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Microwave dielectric property–microstructure relationships in $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions

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Abstract

$Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions were synthesized by the solid state reaction method and the microstructure was studied by using SEM in order to clarify the microwave dielectric property–structure relationship. From the variations in the lattice parameters obtained by Rietveld analysis and the least-squares method, it was clarified that the limit of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions is approximately at $x=0.2$. Grain growth and the reduction of porosity in the samples increased with the composition x. The dielectric constants were constant and the quality factors were extremely increased from 3800 to 42 300 GHz, as the composition x increased from 0 to 0.2. Thus, it was found that the quality factors of the samples were closely related to the morphological changes and a formation of the porosity; the temperature coefficient of resonant frequency of the samples ranged from −35.0 to −56.5 ppm/°C. Moreover, compared to $Y_2Ba(Cu_{1-x}Mg_x)O_5$ compound without cold isotropic pressure (CIP), that with CIP especially exhibited approximately 16% higher $Q{\cdot}f$ value.

Keywords: Alkaline earth oxides; Dielectric properties; MgO; Powders-solid state reaction; X-ray methods

1. Introduction

The demand for the development of dielectric resonators in the high frequency ranges has increased with the rapid progress of wireless communications. At the high frequency application, the microwave dielectric ceramics require low dielectric loss (tanδ), which is the inverse of the unloaded Q, the temperature coefficient of resonant frequency (τ_f) as close as 0 ppm/°C and the low dielectric constant (ε_r). The effects of Zn and Ni substitutions for Cu of $Y_2Ba(Cu_{1-x}M_x)$ O_5 (M = Zn and Ni) solid solutions on the microwave dielectric properties were investigated;[1,2] the highest $Q{\cdot}f$ values of 110 000 GHz was obtained in a $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solution. Moreover, the MgO-doped $Y_2Ba(Cu_{1-x}Zn_x)$ O_5 solid solutions were found to be effective in improving the $Q{\cdot}f$ for x less than 0.5.[3]

Although the microwave dielectric properties of the Mg-substituted $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions have not been reported as described above, those of Y_2BaCuO_5 compound with the alkali earth metal substitution have not been clarified up to date. Then, comparing the ionic radius of Mg with those of Y, Ba and Cu, the partial substitution of Mg for Cu in Y_2BaCuO_5 is expected because the ionic radius of Mg is similar to that of Cu.[4] Thus, the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions were synthesized and the microwave dielectric property–microstructure relationships were investigated in this study.

2. Experimental

High purity (>99.9%) Y_2O_3, $BaCO_3$, CuO and MgO powders were used to synthesize the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions by the conventional solid-state reaction method. These materials were weighted on the basis of the stoichiometry with the compositions x ranging from 0 to 0.4 and mixed with ethanol for 30 min. After calcination at 1000 °C for 10 h in air, they were crushed and ground with the 5 wt%. PVA binder. The pellets, 12 mm in diameter and 7 mm in thickness, were produced with a pressure of 300 MPa by using cold isotropic pressure equipment (CIP), and then sintered at the various temperatures ranging from 1250 to 1270 °C, which were determined by using the differential thermal

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analysis (DTA) and thermogravimetry (TG), for 10 h in air. 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 CuK_α filtered through Ni foil was performed to identify the resulting phases in the samples. The lattice parameters of the solid solutions were obtained by using the Rietveld analysis[5] and the least-squares method. Moreover, Hakki and Coleman's method[6] was used to evaluate the microwave dielectric properties. The microstructure of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions was also investigated by using field emission scanning electron microscopy (FE-SEM).

3. Results and discussion

The XRPD patterns of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ series are shown in Fig. 1. At higher compositions than $x=0.3$, the XRPD profiles showed the presence of the three phases such as Y_2O_3, $Y_4Ba_3O_9$ and unknown phases, whereas those of the samples obtained at the lower compositions had a single phase of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ ($x=0\sim0.2$) solid solutions. Therefore, this result suggests that the limit for x in the solid solutions may be approximately $x=0.2$.

