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Effects of Dy substitution for Y on microwave dielectric properties of High-Q R_2O_3-BaO-ZnO (R = Y and Dy) system

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Abstract

The $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions were synthesized and studied, this paper focused on the relationships between the crystal structure and the improvements in temperature coefficients of resonant frequency (τ_f) caused by Dy substitution for Y. The dielectric constants (ε_r) were slightly increased with increasing the composition x; this result was attributed to the increase in the ionic polarizabilities caused by Dy substitution for Y. The quality factors ($Q{\cdot}f$) were extremely decreased from 165,500 to 29,600 GHz with increasing the composition x. The τ_f values were increased from −44.5 to −1.6 ppm/°C, whereas the temperature coefficients of the dielectric constant (τ_ε) varied from positive to negative values.

Keywords: C. Dielectric properties; B. X-ray method; C. Thermal expansion

1. Introduction

Most recent researches in high-Q ceramics have focused on the development of new dielectric materials for substrates in high-temperature superconducting (HTSC) microwave devices and in microwave dielectric resonators at high frequencies.[1–3] In HTSC devices, the dielectric loss ($\tan\delta = 1/Q$) of the substrate materials must be lower than 10^{-4} at the microwave frequency because the conduction loss of a superconductor such as $YBa_2Cu_3O_{7-x}$(YBCO) is negligibly small.[4] The substrate requires a low dielectric constant, ideally less than 10, to be suitable for the integrated circuit designs. Watanabe et al.[5] reported that Y_2BaZnO_5, which has the crystal structure has an orthorhombic structure (S.G. *Pnma*) with $a = 12.324(4)$Å, $b = 5.706(2)$Å and $c = 7.068(3)$Å, is one of the high-Q materials. These properties of Y_2BaZnO_5 are considered to be suitable use as a dielectric resonator at high frequency or in HTSC devices. However, the temperature coefficient of resonant frequency (τ_f) of the Y_2BaZnO_5 compound has a large negative value and an improvement inτ_f is necessary for the application as a resonator. Moreover, the improvements in τ_f by Dy substitution for Y in Y_2BaCuO_5 compound were found in previous work.[6] Thus, the $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions were synthesized and the effect of Dy substitution for Y on the microwave dielectric properties were investigated in this study.

2. Experimental method

The starting materials were high purity (99.9%) Y_2O_3, Dy_2O_3, $BaCO_3$ and ZnO powders. The mixed materials were calcined at 1050 °C for 20 h in air and milled with 5.0wt% of PVA (polyvinyl alcohol). Pellets 12 mm in diameter and 7 mm in thickness were uniaxially pressed under 100 MPa, and were then sintered at temperatures ranging from 1270 to 1320 °C for 10 h in air. The dielectric constant (ε_r) and the quality factor ($Q{\cdot}f$) of the samples were evaluated by using Hakki and Coleman's method,[7] and the temperature coefficients of resonant frequency (τ_f) were determined from the resonant frequency at 20 and 80 °C. Moreover, X-ray powder diffraction (XRPD) was used to characterize the synthesized phases and the lattice parameters measured at 20 and 80 °C of the samples were refined by using the Rietveld method.[8,9] The thermal expansion coefficients (α_l) of the samples were estimated from the refined lattice parameters at 20 and 80 °C in order to clarify the

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relationships between the τ_f values and the temperature coefficients of dielectric constant (τ_ε). The microstructure of the samples was also investigated by using field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

From the results of XRPD as shown in Fig. 1, it is found that no impurity phase is produced in the entire composition range. Diffraction peak shifts of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions to lower angle of 2θ are observed with increasing composition x. These shifts of the peak to lower angles suggest an increase in the lattice parameters caused by the Dy substitution for Y. The lattice parameters of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions are linearly increased with increasing the composition x, as shown in Fig. 2. These variations in the lattice parameters satisfy Vegard's rule and are attributed to the difference in the ionic radii between Y^{3+} (0.96Å) and Dy^{3+} (0.97Å) ions[10] when the coordination number (C.N.) is seven. Moreover, the average R-O (R = Y and Dy) distances in the R_2O_{11} polyhedra increased with increasing the composition x as shown in Fig. 3, suggesting that the expansion of the volume of the polyhedra is caused by the Dy substitution for Y.

Fig. 4 shows the thermal expansion coefficient (α_l) of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions determined from the lattice parameters refined at 20 and 80 °C, and the details on these values are listed in Table 1. The goodness of fit indicator (s) in the Rietveld analysis ranged from 1.3 to 1.9 in this study. The thermal expansion coefficients of the ceramics, in general, are known to be less than 20 ppm/°C.[11] The α_l values of the samples are almost independent of x as shown in Fig. 4.

