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□ for 2-100h 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 50000 to 189000 GHz with increasing the sintering times from 2 to 50h, a decrease in the quality factor was recognized when the sample was sintered for 100h at the temperature of 1300□. 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 0.05mol in the case of the Y_2BaZnO_5 compound sintered for 100h. Thus, the marked degradation of the quality factor of the sample sintered for 100h is related to the vaporization of Zn which depends on the variations in the sintering time.

Keywords: Powders-solid state reaction, Sintering, X-ray method, Electron microscopy, Dielectric property

Introduction

In the microwave dielectric ceramics, an appropriate dielectric constant (ε_r), a high quality factor (Q□f) and a near zero temperature coefficient of resonant frequency (τ_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, the many types of microwave dielectric ceramics with a high Q□f value and a near zeroτ_f value have not been developed to date[1,2].

As for a recent work which focused on the development of new dielectric materials with high $Q\square f$ 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[3]. In the $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions, it was reported that the $Q\square f$ values increased with increasing the composition x; the grain growth of microstructure in the solid solutions was closely related to an improvement in the $Q\square f$ values[4]. As a result, the $Q\square f$ value of 113000GHz 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.

Experimental method

Samples of the Y_2BaZnO_5 ceramic was prepared by using Y_2O_3, $BaCO_3$ and ZnO powders with 99.9% purity; these powders were calcined at 1000□ for 20h in air after mixing with acetone. The calcined powder was ground with a polyvinyl alcohol and then pressed into a pellet of 12mm in diameter and 7mm thick under a pressure of 100 MPa. Differential 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□ for 2-100h 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 method [5] modified by Kobayashi *et al.*[6]. 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[7,8] 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.

Results and discussion

Figure 1 shows the DTA and TG curves of Y_2BaZnO_5 ceramic after calcining at 1000□ for 20h in air. Any remarkable variations in the DTA and TG curves were not observed in the temperature range of 20°-1300□; however, at the temperature of approximately 1330□, 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□ may be primarily related to the vaporization of Zn. Thus, the Y_2BaZnO_5 ceramic in this study was fabricated at 1300□ in order to avoid the vaporization of Zn and obtain the high relative density.

Figure 2 shows the XRPD patterns of Y_2BaZnO_5 ceramic sintered at a temperature of 1300□ for 2-100h 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 2h was refined in order to determine the theoretical density of the sample; the lattice parameters of the samples sintered for 2h were a=12.336(1)□, b=5.7093(5)□and c=7.0713(6)□, respectively; these lattice parameters refined in this study were similar values to those reported by Michel *et al*[9]. Thus, the theoretical density of Y_2BaZnO_5 ceramic was 6.1412 g/cm^3. Figure 3 shows the variations in the relative density of the samples as a function of sintering time. When increasing the sintering times from 2 to 50h, an increase in the relative density was recognized. In the sample sintered for 50h, the relative density of 97% was obtained; however, the relative density of the samples sintered for 100h was approximately constant in comparison with that of the sample sintered for 50h. Thus, in this case, it is considered that the sintering time of 50h is appropriate to obtain the highest relative density of Y_2BaZnO_5 ceramic when the sintering temperature is 1300□.

The influences of the sintering time on the morphological changes in the Y_2BaZnO_5 ceramic are shown in Fig.4. The grain growth of microstructure in sample was observed with an increasing the sintering times from 2 to 50h; 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 100h was not observed in comparison with that of the sample sintered for 50h. 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 100h 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 was shown in Fig.5. The dielectric constants of the samples ranged from 14.1 to 15.3; at the sintering times from 2 to 50h, the dielectric constant was slightly increased. However, these values were saturated at the sintering times from 50 to 100h. 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.

As for the effect of the sintering time on the temperature coefficient of resonant frequency, the τ_f value of approximately –45ppm/□ was obtained for each sample as shown in Fig.6; a effect of the sintering time on theτ_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 $Q \times f$ 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. 7. With an increasing the sintering times from 2 to 50h, the $Q \times f$ values of the Y_2BaZnO_5 ceramic extremely increased from 50000 to 189000 GHz; as a result, the maximum $Q \times f$ value of 189000 GHz was obtained when the sample was sintered for 50h. The increase in the $Q \times f$ value was closely related to the improvement in the relative density and the grain growth of microstructure in the samples which depended on the sintering time. In the sample sintered for 100h, the $Q \times f$ value was extremely decreased, though the relative density of the sample sintered for 100h was similar to that of the

sample sintered for 50h as described above. However, from the results of EDX analysis of the sample sintered for 100h, 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.8. Then, the goodness of fit indicator was given by the following equation:

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

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[10]. In the case of the samples sintered for 2-50h, the smallest value of the goodness of fit indicator was obtained at x=0 as shown in Fig.8; these results implied that the vaporization of Zn in these samples was not recognized. However, when sintered for 100h, 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 $Y_2BaZn_{0.95}\square_{0.05}O_5$ is appropriate in the sample sintered for 100h; the vaporization of Zn in amounts was suggested to be at least 0.05 mol. Thus, it was recognized that the decrease in the $Q\square f$ value of the samples sintered for 100h as described above was attributed to the vaporization of Zn.

