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Preparation of high-quality transparent Al-rich spinel ceramics by reactive sintering

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ABSTRACT

Transparent Al-rich spinel ceramics ($MgO{\cdot}nAl_2O_3$, n = 1.05–2.5) were prepared by reactive sintering in air followed by the hot isostatic press (HIP). Commercial MgO and γ-Al_2O_3 powders were used as the raw materials, and the effects of composition and HIP temperature on the transmittance and microstructure of resulting samples were investigated. To obtain the high optical quality, extra alumina (n ≥ 1.1) was used to help eliminate residual pores and suppress abnormal grain growth during the sintering process. The appropriate HIP temperature was also critical to realize the single-phase formation and prevent the generation of second-phase precipitates. The resulting samples with n = 1.1 and 1.3 exhibited excellent optical quality and fine grains below 5 μm after HIPed at 1550 °C.

1. Introduction

Transparent magnesium aluminate spinel ceramics have been studied for more than 50 years since the first translucent sample was produced by the General Electric Company in the 1960s [1]. With the emergence of high-quality powders and advanced sintering methods such as hot press (HP) [2], HIP [3], spinel ceramics with high optical quality and large size have been prepared and widely used as transparent armors, high-temperature windows, IR domes and laser hosts [4–6]. Nowadays, the main issues that affect the preparation of transparent spinel ceramics are how to lower costs and further improve the optical quality and mechanical strength of samples [7].

Spinel ($MgO{\cdot}nAl_2O_3$) is the only compound in the MgO-Al_2O_3 phase system, and it has a broad solubility for extra Al_2O_3 at high temperatures [8,9]. However, most studies about transparent spinel ceramics are mainly focused on the near-stoichiometric range. This is because that Al-rich spinel powders are very difficult to be synthesized through traditional wet-chemical methods, i.e. sol-gel [10–12], isopropoxide hydrolysis [13] and co-precipitation [14]. Versus stoichiometric spinel, Al-rich samples generally exhibit superior optical quality [15] and high mechanical strength [16,17]. Transparent Al-rich spinel ceramics with a wide composition range (1 < n < 3) have been successfully prepared by reactive sintering of magnesium and aluminum compounds [18–21]. In these studies, high purity MgO and Al_2O_3 powders are the most commonly used raw materials because of their low prices, high chemical purity and wide sources.

Waetzig et al. [22] prepared transparent spinel ceramics with n = 1–2.5 through pressureless reactive sintering in air and HIP treatment using high-purity MgO and α-Al_2O_3 powders as raw materials. The transmittances of Al-rich samples were much higher than that of stoichiometric sample. However, the HIP treatment was applied at 1750 °C, which caused large average grain sizes of 23–622 μm. Dericioglu et al. [16] hot pressed MgO and α-Al_2O_3 powder mixtures in vacuum at 1400 °C followed by HIP treatment at 1900 °C. The sample with n = 2 exhibited high transmittance and fracture toughness. In general, the preparation of high-quality transparent Al-rich spinel ceramics through reactive sintering of MgO and α-Al_2O_3 powders usually requires high HIP temperatures. This leads to severe grain growth, which is harmful to the mechanical strength and optical quality of resulting samples.

The reaction between MgO and Al_2O_3 occurs by mutual diffusion of magnesium and aluminum ions [23]. The crystal structure of γ-Al_2O_3 was similar to that of spinel. This may be beneficial for the formation of spinel at the low temperature. Watzig et al. demonstrated that γ-Al_2O_3 started to react with MgO at 800 °C, much lower than α-Al_2O_3 (1000 °C)

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Table 1
Pre-sintering temperature, phases after pre-sintering and minimum HIP temperature of Al-rich samples.

n	1.05	1.1	1.3	1.5	2	2.5
Pre-sintering temperature (°C)	1500	1500	1500	1450	1400	1350
Phases after pre-sintering	spinel	spinel	spinel	spinel + α-Al_2O_3	spinel + α-Al_2O_3	spinel + α-Al_2O_3
Minimum HIP temperature (°C)	1500	1500	1500	1550	1650	1800

[24]. Moreover, compared to α-Al_2O_3, the sintering temperature of sample can be obviously decreased because of the higher sintering activity and larger specific surface area of γ-Al_2O_3 [24–26].

Here, transparent Al-rich spinel ceramics ($MgO{\cdot}nAl_2O_3$, $1.05 \le n \le 2.5$) were prepared by reactive sintering in air followed by HIP treatment using high-purity commercial γ-Al_2O_3 and MgO powders as raw materials. The effects of composition (Al_2O_3 / MgO ratio, n) and HIP temperature were intensively studied to find optimal strategies for preparation of transparent spinel ceramics with high optical transmittance and fine grains.

2. Experimental procedures

High-purity MgO (99.99%, 150 nm) and γ-Al_2O_3 (99.99%, 100 nm) powders were used as raw materials. The raw powders were weighed according to different compositions of n = 1.05, 1.1, 1.3, 1.5, 2 and 2.5 ($MgO{\cdot}nAl_2O_3$). Then they were mixed via wet ball milling for 12 h in ethanol using Al_2O_3 balls as the milling medium. After drying at 60 °C for 24 h in oven, the mixed powders were sieved through an 80-mesh screen and calcined at 800 °C to remove the residual organic impurities. The green bodies were shaped through dry pressing at 20 MPa followed by cold isostatic press at 200 MPa for 5 min. To eliminate open pores, the green bodies were pre-sintered in air between 1350 and 1500 °C for 3 h, which varied with the composition of samples. Finally, they were HIPed at 1550–1800 °C for 3 h in argon under a pressure of 200 MPa to obtain transparent samples. After annealing at 1200 °C for 6 h, the samples were double-side mechanical polished to 3 mm thick for further tests.

