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Journal of the European Ceramic Society 26 (2006) 2195–2198
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Fabrication of three-dimensional ceramic photonic crystals and their electromagnetic properties

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Abstract

Fabrication process for three-dimensional ceramic photonic crystals with a diamond structure was investigated. A diamond structure composed of epoxy lattice including SiO_2–TiO_2 ceramic particles at 10 vol.% was fabricated as a precursor by stereolithography. After burning off the epoxy resin in air, the diamond structure of SiO_2–TiO_2 was successfully sintered at 1400 °C for 2.5 h. The linear shrinkage ratio was 50%. Cracks were not found in the sintered diamond structure. Photonic bandgap was observed at around 19 GHz.

Keywords: SiO_2; TiO_2; Sintering; Functional applications; Photonic crystal

1. Introduction

Photonic crystals composed of dielectric lattices form bandgaps for electromagnetic waves.[1–6] These artificial crystals can totally reflect light or microwave at a wavelength comparable to the lattice spacings by Bragg deflection. The two different standing waves vibrating in air and dielectric matrix form higher and lower frequency bands in the first and second Brillouin zones, respectively. The bandgap width can be controlled by varying the structures, filling ratio, and dielectric constant of the lattice. Structural modifications by introducing defects or varying the lattice spacing can control the transmission of light or microwave as well.[7–10]

In the 1970s, multilayered photonic materials were developed by laminating a TiO_2 layer and a SiO_2 layer alternately, resulting in a one-dimensional photonic crystal.[11] After that, a variety of photonic crystals with one or two-dimensional structures were fabricated. In 1990, *Yablonovitch* and *Gmitter* first made three-dimensional photonic crystals called "Yablonovite" by drilling holes at different angles in a slab of dielectric medium and confirmed the formation of the bandgap.[12] The photonic crystal with a diamond structure can form the perfect bandgap, which opens for all crystal directions.[13–16] In our previous study, millimeter order epoxy lattices with a diamond structure were fabricated by using a rapid prototyping method of stereolithography.[17–20] TiO_2-based ceramic particles with high dielectric constant were dispersed into the epoxy lattice. These photonic crystals showed a perfect bandgap in the frequency range of about 16–19 GHz, which prohibited the microwave propagation in all directions.

However, achieving structures with pure ceramics of high dielectric constant has been a technological challenge up to now, even though the photonic crystals in the microwave range are regarded to be easily fabricated compared with those in the optical domain (at the micron scale). Ceramics offer resistance to high temperatures, so the ceramic crystals can control electromagnetic waves having high power. High dielectric constant of ceramics can lead to miniaturize photonic crystal devices because the incident wavelength is reduced to $1/\varepsilon^{1/2}$ in a medium with dielectric constant of ε. Photonic crystals of microwave or millimeter wave range can be applied to multifunctional filters, directional antennas, electromagnetic wave barriers, and other telecommunication devices. Following on our previous experimental work, we focused on fabricating ceramic photonic crystals of diamond structure made from TiO_2 powder mixed with SiO_2 by means of building up the precursor of the crystal form using stereolithography and successive sintering.

2. Experimental

The diamond structure was designed on a computer using a CAD program (Toyota Caelum Co. Ltd., Thinkdesign ver. 5.0). The designed structure was converted into a rapid prototyping

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0955-2219/$ – see front matter © 2006 Published by Elsevier Ltd.
doi:10.1016/j.jeurceramsoc.2005.09.079

format (STL file), sliced into a set of thin sections, and transferred to a stereolithographic machine (D-MEC Co. Ltd., Japan, SCS-300P). This machine forms a three-dimensional object layer-by-layer by scanning a UV laser of 355 nm wavelength over a liquid photopolymer epoxy resin. The thickness of each layer was 100 μm. The ceramic powders of SiO_2–TiO_2 with a particle size of about 10 μm were dispersed into the liquid resin to increase the dielectric constant of the lattice. The amount of ceramic powders was 10 vol.%. It was confirmed by density measurements that the ceramic content did not change after polymerization. The diamond structure is formed with < 100 > direction along the longest edge. It has a rectangular shape with the dimension of 60 mm × 60 mm × 30 mm. The TiO_2 coated with SiO_2 powder has a relatively high dielectric constant and easy sinterability. The TiO_2 particles were surrounded by the same weight of SiO_2. These composite particles have almost spherical shapes. In order to obtain ceramic photonic crystals, the diamond structures of SiO_2–TiO_2/resin formed as the precursor by the stereolithography were heated and the resin was burned out in air at 1100 °C for 1 h, then subjected to sintering at 1400 °C or 1500 °C for 2 h. The relative density of the sintered bodies was measured by Archimedes' method. The microstructure was observed by using SEM. The crystalline phases of the ceramic powders used and sintered bodies were characterized by means of X-ray powder diffraction. The attenuation of microwave transmission through the ceramic photonic crystals was measured in a metal cavity with Network Analyzer (Agilent Technologies, E8364B).[21]