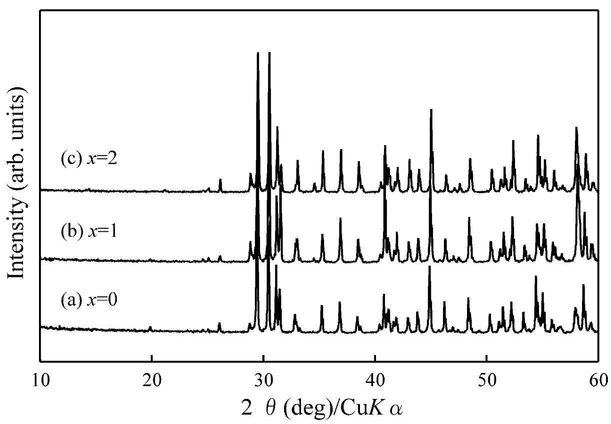

Fig. 1. XRPD patterns of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions at x = 0,1 and 2.

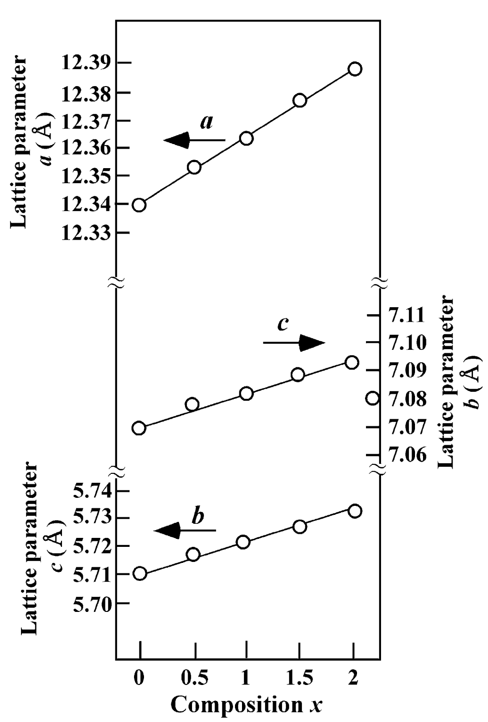

Fig. 2. Effects of Dy substitution for Y on the variations in the lattice parameters of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions as a function of composition x.

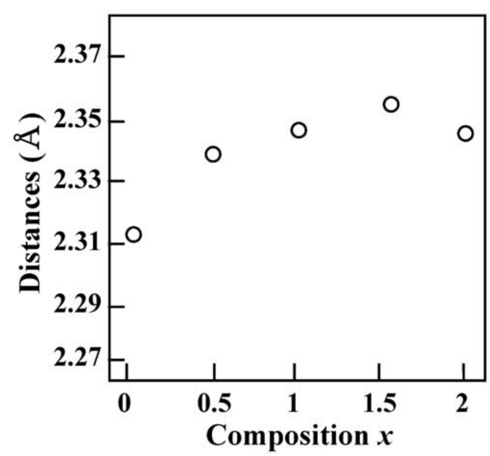

Fig. 3. Variations in the R–O (R = Dy and Y) distances in the R_2O_{11} polyhedron.

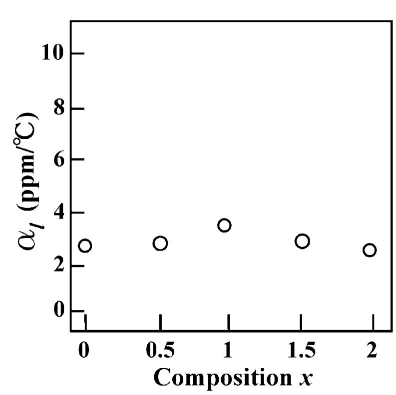

Fig. 4. Thermal expansion coefficient (α_l) of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions estimated from 20 and 80 °C.

The effects of Dy substitution for Y on the dielectric constant and the quality factor of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions are shown in Fig. 5 as a function of composition x; the details on these properties are summarized in Table 2. The ε_r values of solid solutions were slightly increased from 16.1 ($x=0$) to 17.1 ($x=2$). In the microwave region, the dielectric constants of ceramics are known to be affected by the intrinsic ionic polarizabilities (α). According to the ionic polarizabilities of cations reported by Shannon,[12] the value of the ionic polarizability of trivalent Dy ($\alpha_{Dy}^{3+}=4.07$ Å^3) is higher than that of trivalent Y ($\alpha_{Y}^{3+}=3.81$ Å^3). Thus, when increaseing the composition x, we expect an increase in the ionic polarizabilities of the samples. This result is considered to induce the increase in the dielectric constant as shown in Fig. 5. Moreover, the linear increase in the dielectric constants with increasing the ionic polarizabilities of R^{3+} ions (R=Sm, Eu, Gd, Dy, Ho, Er and Tm) was found for R_2O_3-BaO-CuO systems in previous work.[6]

The $Q{\cdot}f$ values of the solid solution are drastically decreased from 165584 to 29669 GHz as shown in Fig. 5. It was reported that the $Q{\cdot}f$ values of microwave dielectric ceramics are affected by defect concentration, impurities, grain size and porosity[13]; therefore, this decrease in the $Q{\cdot}f$ values of the solid solutions may depend on the morphological changes in the samples. However, the significant variations in the microstructure were not observed. In addition, the constituent elements, such as Y, Dy, Ba, Zn were uniformly distributed in the grains, as revealed by the energy dispersive X-ray (EDX) analysis. Thus, the decrease in the $Q{\cdot}f$ values may depend on the crystal structure reported in previous work.[14]

