Fabrication of translucent MgO ceramics using nanopowders

Yi Fang*a, Dinesh Agrawala, Ganesh Skandanb, Mohit Jainb

aMaterials Research Institute, The Pennsylvania State University, 133 Materials Research Laboratory, University Park, PA 16802-4801, USA
bNanopowder Enterprises Inc., 120 Centennial Avenue, Piscataway, NJ 08854-3908, USA

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Abstract

Translucent MgO ceramics have been fabricated by hot-pressing using nanopowder of MgO containing 2–4% LiF as a fugitive additive. Thin circular discs were pressed uniaxially with the LiF-containing nanopowders. The hot-pressing was carried out either in Ar or in vacuum, holding at 1100 °C for 30 to 60 min at either 24 or 45 MPa. The samples were then annealed in air by either conventional or microwave processing. The annealed samples were highly dense and optically translucent.

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1. Introduction

Polycrystalline infrared-transparent MgO is a potential substitute for sapphire IR windows and protectors for sensors. However, fabrication of transparent MgO ceramics is a challenge due to the high sintering temperature required for full densification of MgO. Using a fine MgO powder containing silica and boron oxide, transparent MgO ceramic was fabricated by sintering at 1600 °C for 2 h in vacuum by Misawa et al. [1]. Hot isostatic pressing was used to fabricate solid high purity MgO bodies to 90–95% density with high translucency and a grain size of approximately 0.2 \( \mu \)m [2]. With suitable additives and using hot-pressing, the sinterability of MgO can be substantially enhanced. Rice [3] first reported the fabrication of the transparent MgO ceramics using pressure sintering with LiF additive and found that infrared optical transmission of the transparent polycrystalline MgO fabricated by this method can approach that of a single crystal. The mechanisms of sintering of MgO with additives have been reported earlier [4,5]. According to Hart and et al. [5], densification of MgO with LiF additions depends on the formation of a liquid phase that acts initially as a lubricant for the rearrangement of particles and later a material transport medium for pressure-enhanced liquid-phase sintering. The rate-controlling process in the latter stage is viscous flow of the liquid through grain-boundary channels. After the liquid is distributed as a uniformly thin film between the MgO grains, it can be removed by evaporation, and transparent polycrystalline specimens are produced. Sintering kinetics depends on the reactivity of the powder. Because of the high surface area, nanomaterials are much more reactive than the conventional powders; thus, the sintering behavior of the nanopowders is also quite different. For example, with a hydrothermally synthesized nanocrystalline hydroxyapatite powder, transparent apatite ceramics were fabricated at ambient pressure by Fang et al. [6] by microwave sintering for 5 min. Fang et al. [7] also reported the fabrication of transparent mullite ceramics using aerogels, which are nano-sized powder obtained by drying gels under hypercritical conditions. Fabrication of transparent ceramics of alumina, spinel, ALON, and AlN by microwave sintering was reported by Cheng et al. [8,9]. The present paper reports the fabrication of transparent MgO ceramics using nanopowders with a LiF additive.

2. Experimental procedure

2.1. Starting material

The starting powder used in this study was nanocrystalline MgO (hereafter nano-MgO) produced by Nanopowder Enterprises (Piscataway, NJ 08854) using 99.999% purity...
precursors. The carbon content of the nano-MgO was 0.11%. The powder had high surface area, fine crystallites, and a small aggregate size. LiF suspended in 2-propanol was added to the nano-MgO powder at 2% and 4% by weight (equal to 0.5% and 1% Li by weight), respectively.

2.2. Compaction

In order to obtain as high a green density as possible, 3 wt.% acryloid was used as binder. The binder was dissolved in acetone and then mixed with the MgO powder. Pellets of 12.7 mm diameter, 1 mm thick were pressed uniaxially at 525 MPa with the MgO nanopowders with 0, 2, and 4 wt.% LiF addition, respectively. Pellets of 50.8-mm diameter were also prepared using the same procedure. The green density of the as pressed pellets was 1.9 g/cm³ (53% of the theoretical). The binder was removed by firing the pellets in air at 550 °C for 2 h.

2.3. Hot-pressing

The pellets after binder-burnout were loaded in a graphite die for hot-pressing carried out in Ar atmosphere at 45 MPa, ramping at either 3 or 10 °C/min. The circular discs (one composition each) were separated with graphite spacers. Pressure was applied when the die was cold, the pressure being kept in the entire process, and released during cooling. The hot-pressing conditions are listed in Table 1.

2.4. Annealing

The surface of the as-hot pressed samples was black due to contamination from the graphite die. To remove the graphite and residual LiF, the samples had to be annealed. The samples were annealed conventionally or by microwave processing using the conditions listed in Table 2.

