

# Sintering time dependence of microwave dielectric properties and crystal structure in $Y_2BaZnO_5$ ceramic

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## Abstract

The effect of sintering time on the microwave dielectric properties and crystal structure of the  $Y_2BaZnO_5$  ceramic was investigated in this study. The  $Y_2BaZnO_5$  ceramic was sintered at 1300 °C for 2–100 h in air; the significant variations in the dielectric constant and the temperature coefficient of resonant frequency of the  $Y_2BaZnO_5$  ceramic were not observed with the variations in the sintering time. Although the quality factor of the samples increased from 50,000 to 189,000 GHz with increasing the sintering times from 2 to 50 h, a decrease in the quality factor was recognized when the sample was sintered for 100 h at the temperature of 1300 °C. By refining the site occupancy of Zn in terms of the Rietveld analysis, it was found that the vaporization of Zn in amounts was at least 0.05 mol in the case of the  $Y_2BaZnO_5$  compound sintered for 100 h. Thus, the marked degradation of the quality factor of the sample sintered for 100 h is related to the vaporization of Zn, which depends on the variations in the sintering time.

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## 1. Introduction

In the microwave dielectric ceramics, an appropriate dielectric constant ( $\epsilon_r$ ), a high quality factor ( $Qf$ ) and a near zero temperature coefficient of resonant frequency ( $\tau_f$ ) are required for the commercial applications. Especially, for use in a wireless communication system at high frequency such as a satellite communication system, a low dielectric loss ( $\tan \delta = 1/Q$ ) is required; however, not many types of microwave dielectric ceramics with a high  $Qf$  value and a near zero  $\tau_f$  value have been developed to date.<sup>1,2</sup>

As for a recent work which focused on the development of new dielectric materials with high  $Qf$  in the  $Y_2O_3$ –BaO–MO ( $M = Cu$  and  $Zn$ ) system, the  $Y_2Ba(Cu_{1-x}Zn_x)O_5$  solid solutions which possess the green phase-type structure have been reported to be one of these high- $Q$  dielectric materials.<sup>3</sup> In the  $Y_2Ba(Cu_{1-x}Zn_x)O_5$  solid solutions, it was reported that the  $Qf$  values increased with increasing the composition  $x$ ; the grain growth of microstructure in the solid solutions was

closely related to an improvement in the  $Qf$  values.<sup>4</sup> As a result, the  $Qf$  value of 113,000 GHz was obtained at  $x = 1$ , i.e.,  $Y_2BaZnO_5$ . However, the effects of variations in the sintering time on the crystal structure and microwave dielectric properties have not been clarified to date; it is important to investigate the sintering time dependence on the microwave dielectric properties and crystal structure of the ceramics. Thus, the  $Y_2BaZnO_5$  ceramic was prepared by the solid-state reaction method and the sintering time dependence on the microwave dielectric properties of the  $Y_2BaZnO_5$  ceramic was investigated by the analysis of the crystal structure and the microstructure of the compound.

## 2. Experimental method

Samples of the  $Y_2BaZnO_5$  ceramic were prepared by using  $Y_2O_3$ ,  $BaCO_3$  and  $ZnO$  powders with 99.9% purity; these powders were calcined at 1000 °C for 20 h in air after mixing with acetone. The calcined powder was ground with a polyvinyl alcohol and then pressed into a pellet of 12 mm in diameter and 7 mm thick under a pressure of 100 MPa. Differ-

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ential thermal analysis (DTA) and thermogravimetry (TG) of the  $Y_2BaZnO_5$  ceramic after the calcination were performed in order to decide on an appropriate sintering temperature for the  $Y_2BaZnO_5$  ceramic. Subsequently, these pellets were sintered at  $1300^\circ\text{C}$  for 2–100 h in air on the basis of the results of DTA–TG analysis; the apparent density of the samples was measured in terms of the Archimedes method. The microwave dielectric properties of the samples were measured, using the Hakki and Coleman<sup>5</sup> method, modified by Kobayashi and Katoh.<sup>6</sup> As for the variations in the sintering time on the microstructures of the samples, the site occupancy of Zn was refined by using the Rietveld analysis<sup>7,8</sup> on the basis of  $Y_2Ba(Zn_{1-x}\square_x)O_5$  model. Moreover, the microstructure of the samples was investigated in terms of field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) analysis.

