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Microwave dielectric properties and crystal structure refinements in M (M = Sr, Ca) doped $Nd_2(Ba_{1-x}M_x)ZnO_5$ solid solutions

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Abstract

The microwave dielectric properties and crystal structure stability estimated by the bond valence sum of Nd_2BaZnO_5 ($\varepsilon_r = 22.6$, $\tau_f = 4.6$ ppm/°C, $Q{\cdot}f$ = 12,451 GHz), $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ ($\varepsilon_r = 25.5$, $\tau_f = 26.0$ ppm/°C, $Q{\cdot}f$ = 6185 GHz) and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ ($\varepsilon_r = 26.4$, $\tau_f = 24.0$ ppm/°C, $Q{\cdot}f$ = 6210 GHz) were evaluated in this study. It was clarified that substituting Sr or Ca for Ba induces the decrease of lattice parameters at $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ ($a = 6.7391(4)$, $c = 11.4592(4)$) and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ ($a = 6.7386(4)$, $c = 11.4597(5)$) in comparison with those of Nd_2BaZnO_5 ($a = 6.7391(4)$, $c = 11.4592(4)$) and volume of BaO_{10} polyhedron by Rietveld analysis. In this case, an instability in the crystal structure of $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ is induced by the bond valence difference between Ba and Sr or Ca ions. Our research that the crystal structure instability in particular influences a decrease of the $Q{\cdot}f$ value in this system.

Keywords: Dielectric properties; Powder: solid state reactions; X-ray methods

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1. Introduction

Recently, a low dielectric constant (ε_r) with high quality factor ($Q{\cdot}f$) was required in applications in the high frequency range. In a previous paper,[1] the microwave dielectric properties of $Sm_2Ba(Cu_{1-y}Zn_y)O_5$ ($Pnma$, $y = 0.75$, $\varepsilon_r \approx 17$, $\tau_f \approx 4.6$ ppm/°C, $Q{\cdot}f \approx 42{,}000$ GHz solid solutions were evaluated and the properties were suitable for the application as described above. Then, a new type of crystal structure for Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$, in which Sr or Ca is substituted for Ba, was evaluated as an application to the microwave resonator in this study. In addition, the crystal structures of these oxides are refined by means of the Rietveld method at room temperature in order to evaluate the effect of Sr and/or Ca substitution for Ba on the crystal structure. Also, the atomic valences of the cations Nd, Ba, Sr, Ca and Zn are estimated using the bond valence sum to clarify the influence of the variations in the atomic valence on the microwave dielectric properties.

2. Experimental

Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides were synthesized from high-purity (99.9%) powders of Nd_2O_3, $BaCO_3$, $CaCO_3$, $SrCO_3$, and ZnO, using the conventional solid-state reaction method. The weights of the powders were based on stoichiometry. They were mixed with acetone and were calcined in an alumina crucible at 950°C for 20 h in air. Then, the calcined and crushed powders were ground with an organic binder, and passed through a screen mesh. Samples were formed by applying 100 MPa to obtain the pellet i.e. 12 mm in diameter, 7 mm thick. The sintering temperatures for each oxide were determined by differential thermal analysis (DTA) and thermogravimetry (TG), and then these pellets were sintered at their respective temperatures for 2 h in air. Subsequently, the sintered pellets were polished and annealed at 850°C for 2 h in order to remove any strain. X-ray powder diffraction (XRPD) analysis for these oxides was carried out by using CuK_α radiation filtered through Ni foil. The lattice parameters and crystal structures of these oxides are refined at room temperature by using the Rietveld analysis[2] program "RIETAN".[3] The microwave dielectric properties of the

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samples were measured according to Hakki and Coleman's method.[4]

3. Results and discussion

The crystal structure of Nd_2BaZnO_5 (*I*4/*mcm* No.140) is composed of three polyhedra, NdO_8, BaO_{10}, and ZnO_4. Concerning the NdO_8 polyhedron which is shown in Fig. 1, Nd^{3+} ions are surrounded by two O(1) atoms and six O(2), these O(2) atoms make up a triangular prism. O(1) atoms are joined by the four O(2) atoms, representing the capped prism, i.e. NdO_8 polyhedron, in both sides of the triangular prism. Thus, these NdO_8 polyhedra are linked by the common edges and faces into a $Nd_4O(1)_5O(2)_{16}$ unit shown in Fig. 1. In addition, Ba^{2+} ions are positioned in the center of BaO_{10} polyhedron, which is presented in Fig. 2. Ba^{2+} ions are placed between upper and lower O(1) atoms that are located in the same positions of Ba^{2+} ions in the direction of *a* and *b*-axes, whereas O(2) atoms are linked each other with the rotation on the *c*-axis when positioned in the center of Ba^{2+} ions. Also, Zn^{2+} ions are positioned in the tetrahedral structure, i.e. ZnO_4 with four tetrahedra included in the unit cell of Nd_2BaZnO_5.