The temperature coefficients of resonant frequency varied from −44.5 to −1.6 ppm/°C as shown in Fig. 6. The τ_f value of dielectric ceramics, in general, is known to be related to the variations in the temperature coefficient of dielectric constant and thermal expansion coefficient (α_l) of the ceramics, by the following equation:

$$\tau_f = -\left(\frac{\tau_\varepsilon}{2} + \alpha_l\right) \quad (1)$$

where the α_l values, which is shown in Fig. 4, of the samples were estimated from the refined lattice parameters at 20 and 80 °C. The temperature coefficients of the dielectric constant determined by using Eq. (1) are shown in Fig. 6. The τ_ε values varied from positive to negative value depending on the composition x. Thus, it was found that as Dy substitution for Y in $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions increases it causes a the linear change in τ_ε which ranges from 83 to −1 ppm/°C and this variation plays an important role in controlling the

Table 1
Lattice parameters of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions at 20 and 80 °C

Temp. (°C)	Composition x	Lattice parameters		
		a (Å)	b (Å)	c (Å)
20	0	12.3415(3)	5.7112(1)	7.0725(2)
	0.5	12.3532(7)	5.7159(2)	7.0802(3)
	1	12.3636(10)	5.7215(4)	7.0834(6)
	1.5	12.3766(10)	5.7262(4)	7.0884(5)
	2	12.3885(5)	5.7322(2)	7.0943(3)
80	0	12.3438(4)	5.7121(2)	7.0735(2)
	0.5	12.3558(5)	5.7173(2)	7.0803(2)
	1	12.3664(8)	5.7231(4)	7.0846(5)
	1.5	12.3783(10)	5.7269(4)	7.0899(5)
	2	12.3897(5)	5.7329(2)	7.0960(3)

Table 2
Microwave dielectric properties of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions

Composition x	f (GHz)	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
0	10.081	16.1	165 584	−44.5
0.5	10.065	16.4	64 231	−31.4
1	10.262	16.5	56 601	−21.1
1.5	10.254	16.4	42 363	−11.4
2	9.932	17.2	29 669	−1.7

f: resonant frequency.ε_r: dielectric constant.$Q{\cdot}f$: quality factor.τ_f: tempereture coefficient of resonant frequency.

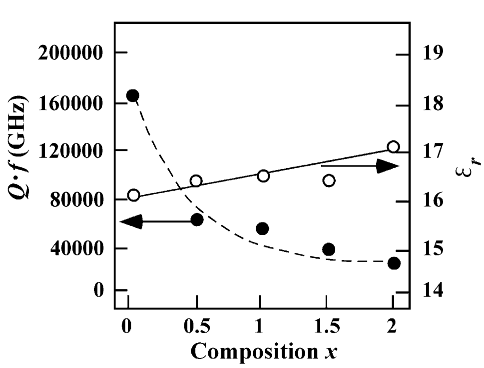

Fig. 5. Dielectric constants (ε_r) and quality factors ($Q{\cdot}f$) of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions.

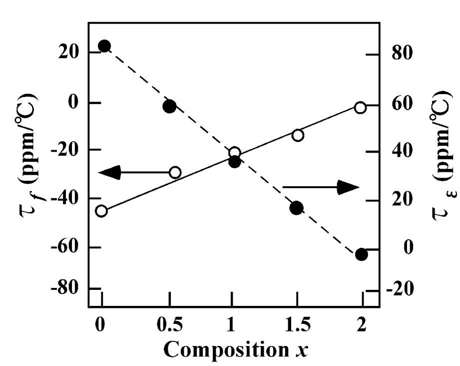

Fig. 6. Temperature coefficients of resonant frequency (τ_f) and temperature coefficients of dielectric constant (τ_ε) of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions.

τ_f values of this system. As a result, the optimum τ_f value was obtained for the sample at $x=2$ (τ_f $=-1.7$ ppm/°C).

4. Conclusion

The microwave dielectric properties and crystal structure of $(Y_{2-x}Dy_x)BaZnO_5$ solid solutions were investigated in this study. All the lattice parameters of the solid solutions were linearly increased by the Dy substitution for Y and the thermal expansion coefficients, which were estimated from the lattice parameters refined at 20 and 80 °C, were almost constant over the whole composition range. The slight increase in the dielectric constants, ranging from 16 to 17, was attributed to the increase in the ionic polarizabilities of Dy^{3+} ions. The $Q{\cdot}f$ values were greatly decreased from 165 000 to 29 000 GHz with increasing the composition x. The temperature coefficient of the dielectric constants varied from 83 to −1 ppm/°C and $\tau_f=-1.7$ppm/°C for $x=2$. Thus, it was found that as the Dy substitution for Y increases a the linear change in τ_ε of the solid solutions also occurs, and this variation exerts an influence on the improvement in the τ_f values of this system.

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