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Spectroscopic study of the discoloration of transparent $MgAl_2O_4$ spinel fabricated by spark-plasma-sintering (SPS) processing

Koji Morita,[a,*] Byung-Nam Kim,[a] Hidehiro Yoshida,[a] Keijiro Hiraga[a,b] and Yoshio Sakka[a]

[a] *Nano-Ceramics Center, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*
[b] *Materials Science and Engineering, Kitami Institute of Technology, 165 Koencho, Kitami, Hokkaido 090-8507, Japan*

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Abstract—Discoloration of spark-plasma-sintered spinel was investigated by spectroscopic techniques and transmission electron microscopy. The discoloration is explained by the combination of carbon contaminations and lattice defects (color centers), which are introduced in the spinel matrix depending on the spark-plasma-sintering conditions. For low heating rates of $\leqslant 10\ ^\circ C\ min^{-1}$, the trace carbonate CO_3 pre-existing in the starting powder remained as glassy carbon within the matrix, irrespective of the sintering temperature. For a high heating rate of $\geqslant 50\ ^\circ C\ min^{-1}$, additional carbon contamination occurred by evaporating the carbon phases from the carbon papers and graphite dies during the heating process, and tended to be enhanced by the increasing heating rate. The present data indicate that the color center (F^+-center) may be generated by the formation of oxygen vacancies, which are mainly introduced by dislocation motion depending on the sintering conditions. Since the rate of sintering, namely the deformation rate, increased with the heating rate, the concentration of the dislocation-related color centers increased with the heating rate, but decreased with the sintering temperature due to the bleaching of the oxygen vacancies. For the present spinel, the discoloration due to the carbon contamination and the formation of F^+-centers deteriorates the light transmission, depending on the sintering conditions.

Keywords: Spark plasma sintering (SPS); Densification; Optical transmission; Ceramic material; Spinels

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1. Introduction

Recently, instead of the well-known hot pressing or hot isostatic pressing (HIP) techniques, the spark-plasma-sintering (SPS) technique [1–4] has been widely utilized for the densification of various types of transparent oxide ceramics [5], such as α-Al_2O_3 [6–12], $MgAl_2O_4$ spinel [13–21], cubic (c-) and tetragonal (t-) ZrO_2 [22–27], MgO [28], Y_2O_3 [29–31] and yttrium aluminum garnet [32,33]. Fig. 1 shows an example of the in-line transmission T_{in} of a spinel, which was obtained by the SPS technique at the low and high heating rates of $\alpha = 10$ and $100\ ^\circ C\ min^{-1}$ [14–16]. The high heating rate has been regarded as the primary advantage of the SPS technique [1–4]. Regarding the transmission of the α-Al_2O_3 and spinel, however, a higher T_{in} value can be achieved by decreasing the heating rate α [6,14]; for the visible wavelength of $\lambda = 550$ nm, T_{in} of the spinel exhibits ~50% for $\alpha = 10\ ^\circ C\ min^{-1}$ though 0% for $\alpha = 100\ ^\circ C\ min^{-1}$ [14–16].

By reducing α to less than $10\ ^\circ C\ min^{-1}$, although the SPSed spinel attains a reasonable T_{in} value of ~50%, the value is much lower than the highest T_{in} (≈87%) obtained using the HIPing technique by Krell et al. [34–36] and the higher T_{in} (>70%) obtained using the SPS technique by Frage et al. [13] and Bonnefont et al. [21], especially in the visible wavelength range. Although the α-dependent T_{in} can be explained by the residual pore size and density [14–16], the T_{in} value limited to less than 50% cannot be explained only by the porosity. The limited T_{in} of the SPSed spinel is likely to be related to discoloration in addition to the porosity, as shown in the insert photo of Fig. 1. According to the previous studies by Krell et al. [34], Meir et al. [18], Bernard-Granger et al. [19], Casolco et al. [23] and Zhang et al. [27], the discoloration has been regarded as a possible source of the limited light transmission. Such a discoloration is known to be a typical phenomenon in the SPS processed oxide ceramics, such as Al_2O_3 [7], ZrO_2 [22] and spinels [18,19], and appears to be more pronounced in the SPS processing than in the HIPing [19]. Since the trace carbon and the point defects (oxygen vacancies) act as a possible light scattering and/or absorption source due to the formation of the color centers [19,38], the discoloration has often been related to the trace carbon contamination [18–20,39] and the oxygen vacancies generated under the vacuum conditions [7,22,27,38].