3. Results and discussion

Fig. 1 shows a precursor of the diamond structure with SiO_2–TiO_2/epoxy and its sintered structure at 1400 °C after burning out epoxy. The linear shrinkage ratio is 50% in each axis. The volumetric shrinkage is about 88%. The relative density of the sintered structure at 1400 °C was 1.3 g/cm^3. When sintered at 1500 °C, it increased to 1.5 g/cm^3. These densities indicate the porous structure. Even the content of ceramic powders is only 10%, the precursor objects shrunk uniformly by the sintering treatment. The homogeneously dispersed powders in epoxy resin seem to assist the uniform shrinkage. However, it was necessary for uniform sintering to optimize the heating conditions of the precursor.

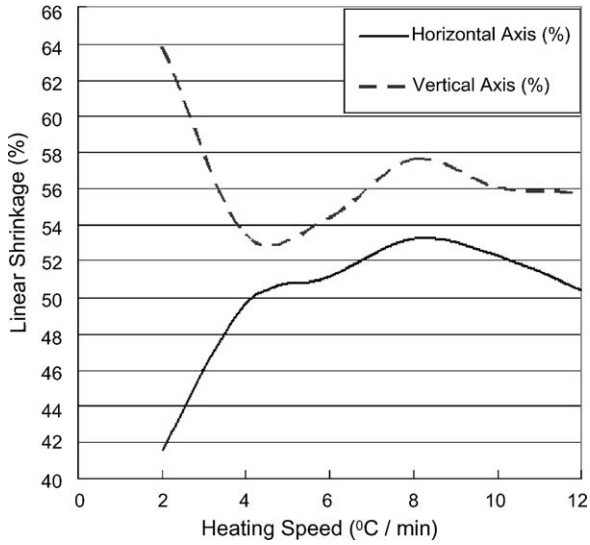

Fig. 2. The linear shrinkage ratios along the horizontal and vertical axes of the precursors as a function of heating ratio.

The precursors were heated in air with various heating ratios at 2, 4, 6, 8 and 10 °C/min up to 1100 °C. The diamond structure of SiO_2–TiO_2 bodies after removing epoxy was crumbly when heated at lower temperatures below 1100 °C. It was necessary to hold diamond structure at 1100 °C for 1 h in order to prevent crumbling. Fig. 2 shows the linear shrinkage ratios along the horizontal and vertical axes of the precursors as a function of heating ratio. When the precursor was heated at 2 °C/min, the shrinkage ratio along the vertical axis was extremely larger than that along the horizontal axis, and the diamond structure was crushed, because the vaporization of epoxy occurred before the adhesion of SiO_2–TiO_2 particles. When heated at 4–10 °C/min, it held almost uniform structures without crushing and breaking. The heating ratio at 8 °C/min was selected as an optimum condition in this time. It gave higher shrinkage ratios. The change of microstructure of the precursors was observed using SEM when heated at 8 °C/min to each temperature from 100 °C to 1500 °C with 100 °C step. There was no change in microstructure below 300 °C as seen in Fig. 3(a). The decomposition of epoxy started at about 400 °C and the color changed from gray to black. The SiO_2–TiO_2 particles coagulated partly at this temperature as seen in Fig. 3(b). The SiO_2–TiO_2 composite particle is composed of TiO_2 covered with amorphous SiO_2. The X-ray

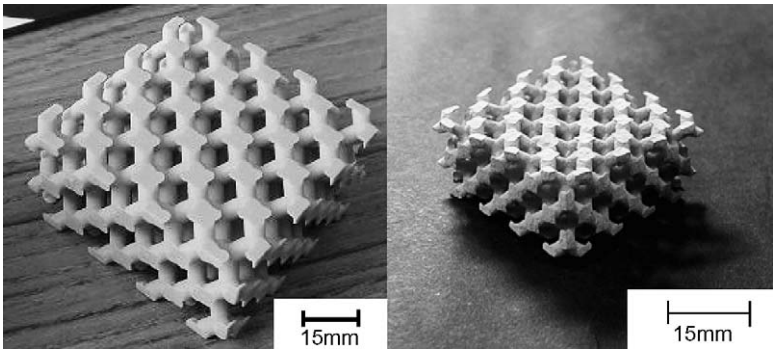

Fig. 1. A precursor of the diamond structure with SiO_2–TiO_2/epoxy (left) and its sintered structure at 1400 °C after burning out epoxy (right).