### 3. Results and discussion

Fig. 1 shows the DTA and TG curves of  $Y_2BaZnO_5$  ceramic after calcining at  $1000^\circ\text{C}$  for 20 h in air. Any remarkable variations in the DTA and TG curves were not observed in the temperature range of 20– $1300^\circ\text{C}$ ; however, at the temperature of approximately  $1330^\circ\text{C}$ , the endothermic and weight loss peaks of the  $Y_2BaZnO_5$  ceramic were observed, as shown in Fig. 1. The variations in the endothermic and weight loss peaks at  $1330^\circ\text{C}$  may be primarily related to the vaporization of Zn. Thus, the  $Y_2BaZnO_5$  ceramic in this study was fabricated at  $1300^\circ\text{C}$  in order to avoid the vaporization of Zn and obtain the high relative density.

From the XRPD patterns of  $Y_2BaZnO_5$  ceramic sintered at a temperature of  $1300^\circ\text{C}$  for 2–100 h in air; any impurity phase was not detected in the samples from their XRPD profiles. By using Rietveld analysis, the lattice parameters of  $Y_2BaZnO_5$  ceramic sintered for 2 h were refined in order to determine the theoretical density of the sample; the lattice parameters of the samples sintered for 2 h were  $a = 12.336(1) \text{ \AA}$ ,  $b = 5.7093(5) \text{ \AA}$  and  $c = 7.0713(6) \text{ \AA}$ , respectively; these lattice parameters refined in this study were similar values to those reported by Michel and Reveau.<sup>9</sup> Thus, the theoretical density of  $Y_2BaZnO_5$  ceramic was  $6.1412 \text{ g/cm}^3$ . Fig. 2

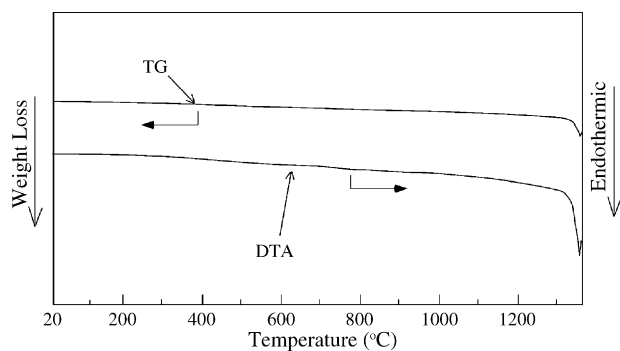


Fig. 1. DTA–TG curves of  $Y_2BaZnO_5$  powder after calcining at  $1000^\circ\text{C}$  for 20 h in air.

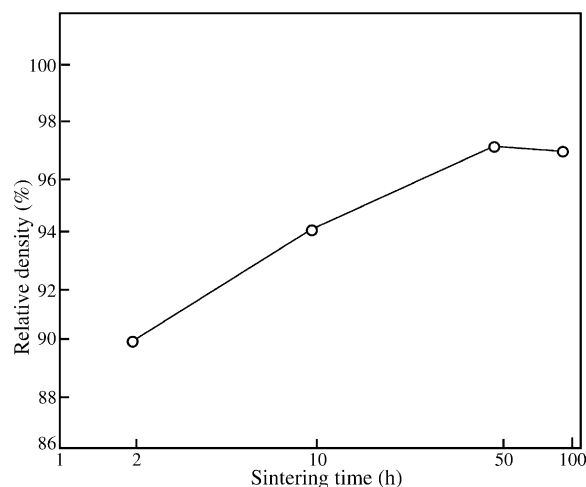


Fig. 2. Variation in apparent density of  $Y_2BaZnO_5$  ceramic sintered at  $1300^\circ\text{C}$  as a function of sintering time.

shows the variations in the relative density of the samples as a function of sintering time. When increasing the sintering times from 2 to 50 h, an increase in the relative density was recognized. In the sample sintered for 50 h, the relative density of 97% was obtained; however, the relative density of the samples sintered for 100 h was approximately constant in comparison with that of the sample sintered for 50 h. Thus, in this case, it is considered that the sintering time of 50 h is appropriate to obtain the highest relative density of  $Y_2BaZnO_5$  ceramic when the sintering temperature is  $1300^\circ\text{C}$ .

From the FE-SEM observation, the grain growth of microstructure in sample was observed with increasing the sintering times from 2 to 50 h; in the grains of these samples, the EDX results showed that the elements, such as Y, Ba, Zn and O were uniformly distributed on the basis of the stoichiometric composition of  $Y_2BaZnO_5$  compound. However, the grain growth of microstructure in the sample sintered for 100 h was not observed in comparison with that of the sample sintered for 50 h. Moreover, the deviation of the elements from the stoichiometric composition was observed from the results of EDX analysis; especially with the element Zn, the deviation from the stoichiometric composition was remarkable. From these results, it is considered that the variations in the sintering time may exert an influence on the vaporization of Zn, though the XRPD pattern of the sample sintered for 100 h did not perceptibly indicate the impurity phase as described above.