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□ for 2-50h increased from 50000 to 189000 GHz. However, when the sample was sintered at 1300□ for 100h, the quality factor of the sample was 113000 GHz. From FE-SEM and EDX results, the grain growth of microstructure in the samples was observed with increasing the

sintering times from 2 to 50h; the increase in the $Q \times f$ values of the samples as described above is related to the grain growth of microstructure in the samples. In the case of the samples sintered for 100h, 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 $Q \times f$ values of the samples by the variations in the sintering time is closely related with the Zn vaporization.

References

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Figure Captions

Fig.1 DTA-TG curves of Y_2BaZnO_5 powder after calcining at 1000□ for 20 h in air.

Fig.2 XRPD patterns of Y_2BaZnO_5 ceramic sintered at 1300□ for 2-100h in air.

Fig.3 Variation in apparent density of Y_2BaZnO_5 ceramic sintered at 1300□ as a function of sintering time.

Fig.4 FE-SEM photographs of Y_2BaCuO_5 ceramic sintered at 1300□ for 2-100h in air.

Fig.5 Relationship between dielectric constant and sintering time of Y_2BaZnO_5 ceramic sintered at 1300□ in air.

Fig.6 Variations in temperature coefficient of resonant frequency of Y_2BaZnO_5 ceramic sintered at 1300□ for 2-100h in air.

Fig.7 Sintering time dependence of Q□f value of Y_2BaZnO_5 ceramic as a function of sintering time.

Fig.8 Goodness of fit indicator in Rietveld analysis of $Y_2Ba(Zn_{1-x}□_x)O_5$ ceramic sintered for 2 and 50h.

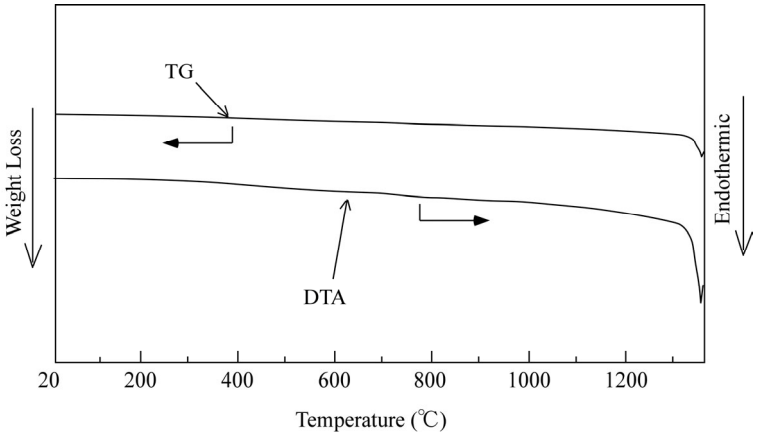

TG
DTA
Weight Loss
Endothermic
20
200
400
600
800
1000
1200
Temperature (℃)

Fig.1

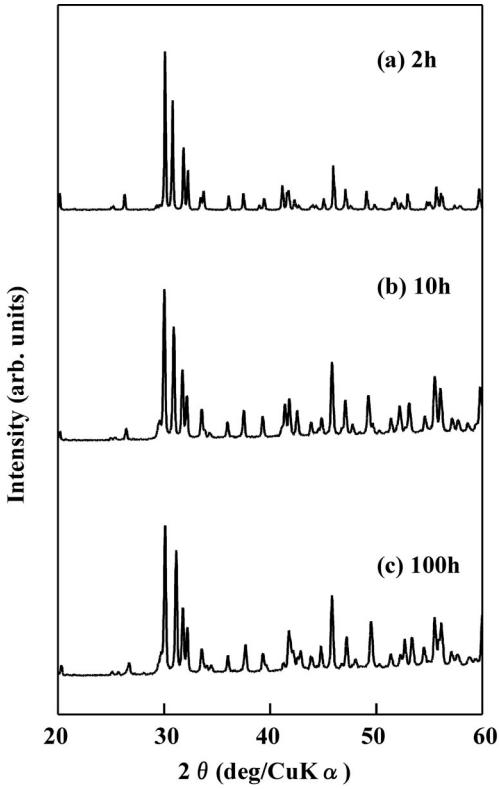


Fig.2

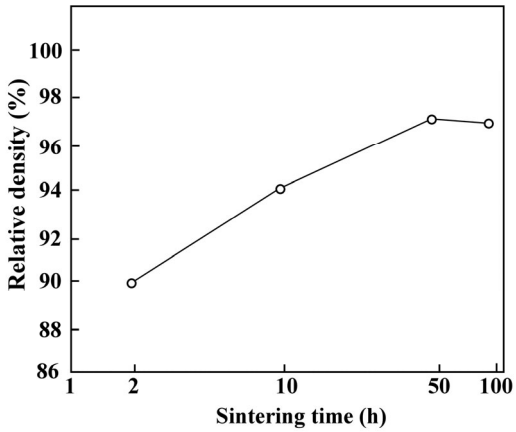
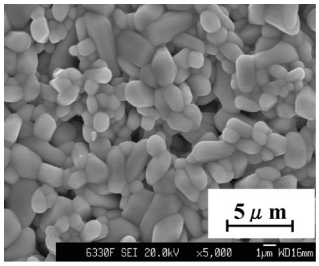
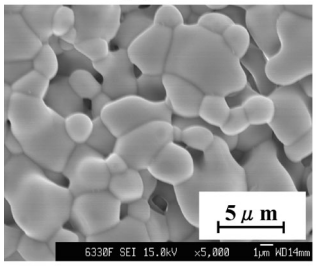