In order to fully utilize the SPS technique for industrial applications, especially for the optical industries, an understanding of the discoloration sources is necessary. The present study was therefore performed to examine the formation of carbon contamination and oxygen vacancies in the SPS processed transparent $MgAl_2O_4$ spinel. In this

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[*] Corresponding author; e-mail: MORITA.Koji@nims.go.jp

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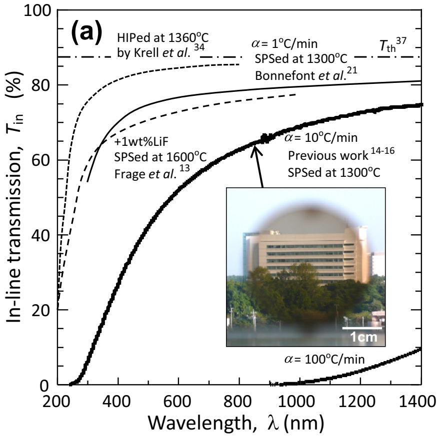

Fig. 1. In-line transmission T_{in} of spinels, which are SPSed at 1300 °C for 20 min and at $\alpha = 10$ °C min^{-1} and 100 °C min^{-1} [14–16], plotted as a function of wavelength λ. The theoretical transmission, T_{th}, expected for a single $MgAl_2O_4$ spinel crystal [37] is shown by the dash-dotted line. The light transmissions of a 1 wt.% LiF doped [13] (broken line) and undoped spinels [21] (thin solid line), which are SPSed at 1600 °C with $\alpha \approx 10$ °C min^{-1} for the former and at 1300 °C with $\alpha \approx 1$ °C min^{-1} for the latter, respectively, and a submicrograined spinel with $d \approx 0.4$ μm [34] (dotted line), which are HIPed at 1360 °C, are also shown for comparison. The data of the 1 wt.% LiF doped spinel with $w = 2.5$ mm [13], undoped spinel with $w = 2.3$ mm [21] and submicrograined spinel [34] with $w = 5$ mm were normalized at the same thickness of $w = 1.8$ mm using the following equation of $T_{in,1} = (1 - R)^2\,[T_{in,2}/(1 - R)^2]^{w1/w2}$, where R is the reflection loss ($R = 0.068$ [37]) and $T_{in,1}$ and $T_{in,2}$ are the in-line transmissions for the specimen thickness of w_1 and w_2, respectively. The insert photo is a transparent spinel disk with a 30 mm diameter obtained by SPS processing at $\alpha = 10$ °C min^{-1} and 1300 °C for a 20 min soak.

study, spectroscopic techniques were employed to examine possible sources of the discoloration.

2. Experimental procedures

A stoichiometric magnesium aluminate spinel ($MgAl_2O_4$) powder was consolidated using an SPS machine (SPS-1050, SPS Syntex Inc., Kawasaki, Japan) under vacuum. The details are described elsewhere [14–16].