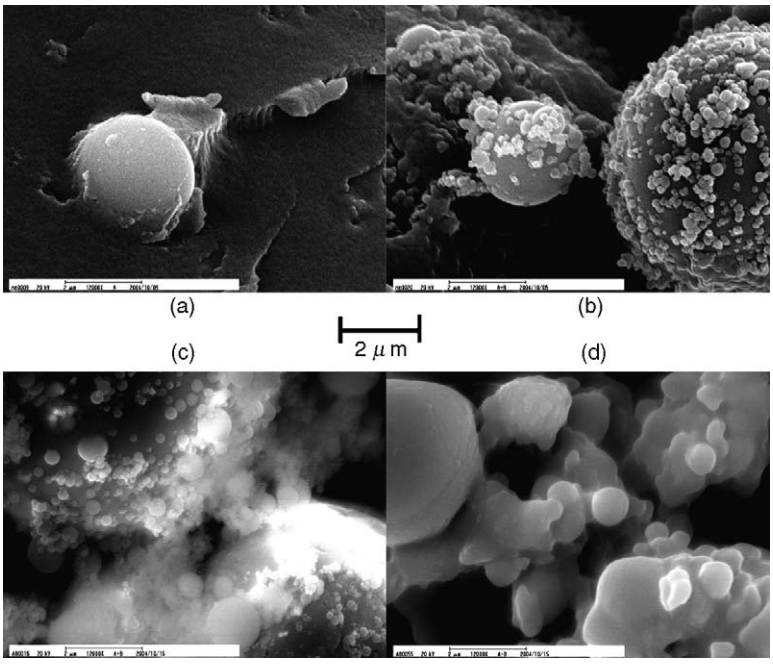

Fig. 3. Microstructure change depending on heating treatment: (a) 100 °C; (b) 400 °C; (c) 900 °C; and (d) 1400 °C.

powder diffraction showed that the composite powders consist of anatase phase of TiO_2 and amorpous SiO_2 with a minor phase of rutile. Fine particles precipitated on the surface at 400 °C may be crystalline silica. When heated at temperatures from 700 °C to 1000 °C, the epoxy is burn out and the color changed to white. The SiO_2–TiO_2 diamond structure was crumbly. The adhesion of SiO_2–TiO_2 particles was observed at 900 °C as seen in Fig. 3(c). The color changed to light blown at over 1100 °C. The network of SiO_2–TiO_2 particles was observed at over 1400 °C. The crystalline phases changed to rutile and crystoballite?

In electromagnetic measurement along the long edge direction (<100>) of the ceramic diamond structures sintered at 1400 °C and 1500 °C, the dips of the attenuation over −25 dB were observed at around 19 GHz as shown in Fig. 4. Of course, the bulk sample did not show such dips. These attenuations of transmission amplitude suggest the bandgap formation. The ceramic diamond structure sintered at 1500 °C had higher density than that sintered at 1400 °C, which may give a higher contrast of dielectric constant between the lattice and air resulting in the deep bandgap.

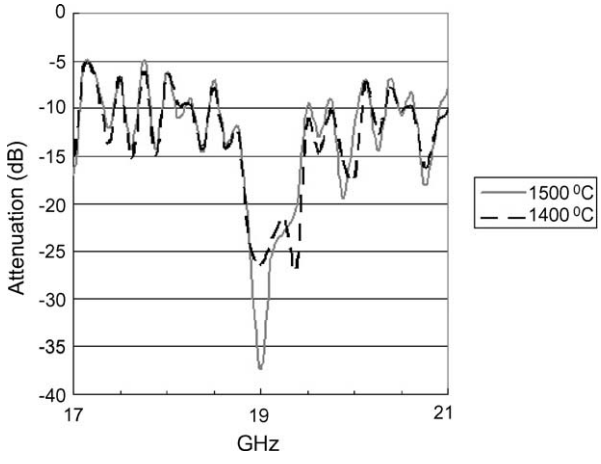

Fig. 4. Electromagnetic measurement of the ceramic diamond structures sintered at 1400 °C and 1500 °C.

4. Conclusions

Three-dimensional ceramic photonic crystals with a diamond structure were successfully fabricated. A diamond structure composed of epoxy lattice including SiO_2–TiO_2 ceramic particles at 10 vol.% was formed as a precursor by stereolithography. After burning off the epoxy resin in air, the diamond structure of SiO_2–TiO_2 could be sintered at around 1500 °C. The linear shrinkage ratio was 50%. Cracks were not found in the sintered diamond structure. The photonic bandgap was observed at around 19 GHz.

Acknowledgement

This work is partially supported by the grant for the 21st Century's COE program "Center of Excellence for Advanced Structural and Functional Materials Design" under the auspice of the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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