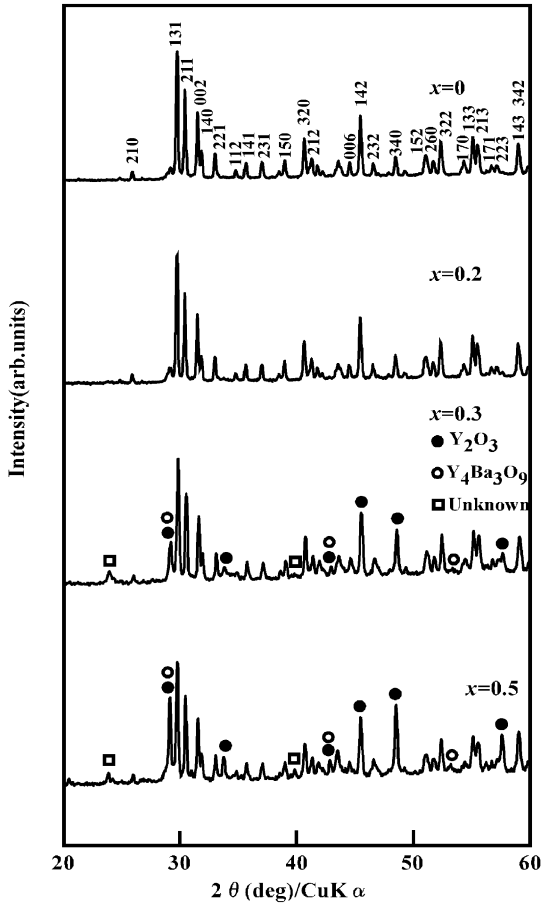

Fig. 1. XRPD patterns of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions.

Figure 2 shows the lattice parameters of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ series as a function of composition x. The lattice parameters, a and b, increased linearly as the compositions x ranging from 0 to 0.2, although these values saturated at compositions higher than $x=0.2$ as shown in Fig. 2. These results indicate that the samples satisfy Vegard's rule at the compositions ranging from 0 to 0.2; the limit of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions is approximately $x=0.2$. The single phase region of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions is more limited in comparison with those of the samples with the M (M = Ni and Zn) substitutions for Cu, although the ionic radius of Mg is approximately equal to those of the Ni, Cu and Zn ions. However, as the electronegativity[7] of the Mg ion (1.31) differs from that of the Cu ion (1.90) in comparison with those of the Zn (1.65) and Ni ions (1.91), the difference in the electronegativities of Cu and Mg may exert an influence on the formation of a solid solution. Moreover, these variations in the lattice parameters of the samples in the single phase region ($0\leqslant x\leqslant 0.2$) show a similar tendency to those of the $Y_2Ba(Cu_{1-x}Ni_x)O_5$ ($0\leqslant < x\leqslant 0.85$) and $Y_2Ba(Cu_{1-x}Zn_x)O_5$ ($0\leqslant x\leqslant 1$) solid solutions.[1,2] The variations in the atomic distances of the the M-O (M = Ni, Cu and Zn), which composes the MO_5 pyramid, exert an influence on those of the lattice parameters; the

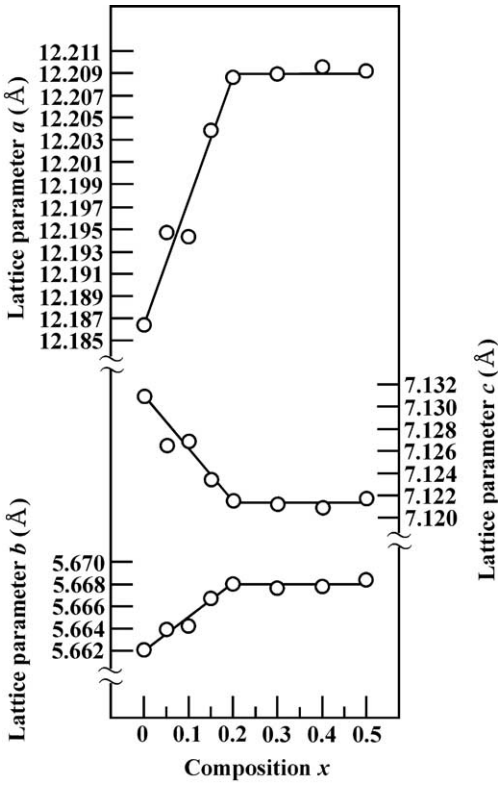

Fig. 2. Lattice parameters of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions as a function of composition x.

