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Dielectric property–microstructure relations in Co-O doped $(Y_{2-x}Sm_x)BaCuO_5$ ceramics

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Abstract

The effect of CoO doping on the microwave dielectric property and the microstructure of $(Y_{2-x}Sm_x)BaCuO_5$ ceramics have been investigated. The limits of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ($x=0$,1 and 2) solid solutions were approximately $y=0.1$ and the deviations of the valences in cations determined by using bond valence sum may be related to the formation of the solid solutions. It was found that high $Q{\cdot}f$ values were obtained by the Co substitution for Cu in the $(Y_{2-x}Sm_x)BaCuO_5$ ceramics, whereas the τ_f values were not improved. In the Sm-substituted $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics, the optimum value of τ_f which was closest to 0 ppm/°C was −6.3 ppm/°C for $x=2$. The reduction of porosity in the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics at compositions lower than $y=0.01$ was recognized; it was found that these morphological changes in the ceramics were closely related to the increase of the $Q{\cdot}f$ values. Thus, the optimum dielectric properties, i.e. $\varepsilon_r=16.8$, $Q{\cdot}f=90732$ GHz and $\tau_f=-9.2$ ppm/°C, were obtained in the $Sm_2Ba(Cu_{0.99}Co_{0.01})O_5$ ceramics by using cold isotropic pressing (CIP).

Keywords: Dielectric properties; Grain growth; Powders–solid state reaction; X-ray methods; Y_2O_3; $(YSm)BaCuO_5$

1. Introduction

Recently, high power filters with very low dielectric loss (tanδ) have become required for the Ku-band and Ka-band satellite microwave communications in the frequency range of 10–30 GHz.[1] One main characteristic of the components is the low tanδ, i.e. high Q, and high temperature stability. Thus, the development of microwave dielectric ceramics with high quality factor ($Q{\cdot}f$) and temperature coefficient of the resonant frequency (τ_f) close to 0 ppm/°C are required for the application of filters and resonators at high frequency.

The solid solutions with the Sm substitution for Y, i.e. $(Y_{2-x}Sm_x)BaZnO_5$ ($0<x<2$), are effective in obtaining the appropriate temperature coefficient of resonant frequency and the quality factor ($\tau_f=-4.70$ ppm/°C, $Q{\cdot}f=24\,036$ GHz at the composition $x=2$).[2] Though the effect of the Zn and Ni doping of the Y_2BaCuO_5 compound have been studied[3,4] and the improvement of the $Q{\cdot}f$ values was especially reported, the properties of the Y_2BaCuO_5 compound with the other transition metal doping, for example, Co, have not been clarified to date. Thus, to obtain high Q materials with a near zero temperature coefficient of resonant frequency, the dielectric properties of $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics with and without cold isotropic pressure (CIP) have been studied. Moreover, the effects of the Co substitution for Cu on the instability of the crystal structures which arise from the variations in the valences of cations have been analyzed in terms of the bond valence sum.[5]

2. Experimental

The $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics were prepared by the solid-state reaction method, using Y_2O_3, Sm_2O_3, $BaCO_3$, CuO and CoO powders of 99.9% purity. The starting materials were determined on the basis of the stoichiometric compositions and mixed with ethanol for 30 min. Then, they were crushed and ground with the 5 wt.% PVA binder after calcining these powders in air for 20 h. The pellets, 12 mm in diameter and 7 mm in thickness, were obtained by using CIP equipment under the pressure of 300 MPa, and then sintered

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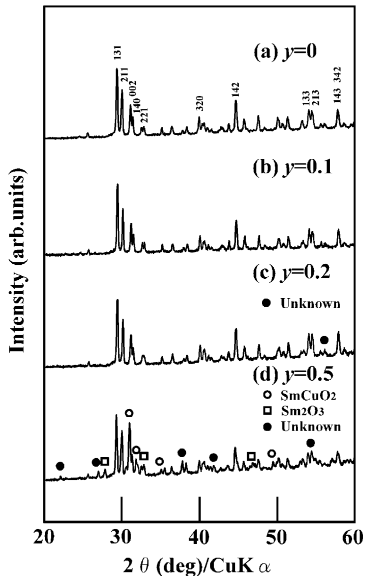