Relative density (%)
100
98
96
94
92
90
88
86
1
2
10
50
100
Sintering time (h)

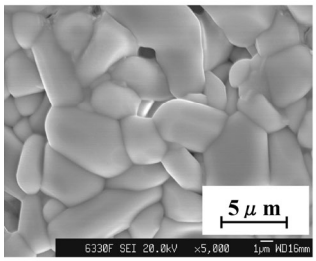
Fig.3



(a) 2 h



(b) 50h



(c) 100 h

Fig.4

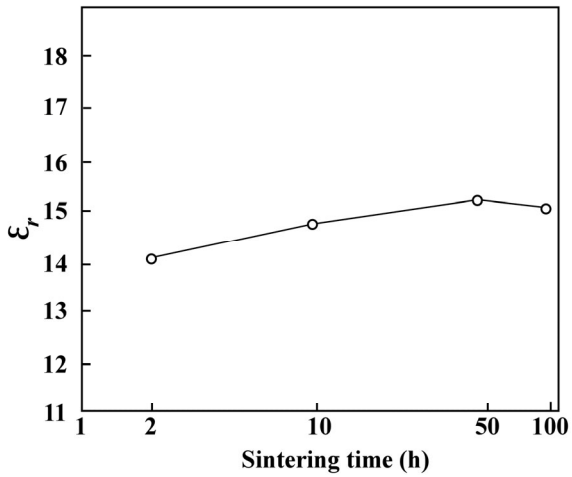

18
17
16
15
14
13
12
11
ε_r
1
2
10
50
100
Sintering time (h)

Fig.5

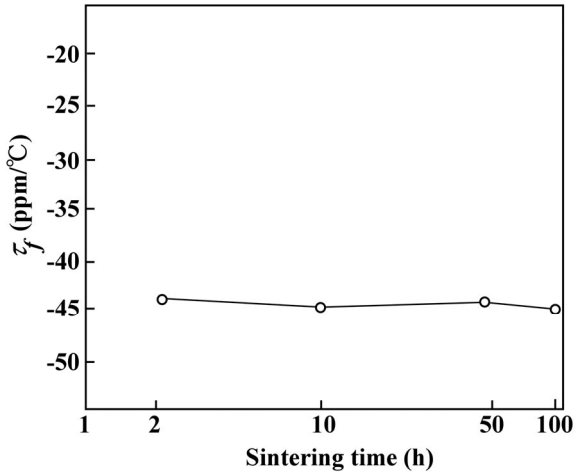


Fig.6

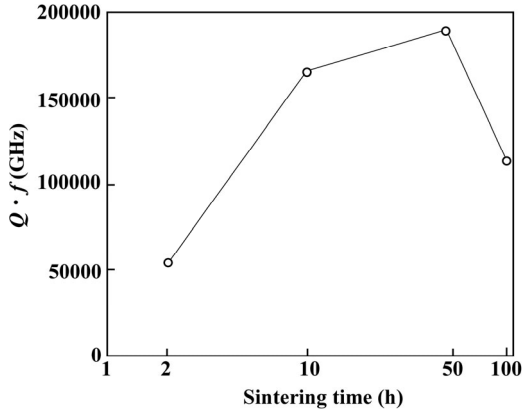

200000
150000
100000
50000
0
Q · f (GHz)
1
2
10
50
100
Sintering time (h)

Fig.7

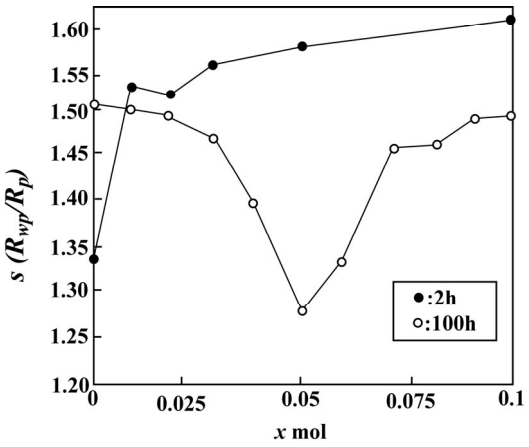

1.60
1.55
1.50
1.45
1.40
1.35
1.30
1.25
1.20
s (Rwp/Rp)
0
0.025
0.05
0.075
0.1
x mol
●:2h
○:100h

Fig.8