differences of the ionic radii of Ni, Cu and Zn ions are closely related to the variations in the atomic distances of the *M*-O. When the Cu ion was substituted for the Zn ion, the bottom plane of the MO_5 pyramid was expanded as shown in Fig. 3, and then the atomic distance of the *M*-O(3) was decreased. The expansion of the bottom plane leads to the increase in the lattice parameter, *a* and *b*, while the decrease in the atomic distance of the *M*-O(3) induces the decrease in the lattice parameter *c*. From these results, in the case of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ ($0 \leqslant x \leqslant 0.2$) solid solutions, it is suggested that the Mg substitution for Cu may exerts an influence on the variations in the atomic distances of the MO_5 pyramid because the ionic radius of the Mg ion (0.66 Å) is larger than that of the Cu ion (0.65 Å) under the same coordination number (C.N. = 5);[4] these variations in the atomic distances of the MO_5 pyramid are considered to induces the increase in the lattice parameters, *a* and *b*, and the decrease in that of *c* as shown in Fig. 3. The unit cell volumes of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions at the compositions ranging from 0 to 0.2 are also linearly increased as shown in Fig. 4. The expansion of the unit cell volume is attributed to the difference in the ionic radii of the Cu and Mg ions. Basically, the Mg substitution for Cu leads to the variations in the atomic distances of the MO_5 pyramids, which is directly related to the variations in the lattice parameters and the unit cell volume.

The microwave dielectric properties of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions are shown in Fig. 5 as a function of the composition *x* and the details on these properties are listed in Table 1. The $Q{\cdot}f$ values of these samples increased extremely from 3831 to 44 669 GHz with increasing the compositions up to $x = 0.2$, whereas those of the samples obtained at a higher compositions than $x = 0.2$ were decreased. In general, it is known that the lattice defects (vacancies and dislocations), second phases, porosity, and other microstructure-related defects strongly exert an influence on the $Q{\cdot}f$ values. The decrease in the $Q{\cdot}f$ values at the compositions higher than $x = 0.2$ is due to the formation of the second phases which were obtained from the XRPD analysis as shown in Fig. 1. At compositions lower than $x = 0.2$, the highest $Q{\cdot}f$ value was 44 669

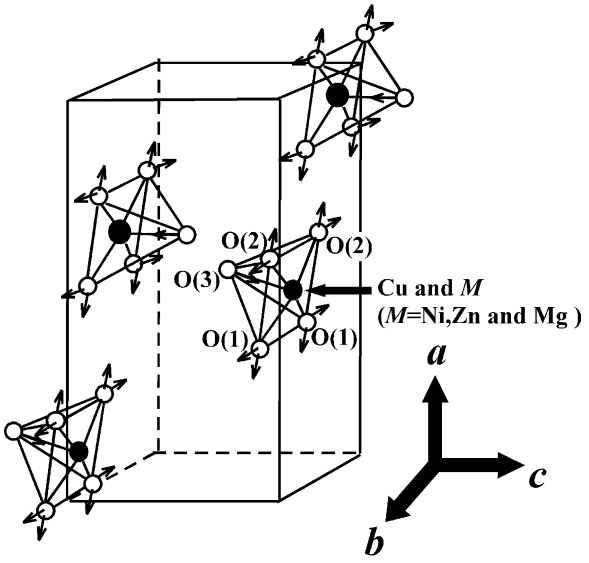

Fig. 3. Variations in the interatomic distances of MO_5 (M = Cu, Ni, Zn and Mg) pyramids in the unit cell.

