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Effect of two-step sintering on the microwave dielectric properties of $Zn_{1.8}SiO_{3.8}$ ceramics

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Abstract

The microwave dielectric properties of $Zn_{1.8}SiO_{3.8}$ ceramics were investigated as a function of sintering conditions. A single-phase willemite structure was confirmed for $Zn_{1.8}SiO_{3.8}$ ceramics prepared by single-step or two-step sintering. In the two-step sintering, the first step was for grain growth and the second step was for densification. The densification temperature selected was 1250 °C, which showed the maximum densification rate by dilatometry analysis. Using two-step sintering, the specimens sintered at 1400 °C for 5 min and held at 1250 °C for 4–12 h showed a lower quality factor (*Qf*) than the specimens sintered at 1350 °C for 5 min and held at 1250 °C for 4–12 h. This result could be attributed to the higher density of the latter group of specimens. For the specimen sintered at 1350 °C for 5 min and held at 1250 °C for 4 h (two-step sintering), the *Qf* value was higher (187,600 GHz) than that of the specimen sintered at 1350 °C for 4 h (single-step sintering). However, all specimens showed quite similar dielectric constant (*K*) and temperature coefficients of resonant frequency (*TCF*).

Keywords: C. Dielectric properties; Two-step sintering; Willemite; $Zn_{1.8}SiO_{3.8}$

1. Introduction

Dielectric materials applicable to components at microwave frequencies should have a high quality factor (*Qf*) for frequency selectivity, a low dielectric constant (*K*) for fast signal speed, and a near-zero temperature coefficient of resonant frequency (*TCF*) for thermal stability.

In recent years, a number of dielectric ceramics with low *K* and high *Qf* values have been investigated, such as Al_2O_3 [1], $MgAl_2O_4$ [2], $ZnAl_2O_4$ [3], and Mg_2SiO_4 [4]. In particular, Zn_2SiO_4 ceramic systems have been widely studied due to their high *Qf* values. Guo et al. [5] reported that Zn_2SiO_4 ceramics exhibited a low *K* value of 6.6, a high *Qf* value of 219,000 GHz, and a *TCF* value of −61 ppm/°C. Also, $Zn_{1.8}SiO_{3.8}$ ceramics showed improved microwave dielectric properties, with a *K* value of 6.6, a *Qf* value of 147,000 GHz, and a *TCF* value of −22 ppm/°C [6]. However, Zn_2SiO_4 ceramics with a low *Qf* value of approximately 35,000 GHz have also been reported [7,8], a difference that could be attributed to differences in the microstructural characteristics of the specimens.

A homogeneous microstructure with small grains was observed for the Zn_2SiO_4 ceramics with a high *Qf* value, whereas exaggerated grain growth was confirmed for the Zn_2SiO_4 ceramics with a low *Qf* value. From these results, the *Qf* value of Zn_2SiO_4 ceramics strongly depended on the microstructural characteristics of the specimens. Therefore, control of the microstructural characteristics of Zn_2SiO_4 ceramics should be investigated in order to obtain Zn_2SiO_4 ceramics with a high *Qf* value. The microstructural characteristics could be controlled by the addition of a dopant, the substitution of ions, and the sintering process [9,10]. In this study, control of the sintering process was employed in order to limit the formation of a secondary phase of Zn_2SiO_4, which could occur using the other methods.

There are several sintering processes capable of controlling the microstructural characteristics of ceramics, such as rapid-rate sintering [11], rate-controlled sintering [12], two-step sintering, and so on [13]. In particular, two-step sintering has

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been widely applied to many materials owing to its ability to effectively control the grain growth (the first step) and densification of ceramics (the second step). It is reported [13–17] that a homogeneous microstructure with small grains can be obtained by the two-step sintering process, which could be applied to improve the *Qf* value of Zn_2SiO_4 ceramics.

In this study, the microstructure characteristics and microwave dielectric properties of $Zn_{1.8}SiO_{3.8}$ ceramics sintered by two-step sintering were investigated as a function of the first-step temperature and the holding time at the second step.

2. Experimental procedure

High-purity (99.9%) oxide powders of ZnO and SiO_2 were used as the raw materials. The powders were weighed in the mole ratios of Zn_2SiO_4 and $Zn_{1.8}SiO_{3.8}$, and mixed in ethanol by ball milling for 24 h. The powders were calcined at 1150 °C for 3 h and then milled again for 24 h. The dried powders were pressed isostatically into 10-mm-diameter disks at 1500 kg/cm^2. Sintering of the pellets was carried out by the single-step or two-step sintering method. For the single-step sintering method, the heating rate was maintained at 3 °C/min, and the pressed pellets were sintered at 1350–1400 °C for 4 h. For the two-step sintering method, the pressed pellets were sintered at 1350–1400 °C for 5 min at a heating rate 3 °C/min and then rapidly cooled to a lower second-step temperature of 1250 °C at a heating rate 25 °C/min. The pressed pellets were then held at 1250 °C for 4, 8, and 12 h. The linear shrinkage data as a function of temperature was simultaneously recorded by a dilatometer (DIL 402C, NETZSCH, Germany).

