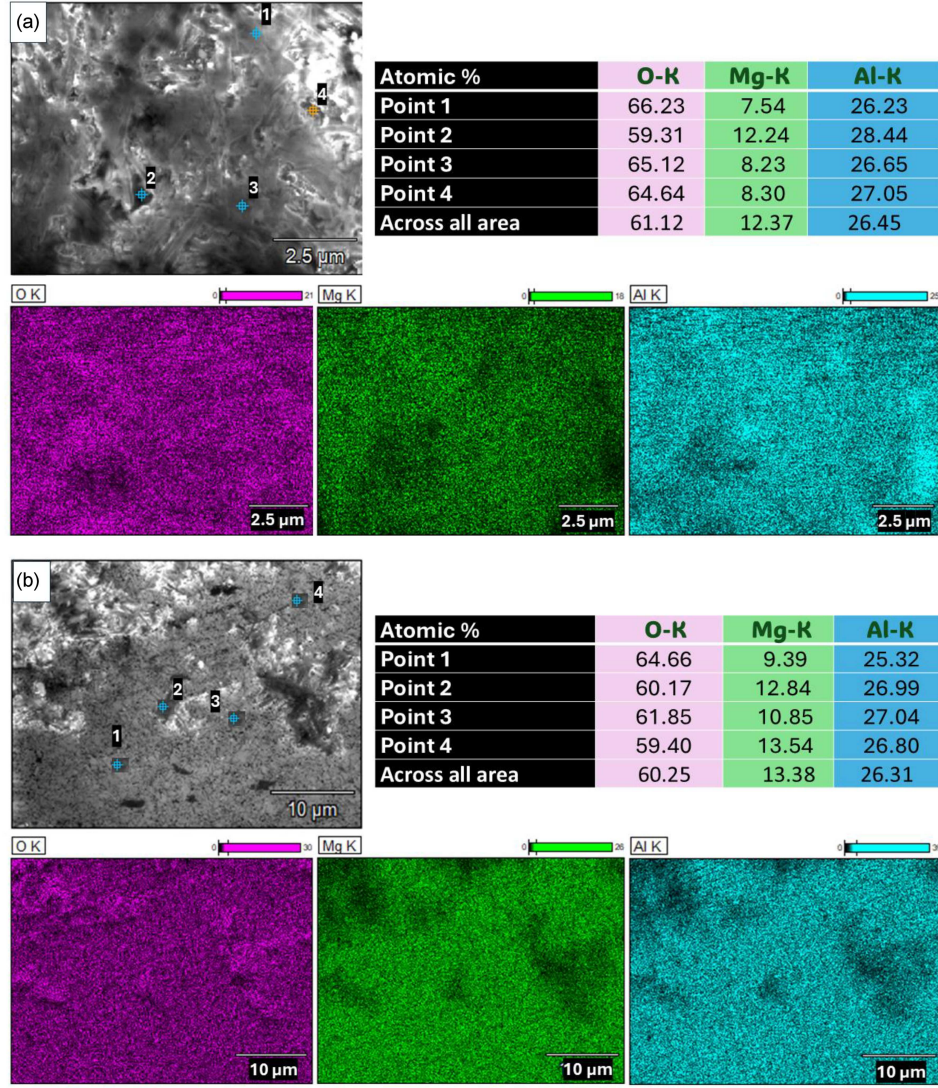


Fig. 5. SEM-EDX analysis of  $MgO-Al_2O_3$  samples sintered at 1000°C (a) and 1600°C (b).

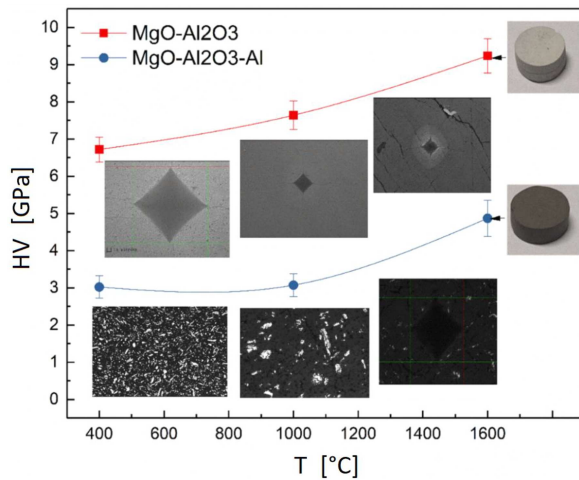


Fig. 6. Vickers hardness versus sintering temperature for  $MgO-Al_2O_3$  and  $MgO-Al_2O_3-Al$  samples, as well as their general view and macrostructure.

and kinetic parameters (in particular, the need to reduce the heating rate and increase the holding time) to minimize crack formation and improve the structural and mechanical properties of the sintered spinel materials.

#### 4. Conclusions

The possibility of obtaining spinel samples from the starting powders of aluminum and magnesium oxides at high temperatures and pressures has been investigated. It was found that the temperature interval of spinel formation at a pressure of 2.0 GPa is at least 1000–1600°C. Increasing the pressure to 5.0–7.5 GPa does not allow obtaining spinel-based samples even at a sintering temperature of 1900°C [12]. Therefore, it can be concluded that to synthesize spinel from a mixture of alumina micropowder and magnesia nanopowder with

optimal physical properties and maximum spinel content, the HPHT process pressure should be above 2.0 GPa but below 5.0 GPa, and the sintering temperature should be at least 1000°C (which is still significantly lower than the solid-phase sintering temperature). To minimize microstructural heterogeneity, it is advisable to adjust the heating rate and extend the holding time during the sintering process. Such an approach will facilitate more thorough diffusion processes and, as a result, minimize the residual presence of aluminum oxide and increase the spinel content in the produced samples. An open question remains regarding the replacement of aluminum by other components (e.g., yttrium oxide [22] or zirconium oxide), the addition of which will also enhance the diffusion processes but will not reduce the hardness of the samples.

Consideration of the possibility of synthesizing magnesium–aluminum spinel from initial nanopowders of magnesium and aluminum oxides is essential because the use of nanopowders will allow the improvement of the mechanical properties of the samples through the implementation of Hall–Petch and other mechanisms [19]. In addition, it could lead to the production of optically transparent samples by minimizing porosity and preventing significant grain growth during the sintering process [23, 24].

### Acknowledgments

This contribution was created under the support project “Development of a technology to produce transparent spinel for optical applications” (state registration number 602430). The project was financed by the Ministry of Science and High Education for Łukasiewicz Research Network — Krakow Institute of Technology. The work was also partially supported by the Polish National Science Centre (project no. 2024/53/B/ST11/01108).

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