Briefly, a high purity spinel powder (TSP-15, Taimei Chemical Co. Ltd, Tokyo, Japan) having a commercial purity of >99.97% and a particle size of 100–300 nm was used as the starting material. The as-received powder was placed in a graphite die with a 30 mm inner diameter. The powder and the die were separated by carbon papers. The graphite die was covered with a thermal insulator carbon felt to suppress any heat losses from the surface. The SPS was carried out at a uniaxial pressure of 80 MPa, a heating rates of $\alpha = 10$ °C min^{-1} and a temperature of $T = 1300$ °C for a 20 min soak time as the reference condition, which can attain higher transmissions [14]. In order to examine the effect of the SPS conditions on the carbon contamination and vacancy formation, sintering was also performed at 80 MPa for a 20 min soak time at several heating rates of $\alpha = 2$–100 °C min^{-1} and temperatures of $T = 1200$–1500 °C. The SPS processing was conducted by measuring the surface temperature of the graphite die using an optical pyrometer through a window made in the carbon felt. By this procedure, we fabricated a disk with a 30 mm diameter and 3 mm thickness.

For the optical and phase characterization, square plates with the dimensions of 12 × 12 mm were machined from the center of the SPSed circular disks. For the measurement of the in-line transmission T_{in}, both surfaces of the plates were carefully mirror-polished with diamond pastes and finished with 1 μm paste. During the polishing procedures, the thickness of the square plate was reduced to ~1.8 mm. T_{in} measurements were conducted using a double-beam spectrophotometer (SolidSpec-3700DUV, Shimazu Co. Ltd, Japan) equipped with an integrating sphere.

The phases present in the powder and the SPSed spinel were characterized by Raman spectroscopy (Horiba-Jobin-Yvon T64000, Horiba Co. Ltd, Japan) using an Ar laser ($\lambda = 514.5$ nm) operated at 0.1 W and by Fourier transform infrared (FT-IR) spectroscopy (FT/IR-6200; JASCO Co. Ltd, Japan). For the measurement of the bulk samples, the Raman spectrum was carefully taken from the inside after mechanically polishing the surface area. Each measurement was carried out at room temperature, the recording time was 40 s and the number of accumulations was 10. For the FT-IR measurements, the powder was diluted with KBr and analyzed by the diffuse reflectance infrared Fourier transform (DRIFT) technique. The lattice defects, such as the oxygen vacancies, were characterized by an electric spin resonance spectrometer (ESR: JES-FA100, JEOL Co. Ltd., Japan) at room temperature by operating at 1 mW. A rectangular rod with the size of ~1.8 × 2.5 × 20 mm, which was prepared from the center of the SPSed circular disks, was inserted into a quartz cell tube with a 5 mm inner diameter and placed in the resonant cavity of the spectrometer. The magnetic field was swept over the range of 326 ± 10 mT, with a sweep time of 15 min, a time constant of 0.3 s and the number of spectral accumulations = 2.

The microstructures were examined around the center of the circular disks using a transmission electron microscope (TEM). For the TEM observations, thin sheets with a thickness of ~500 μm were cut using a low speed diamond cutter, and mechanically polished to a thickness of ~100 μm, followed by further thinning using an Ar ion-milling

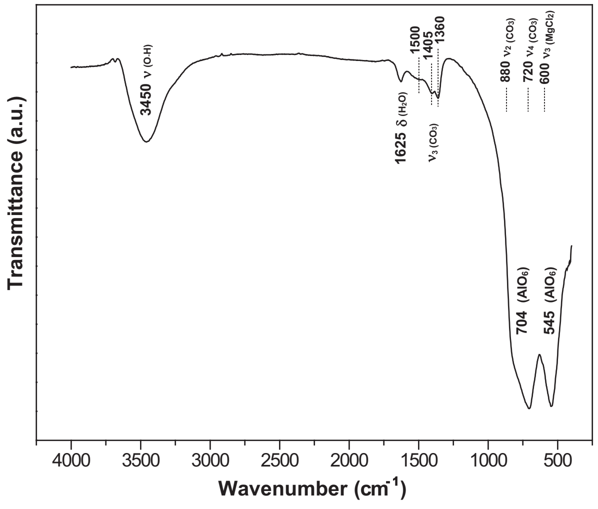

Fig. 2. FT-IR spectrum of the starting spinel powder in the region of 400–4000 cm^{-1}.