The apparent densities of the sintered specimens were measured using the Archimedes method. The relative densities of the sintered specimens were obtained from the apparent density and the theoretical values. Powder X-ray diffraction analysis (XRD) (Model D/Max-3C, Rigaku, Japan) was used for the phase identification. The microstructures of the sintered specimens were observed using a scanning electron microscope (SEM) (JSM-6500F, JEOL, Japan). The chemical compositions of the sintered specimens were analysed by energy dispersive spectrometer (EDS) (JSM-6500F, JEOL, Japan).

The dielectric constant (*K*) and quality factor (*Qf*) of the sintered specimens were measured by the post-resonant method developed by Hakki and Coleman [18] using a network analyser. The temperature coefficient of resonant frequency (*TCF*) of the sintered specimens was measured by the cavity method [19] in the temperature range from 20 to 80 °C.

3. Results and discussion

3.1. Preparation of Zn_2SiO_4 ceramics and two-step sintering process

Complete interaction between SiO_2 and ZnO was difficult owing to the very stable structure of crystalline SiO_2, resulting in the formation of a ZnO secondary phase [20]. However,

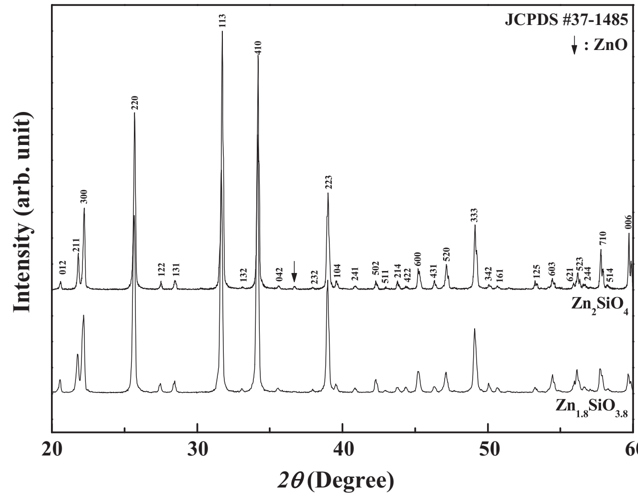

Fig. 1. X-ray diffraction patterns of $Zn_{1.8}SiO_{3.8}$ and Zn_2SiO_4 ceramics sintered at 1350 °C for 4 h.

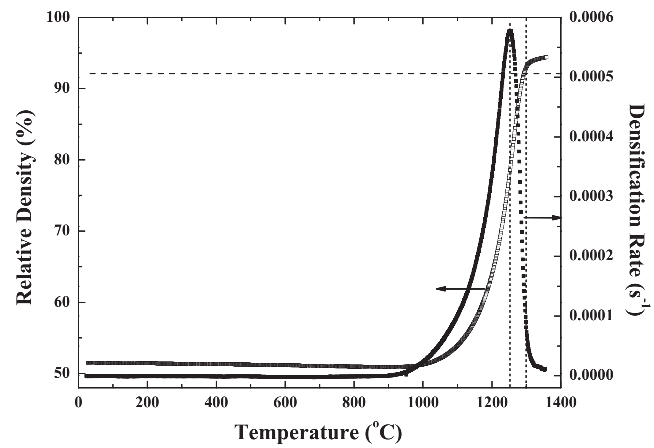

Fig. 2. Densification curves of the $Zn_{1.8}SiO_{3.8}$ ceramics.

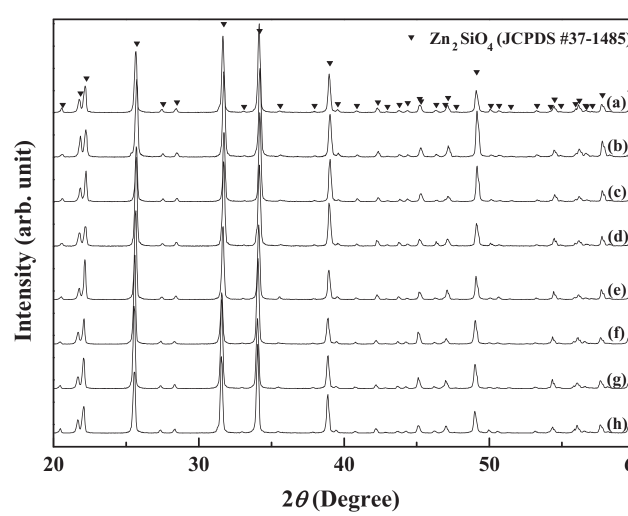

Fig. 3. X-ray diffraction patterns of $Zn_{1.8}SiO_{3.8}$ specimens sintered at (a) 1350 °C for 4 h, (b)1350 °C for 5 min and held at 1250 °C for 4 h, (c) 8 h, (d) 12 h, (e) 1400 °C for 4 h, (f) 1350 °C for 5 min and held at 1250 °C for 4 h, (g) 8 h, and (h) 12 h.