The in-line transmittances of polished samples were tested with a UV–VIS–NIR spectrometer (Carry 5000 spectrophotometer, Varian, Seattle, USA) in the range of 190–1100 nm. Scanning electron microscopy (JSM-6390, JEOL, Tokyo, Japan) was used to observe the microstructure of samples. The average grain sizes of samples were measured by common linear intercept analysis from the SEM images. Optical microscopy (BX51 system microscope, Olympus, Tokyo, Japan) and EDS (SwiftED3000, Hitachi, Tokyo, Japan) were used to analyze the homogeneity of the resulting transparent samples.

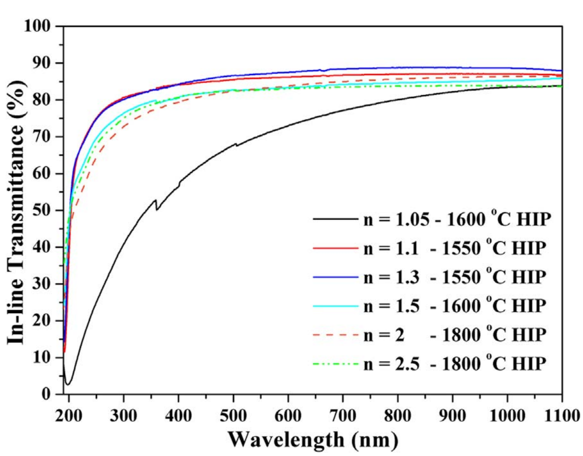

Fig. 1. In-line transmittances of the transparent alumina-rich spinel samples sintered under optimal conditions. (3 mm thick, $1.05 \le n \le 2.5$).

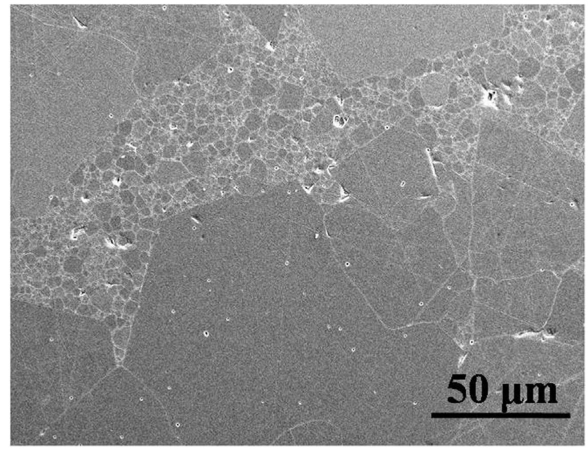

Fig. 2. Thermally etched surface of the transparent spinel sample with n = 1.05, which HIPed at 1600 °C.

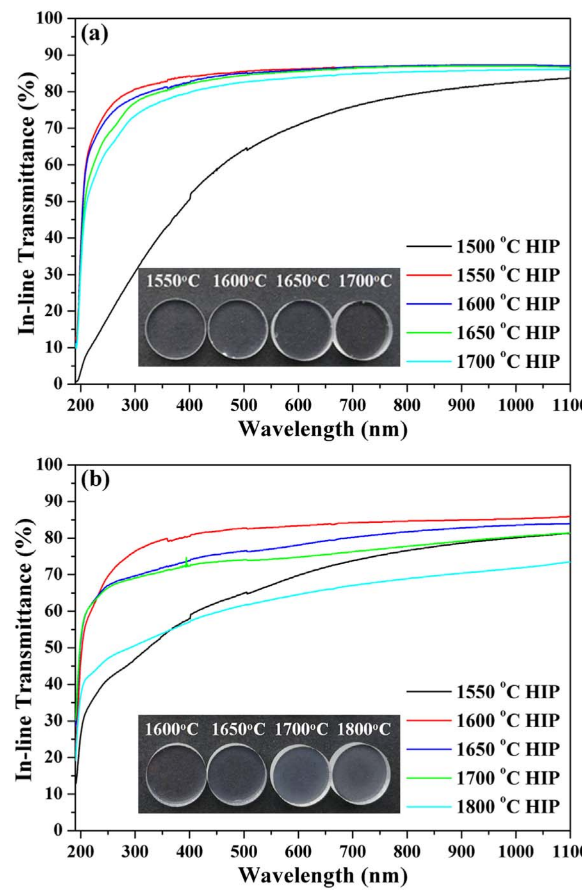

Fig. 3. In-line transmittances and pictures of the 3 mm thick transparent spinel samples with n = 1.1 and 1.5 (a: n = 1.1, b: n = 1.5).

3. Results and discussions

3.1. Effect of composition

Table 1 shows the effects of composition on the pre-sintering and HIP temperatures. We can see that the pre-sintering temperature of samples with n = 1.05–1.3 was 1500 °C, much higher than the phase