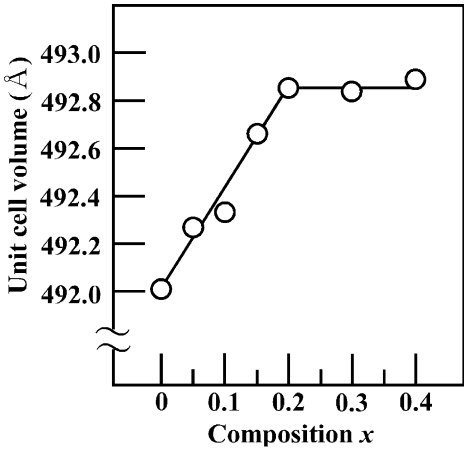

Fig. 4. Unit cell volume of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions as a function of composition *x*.

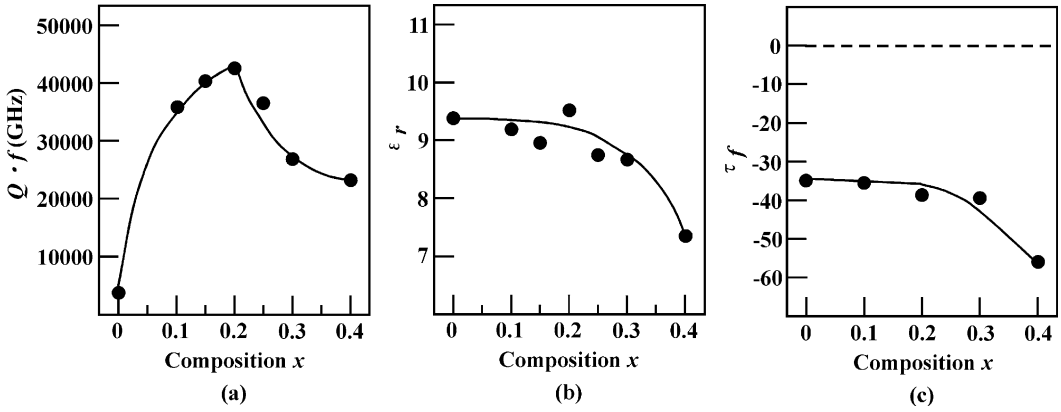

Fig. 5. Microwave dielectric properties of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions.

Table 1
Microwave dielectric properties of $Y_2Ba(Cn_{1-x}Mg_x)O_5$

x	D_r (%)	f (GHz)	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
0	84.0	12.021	9.4	3831	−35.0
0.1	84.4	12.624	9.2	36 795	−35.6
0.2	85.4	12.488	9.53	42 287	−38.8
0.3	–	13.646	8.7	27 401	−39.1
0.4	–	12.968	7.4	25 320	−56.5

x, composition; D_r, relative density; f, resonant frequency; ε_r, dielectric constant; $Q{\cdot}f$, quality factor; τ_f, temperature coefficient of resonant frequency.

Table 2
Microwave dielectric properties of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ using CIP

x	D_r (%)	f (GHz)	ε_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
0	85.8	13.492	8.3	53 361	−39.5
0.1	91.8	14.520	7.72	37 506	−37.6
0.2	92.7	12.858	9.86	49 179	−40.1
0.3	–	12.135	10.6	29 260	−44.3
0.4	–	14.579	7.7	14 031	−48.0

x, composition; D_r, relative density; f, resonant frequency; ε_r, dielectric constant; $Q{\cdot}f$, quality factor; τ_f, temperature coefficient of resonant frequency.