2.5. Characterization

The green powder was characterized for phase purity and crystallite size by powder X-ray diffraction (XRD,

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Hot-pressing conditions</th>
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<tbody>
<tr>
<td>Batch</td>
<td>LiF%</td>
</tr>
<tr>
<td>A</td>
<td>0; 2; 4</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Annealing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>Microwave in air</td>
</tr>
<tr>
<td>1000 °C × 2 h</td>
<td>1000 °C × 30 min</td>
</tr>
</tbody>
</table>

*a For samples made in hot-pressing batch C (Table 1) only.

Scintag Diffractometer, Sunnyvale, CA, Cu Ka) at a scan rate of 2°/min 2θ. Specific surface area was measured on a micrometric single point BET in nitrogen atmosphere. The morphology of the powder was studied by scanning electron microscopy (SEM, Hitachi S-3500N) and transmission electron microscopy (TEM, Hitachi). The density of the sintered samples was determined using Archimedes principle.
3. Results and discussion

3.1. Starting powder

Powder X-ray diffraction (Fig. 1) shows that the starting powder is pure crystalline periclase phase of MgO. The crystallite size was determined based on the powder XRD data using the Scherrer equation [10]

\[ B = \frac{0.9 \lambda}{(t \cos \theta)} \]

where \( \lambda \) is the wavelength of X-ray (1.5406 Å), \( B \) is full width at half maximum (FWHM) of the broadened diffraction line on the 2\( \theta \) scale (radians), and \( t \) is the diameter of the crystallites. The average value of the crystallites is 238 ± 21 Å, or 23.8 ± 2.1 nm. This indicates that the powder was truly nano-sized. The surface area of the starting powder was found to be 75 m\(^2\)/g. The SEM and TEM micrographs of the nanopowder are shown in Fig. 2. Accordingly, the aggregate size of the starting powder was about 200 nm.

3.2. Sintered samples

When separating from the graphite spacers, the as-hot-pressed samples in batch A (Table 1) broke into pieces whereas the samples in batches B and C remained intact. After annealing, the samples made from the LiF-containing nanopowders were translucent, whereas those without LiF were opaque. This indicates that LiF is the key factor for achieving transparency. Fig. 3 displays some of the as-annealed samples.

Figs. 4 and 5 show the influence of the original LiF content and annealing method on the grain growth of the transparent MgO. The influence of microwave annealing on grain size is shown in Table 3. First, in conventional annealing (1000 °C, 2 h), the increase of LiF in MgO from 2% to 4% increased the grain size from 1 to 3 μm. Secondly, microwave annealing at 1000 °C for 30 min at least doubled the grain size, from 1 to 2 μm for the MgO containing 2% LiF, and from 3 μm to more than 6 μm for the MgO containing 4% LiF. The secondary recrystalliza-
tion phenomenon is evidenced in the microwave-annealed sample starting with 4% LiF. As the grains grew, the smaller grains disappeared and the larger grains became even larger. The decrease in grain boundaries would help the removal of LiF.

The hot-pressed MgO is translucent and slightly cloudy, supposedly due to the trapped LiF. Considering that the hot-pressing time, 60 min, was short, extending the hot-pressing time might help further improve the transparency. EDS on the annealed samples did not reveal any LiF since the content was too small. The analysis of Li contents in an as-hot-pressed sample of batch C that had a transparent core and opaque edges showed a difference in Li content. The center had 400 ppm, while the edges had 2900 ppm of Li after hot-pressing. While the initial Li content was 1%, hot-pressing at 1100 °C for 5 min had 1700 ppm Li, and that hot-pressed at 1100 °C for 60 min had 400 ppm Li. In order to achieve fully dense MgO, the sintering temperature should not be too high, otherwise LiF would evaporate and leave the sample prematurely. Therefore, hot-pressing technique at lower temperature was used here.

4. Summary

Translucent MgO ceramics have been fabricated in this study by hot-pressing followed by conventional or microwave annealing of the specimens made of nano-sized high purity MgO powder containing 2–4% LiF as a fugitive additive. Without LiF, the samples sintered under identical conditions were opaque, indicating that the fugitive LiF played a key role in achieving the translucency. Presence of LiF as a liquid phase facilitated grain rearrangement and substantially enhanced mass diffusion, and thus densification of MgO. Complete removal of LiF after sintering is necessary to achieve transparent MgO besides full densification.

References


Table 3

<table>
<thead>
<tr>
<th>Annealing conditions</th>
<th>2% LiF</th>
<th>4% LiF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional: 1000 °C × 2 h</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Microwave: 1000 °C × 30 min</td>
<td>2</td>
<td>&gt;6</td>
</tr>
</tbody>
</table>

Fig. 5. SEM micrographs showing the as-sintered surface of the translucent MgO ceramics made from the nano-MgO powder containing 4% LiF by hot-pressing at 900 °C for 30 min then 1100 °C for 30 min, followed by (a) conventional annealing at 1000 °C for 2 h, and (b) microwave annealing at 1000 °C for 30 min.