The relationship between the dielectric constant of  $Y_2BaZnO_5$  ceramic and the sintering time is shown in Fig. 3. The dielectric constants of the samples ranged from 14.1 to 15.3; at the sintering times from 2 to 50 h, the dielectric constant was slightly increased. However, these values were saturated at the sintering times from 50 to 100 h. Since the variations in the dielectric constant showed a similar tendency to those of the relative density, it was considered that the relative density, which arose from the variations in the sintering time improved the dielectric constant of  $Y_2BaZnO_5$  ceramic.

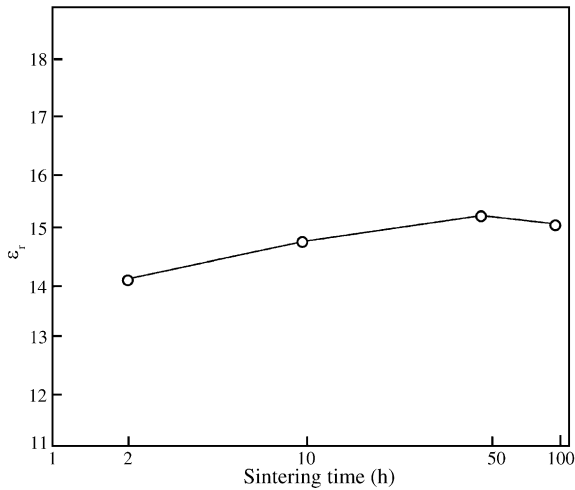


Fig. 3. Relationship between dielectric constant and sintering time of  $Y_2BaZnO_5$  ceramic sintered at  $1300\text{ }^\circ\text{C}$  in air.

As for the effect of the sintering time on the temperature coefficient of resonant frequency, the  $\tau_f$  value of approximately  $-45\text{ ppm}/^\circ\text{C}$  was obtained for each sample, as shown in Fig. 4; a effect of the sintering time on the  $\tau_f$  values of the  $Y_2BaZnO_5$  ceramic was not observed. Thus, it is considered that the sintering time is independent of the temperature coefficient of resonant frequency of the  $Y_2BaZnO_5$  ceramic in this case.

The significant variations in the  $Qf$  values of the  $Y_2BaZnO_5$  ceramic as a function of sintering time were observed in this study, and this sintering time dependence is shown in Fig. 5. With an increasing the sintering times from 2 to 50 h, the  $Qf$  values of the  $Y_2BaZnO_5$  ceramic extremely increased from 50,000 to 189,000 GHz; as a result, the maximum  $Qf$  value of 189,000 GHz was obtained when the sample was sintered for 50 h. The increase in the  $Qf$  value was closely related to the improvement in the relative density and the grain growth of microstructure in the samples, which de-

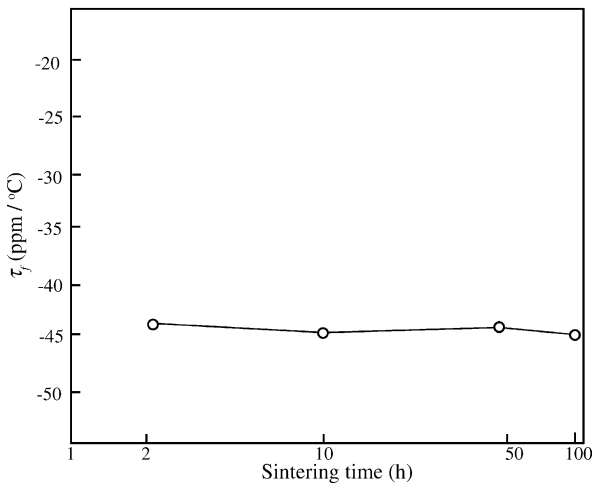


Fig. 4. Variations in temperature coefficient of resonant frequency of  $Y_2BaZnO_5$  ceramic sintered at  $1300\text{ }^\circ\text{C}$  for 2–100 h in air.