Fig. 1. XRPD patterns of $Sm_2Ba(Cu_{1-y}Co_y)O_5$ solid solutions.

for 10 h in air at various temperatures determined by differential thermal analysis (DTA) and thermogravimetry (TG). These sintered pellets were polished and annealed at 850 °C for 2 h in order to eliminate any strain. X-ray powder diffraction (XRPD) using the CuK_α filtered through the Ni foil was performed to identify the phases in the samples. The crystal structures of the solid solutions were refined by using the Rietveld analysis.[6] The Hakki and Coleman method[7] was used in order to evaluate the microwave dielectric properties. The apparent densities of the ceramics were measured according to the Archimedes method. The microstructure of the sintered pellets was also investigated by using field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray analysis (EDX).

3. Results and discussion

The XRPD patterns of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics are shown in Fig. 1. All the samples with the compositions ranging from 0 to 0.1 showed a single phase, whereas those synthesized at the higher composition than $y=0.1$ contained five impurity phases such as Y_2O_3, $Y_2Ba_4O_7$, $SmCuO_2$, Sm_2O_3 and an unknown phase. Therefore, these results suggest that the limit of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics may be approximately $y=0.1$.

Though the ionic radius[8] and electronegativity[9] of the Co ion are approximately equal to those of the Cu ion, the limit of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics was approximately $y=0.1$ and these samples did not form the solid solutions over the whole composition range. Thus, the instability of the crystal structure which arises from Co substitution for Cu may exert an influence on the formation of the solid solutions. The instability index of the R_2BaCuO_5 (R = Y, Lu, Yb, Tm, Er, Ho and Dy) ceramics were reported by Salinas et al.[10] in terms of the bond valence sum. Therefore, in order to clarify the effect of the Co substitution for Cu on the instability of the crystal structure, the valence of cations in the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics were determined by using the Eqs. (1) and (2):

$$s = \exp\left[\left(R_0 - R_{ij}\right)/0.37\right] \tag{1}$$

$$V_i = \sum_j s_{ij} \tag{2}$$

where s is the bond valence, R_0 is bond valence parameters and R_{ij} is the length of the bond between atoms i and j. Though the theoretical valence of Cu ion in the $Y_2Ba(Cu_{1-y}Co_y)O_5$ ($y=0$ to 0.1) is +2, those of Cu estimated by the bond valence sum vary from 1.78 to 1.68 as shown in Table 1. Moreover, with the Co substitution for Cu, the valences of the Sm ion in the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics at $y=0.1$ deviated from the theoretical value of +3 in comparison with those of the Sm_2BaCuO_5 ceramics. Therefore, it suggests that the instability of the crystal structures is caused by the Co substitution for Cu and the limit of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ solid solutions may be restricted.

The microwave dielectric properties of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics are shown in Fig. 2. As the composition x increases in the $(Y_{2-x}Sm_x)Ba(Cu_{0.99}Co_{0.01})O_5$ ceramics ($x=0$ to 2), the $Q\cdot f$ and τ_f values

Table 1
Bond valance sum obtained for the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics

	Y_2BaCuO_5		$Y_2Ba(Cu_{0.9}Co_{0.1})O_5$		Sm_2BaCuO_5		$Sm_2Ba(Cu_{0.9}Co_{0.1})O_5$	
	Bond valance							
	Y (1)	3.15	Y (1)	3.01	Sm(1)	3.14	Sm(1)	3.76
	Y (2)	3.00	Y (2)	3.29	Sm(2)	3.17	Sm(2)	3.67
	Ba	1.96	Ba	1.89	Ba	1.85	Ba	1.90
	Cu	1.78	Cu	1.68	Cu	1.63	Cu	1.79
			Co	1.74			Co	1.74
Total		9.90		9.86		9.81		11.12

vary from 67 057 to 39 018 GHz and from -34.0 to −7.3 ppm/°C, respectively. The $Q{\cdot}f$ values of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics noticeably increased from 11 296 to 39 018 GHz with increasing compositions up to $y = 0.01$, whereas those of the samples having higher compositions than $y = 0.01$ decreased. With increasing compositions y ranging from 0 to 0.2, the $Q{\cdot}f$ values of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ($x = 0$ and 1) ceramics show the same tendency with those of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics and the maximum $Q{\cdot}f$ values of those at $x = 0$ and 1 were 67 057 and 46 698 GHz, respectively. The samples obtained by the Sm substitution for Y and the Co substitution for Cu, exhibited the desirable microwave dielectric properties, especiallyτ_f and $Q{\cdot}f$. Though theτ_f values of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics exhibited the near-zero temperature coefficient of the resonant frequency, the $Q{\cdot}f$ values of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics were smaller than those of the $Y_2Ba(Cu_{1-y}Co_y)O_5$ ceramics. In general, the $Q{\cdot}f$ values of the microwave dielectric ceramics are known to be affected by the grain growth, porosity, impurities, lattice defect, etc.[11] The lower $Q{\cdot}f$ values of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics than those of the $Y_2Ba(Cu_{1-y}Co_y)O_5$ ceramics may depend on the sinterbility of the ceramics. Thus, in order to improve the $Q{\cdot}f$ values of $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics, much denser $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics were prepared by using CIP. The microwave dielectric properties of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics prepared with CIP are listed in Table 2. As a result, the apparent densities and the $Q{\cdot}f$ values of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics with CIP are higher than those without CIP. Therefore, it suggests that the improvements in the apparent density by using CIP are effective in increasing the $Q{\cdot}f$ values; the microwave dielectric properties of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics with CIP are: $\varepsilon_r = 16.8$, $Q{\cdot}f = 90\,732$ GHz and $\tau_f = -9.2$ ppm/°C.

The microstructure of the samples were observed by means of FE-SEM and EDX analysis in order to evaluate the effects of Co substitution for Cu on the microstructure. Fig. 3 shows SEM photographs of the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics ($y = 0$ to 0.2) after different

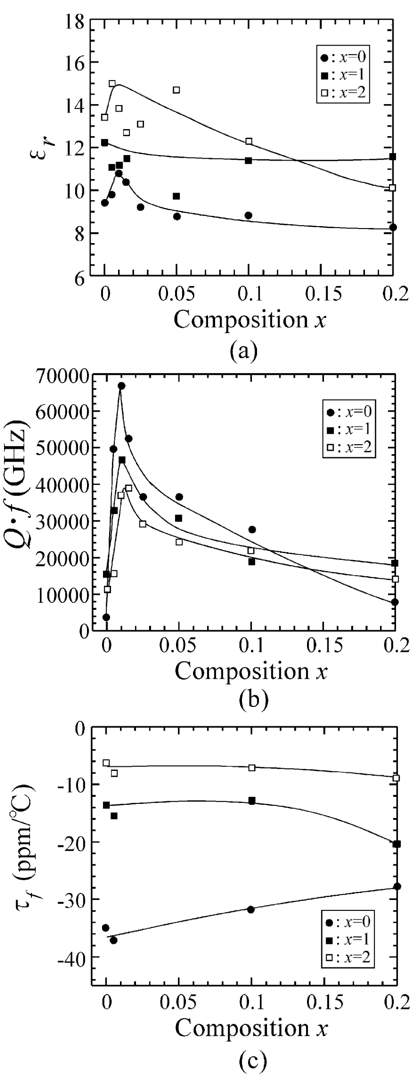

Fig. 2. Microwave dielectric properties of $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics.