GHz at the composition $x=0.2$; the densified samples were also obtained at the same composition. Thus, since such a improvement in the $Q{\cdot}f$ values coincides with the tendency of the higher density of the samples, the morphological changes in the samples caused by the Mg substitution for Cu may play an important role in improving the $Q{\cdot}f$ values. The ε_r and τ_f values of the samples were almost the constant values at the single phase region and the variations in these values were not recognized by the Mg substitution for Cu. The slight decreases in these properties at compositions higher than $x=0.2$ were attributed to the presence of the second phases. Although it was found that the Mg substitution for Cu was effective in improving the $Q{\cdot}f$ values of this system, the relative densities (D_r) of the samples were still low values and the improvements in the $Q{\cdot}f$ values of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ were expected by obtaining the samples with the higher relative densities. In this study, an additional experiment was performed by using CIP in order to improve the density of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solution. The microwave dielectric properties of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ series with CIP were listed in Table 2. As a result, the relative densities of the samples with CIP are higher than those without CIP. Then, by using CIP, higher $Q{\cdot}f$ values at the compositions ranging from 0 to 0.2 were obtained as listed in Table 2. From these results, the optimum microwave dielectric properties of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ series are: $\varepsilon_r=9.8$, $Q{\cdot}f=49179$ GHz and $\tau_f=-40.1$ ppm/°C for the sample of the composition $x=0.2$ with CIP.

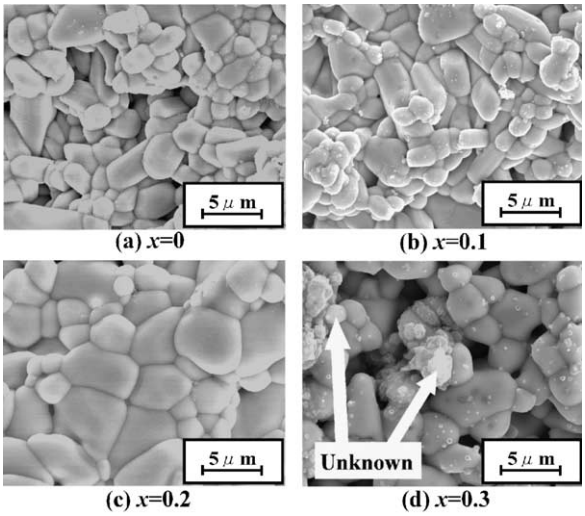

Fig. 6. FE-SEM micrographs of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions as a function of composition x.

The typical FE-SEM photographs of the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ series sintered at the optimum temperatures (1250 °C for $x=0$, 1260 °C for $x=0.1$ and 0.2; 1270 °C for $x=0.3$) for 10 h in air are shown in Fig. 6. The morphological changes, i.e., the densifications and grain size of the samples with CIP were extremely improved in comparison with those of the samples without CIP; the microstructure with the highest relative density was obtained for $x=0.2$. From the EDX analysis, deviations from the stoichiometry of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ in solid solutions was not observed in the specimens with the compositions ranging from 0 to 0.2. However, the second phases precipitated at the grain boundary of the $Y_2Ba(Cu_{0.7}Mg_{0.3})O_5$ were observed as shown in Fig. 6(d). Thus, the FE-SEM photographs revealed that the changes in the morphology of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions are extremely depend on the variations in the composition x and the relative density.

4. Conclusion

The effects of the variations in the microstructure on the microwave dielectric properties were evaluated in order to clarify the structure–microwave dielectric property relations in the $Y_2Ba(Cu_{1-x}Mg_x)O_5$ ceramics. The limit of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ solid solutions was found to be approximately $x=0.2$ on the bases of the variations in the lattice parameters. At the composition x ranging from 0 to 0.2, the lattice parameters, a and b, increased with the increase of the composition x, whereas the lattice parameter, c, decreased and Vegard's rule was satisfied. The improvements in $Q{\cdot}f$ values of the samples were recognized at $x=0.2$; these results are considered to relate with the morphological changes in the samples with CIP which depend on the variations in

the composition x. Consequently, the D_r values varied from 89.3 to 92.7% at the compositions ranging from 0 to 0.2. The optimum dielectric properties, i.e., $Q{\cdot}f = 49\,179$ GHz, $\varepsilon_r = 9.86$ and $\tau_f = -40.1$ ppm/°C, of $Y_2Ba(Cu_{1-x}Mg_x)O_5$ ceramics with CIP were obtained at $x = 0.2$.

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