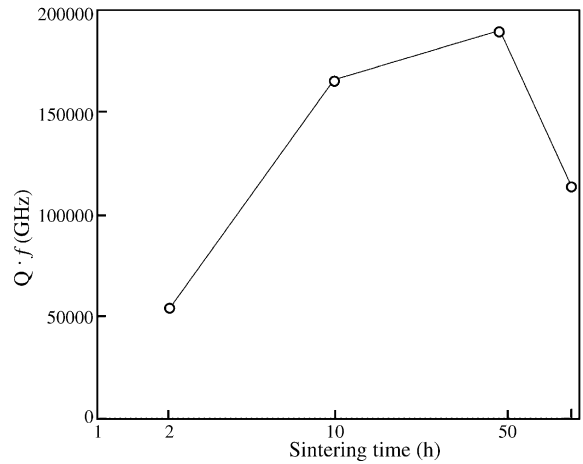


Fig. 5. Sintering time dependence of  $Qf$  value of  $Y_2BaZnO_5$  ceramic as a function of sintering time.

ended on the sintering time. In the sample sintered for 100 h, the  $Qf$  value was extremely decreased, though the relative density of the sample sintered for 100 h was similar to that of the sample sintered for 50 h, as described above. However, from the results of EDX analysis of the sample sintered for 100 h, the deviation from the stoichiometric composition was recognized, as described above; this result implies the possibility of the vaporization of Zn, which is closely related to the variations in the sintering time. Thus, in order to clarify the possibility of the vaporization of Zn caused by the variations in the sintering time, the site occupancy of Zn in the  $Y_2BaZnO_5$  ceramic was refined by using the Rietveld analysis. In this study, the site occupancy of Zn was refined on the basis of the  $Y_2Ba(Zn_{1-x}\square_x)O_5$  model; the goodness of fit indicator ( $s$ ) of the Rietveld analysis was determined as a function of  $x$ , as shown in Fig. 6. Then, the goodness of fit

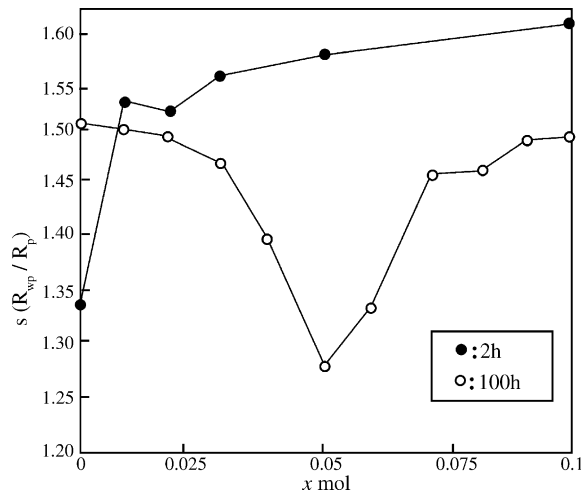


Fig. 6. Goodness of fit indicator in Rietveld analysis of  $Y_2Ba(Zn_{1-x}\square_x)O_5$  ceramic sintered for 2 and 100h.

indicator was given by the following equation:

$$s = \frac{R_{wp}}{R_p} \quad (1)$$

where  $R_{wp}$  and  $R_p$  represent the reliability factors for the weighted pattern and the pattern, respectively. The details on these reliability factor and goodness of the fit indicator are given elsewhere.<sup>10</sup> In the case of the samples sintered for 2–50 h, the smallest value of the goodness of fit indicator was obtained at  $x = 0$  as shown in Fig. 6; these results implied that the vaporization of Zn in these samples was not recognized. However, when sintered for 100 h, the  $s$  values of the sample were decreased with increasing the composition  $x$  from 0 to 0.05; subsequently the  $s$  value of 1.25 was obtained at  $x = 0.05$ . Therefore, from these results, it is considered that the model of  $Y_2BaZn_{0.95}□_{0.05}O_5$  is appropriate in the sample sintered for 100 h; the vaporization of Zn in amounts was suggested to be at least 0.05 mol. Thus, it was recognized that the decrease in the  $Qf$  value of the samples sintered for 100 h as described above, was attributed to the vaporization of Zn.

#### 4. Conclusions

The effects of the sintering time on the microwave dielectric properties and crystal structure of  $Y_2BaZnO_5$  ceramic were investigated in this study. The quality factors of the  $Y_2BaZnO_5$  ceramics sintered at 1300 °C for 2–50 h increased from 50,000 to 189,000 GHz. However, when the sample was sintered at 1300 °C for 100 h, the quality factor of the sample was 113,000 GHz. In the case of the samples sintered for 100 h, the deviation from the stoichiometric composition of

$Y_2BaZnO_5$  ceramic was recognized from the result of EDX analysis. Moreover, in the Rietveld analysis, the refined site occupancy of Zn was found to be 0.95; the effect of the sintering time on the Zn vaporization in the  $Y_2BaZnO_5$  ceramic was suggested. Thus, it is considered that the decrease in the  $Qf$  values of the samples by the variations in the sintering time is closely related with the Zn vaporization.

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