Table 2
Microwave dielectric properties of $Sm_2Ba(Cu_{1-y}Co_y)O_5$ using CIP

y	d (g/cm^3)	f (GHz)	ε_r	$Q{\cdot}f$ (GHz)	ρ_f (ppm/°C)
0	6.884	9.880	16.5	53 257	−5.2
0.005	6.611	10.075	16.1	87 826	−8.2
0.01	6.848	9.918	16.8	90 732	−9.2
0.015	6.450	10.309	15.5	59 296	−8.1

y, composition; d, density; f, resonant frequency; ε_r, dielectric constant; $Q{\cdot}f$, quality factor; τ_f, temperature cosfficient of resonant frequency.

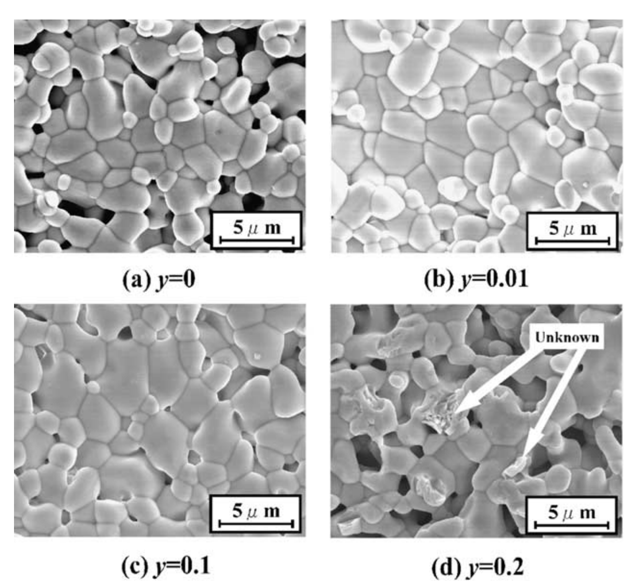

Fig. 3. FE-SEM photographs of $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ($y = 0$ to 0.2) ceramics.

sintering temperatures for 10 h. There is much porosity in the Sm_2BaCuO_5 ceramics after sintering at the optimum temperatures determined from DTA [Fig. 3 (a)]. However, as shown in Fig. 3(b), the $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics are denser than the Sm_2BaCuO_5 ceramics; the EDX results imply that small amounts of Cu may be substituted by Co in the $Sm_2Ba(Cu_{0.99}Co_{0.01})O_5$ ceramics. In the samples at $y=0.2$, there is evidence of the formation of an unknown phase [marked by the arrow in Fig. 3(d)] which deviates from the perfect cation stoichiometry in the composition. Thus, the FE-SEM photographs revealed that the changes in the microstructure of $Sm_2Ba(Cu_{1-y}Co_y)O_5$ ceramics strongly depend on the variations in the composition x. From these results, it was found that the Sm substitution for Y, and Co substitution for Cu are effective in improving theτ_f and $Q{\cdot}f$ values; the morphological changes in the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ceramics, which depend on the composition y, play an important role in increasing the $Q{\cdot}f$ values.

4. Conclusion

From XRPD patterns, it was recognized that small amounts of Cu were substituted by Co and the limits of the $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ ($x=0$, 1 and 2) solid solutions were approximately $y=0.1$. The limit of the solid solutions may be attributed the instability of the crystal structure which was estimated by using the bond valence sum. The Co substitution for Cu in $(Y_{2-x}Sm_x)Ba(Cu_{1-y}Co_y)O_5$ was effective in obtaining a high-density microstructure; this led to an improvement in the $Q{\cdot}f$ values. Moreover, the Sm substitution for Y was effective in improving the τ_f values. Thus, the $Sm_2Ba(Cu_{0.99}Co_{0.01})O_5$ ceramics with CIP exhibit the optimum microwave dielectric properties; $\varepsilon_r=16.8$, $Q{\cdot}f=90732$ GHz and $\tau_f=-9.2$ ppm/°C.

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