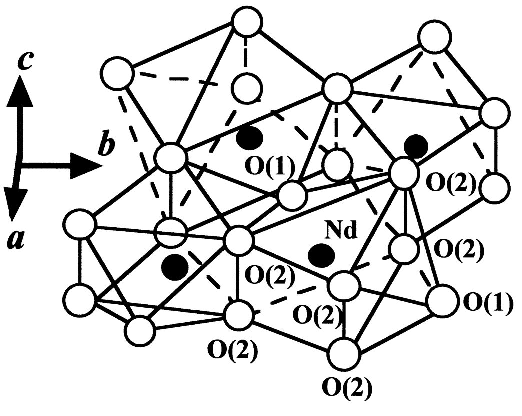

Fig. 1. NdO_8 polyhedron structure.

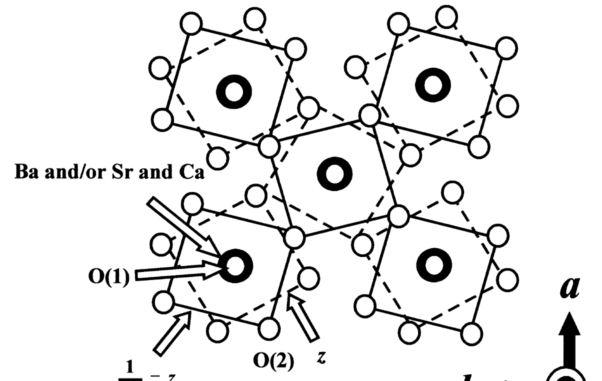

Fig. 2. Crystal structure of BaO_{10} polyhedron along the *c*-axis.

XRPD patterns of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides are shown in Fig. 3. No impurity phase was detected in these patterns. Thus, it is shown that $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides may consist of a single phase, suggesting the partial substitution of Sr and/or Ca for Ba ions. For the purpose of the evaluation of the influence on the crystal structure of Sr and/or Ca substitution for Ba, the structure parameters of these oxides were refined, using the Rietveld method. In this study, the initial structure parameters i.e. the lattice parameters and atomic coordinates, reported by M. Taibi et al.[5] were used in order to refine the crystal structure. As a result of the Rietveld analysis, the reliability factor for the weighted patterns (R_{wp}) and those for the patterns (R_p) of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides are 8.40, 6.55, 6.70, 5.00, 7.37 and 5.39%, respectively.

Table 1 shows the lattice parameters and unit cell volumes of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides, respectively. These volumes of $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides are decreased in comparison with those of Nd_2BaZnO_5 oxide. These decreases are attributed to the difference in the ionic radii between Ba and *M* (*M* = Sr or Ca). It is considered that these decreases of the lattice parameters resulting from Sr or Ca substitution for Ba will be reflected by the variations in the atomic distances between the cations and oxygen atoms. Thus, the atomic distances between cations and oxygen atoms were determined on the basis of the refined atomic coordinates obtained in this study. By Sr and/or Ca substitution for Ba, the positions of Sr^{2+} and Ca^{2+} ions

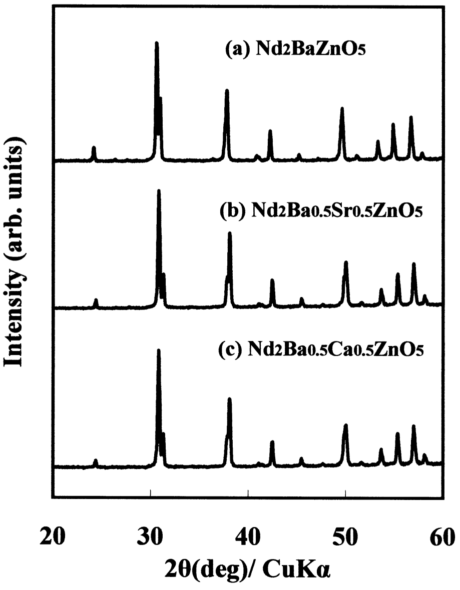

Fig. 3. XRPD patterns of (a) Nd_2BaZnO_5, (b) $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and (c) $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$.

Table 1
Lattice parameters and the unit cell volumes of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$

Samples	Nd_2BaZnO_5	$Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$	$Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$
Lattice parameter *a* (Å)	6.7616 (2)	6.7391 (4)	6.7386 (2)
Lattice parameter *c* (Å)	11.5469 (4)	11.4592 (4)	11.4597 (5)
Unit cell volume (Å^3)	527.91 (7)	520.43 (3)	520.38 (3)

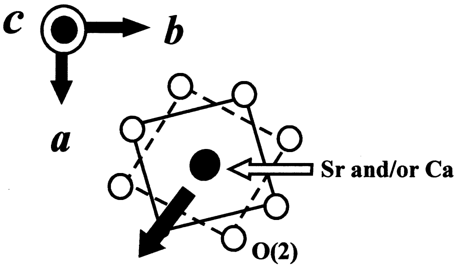

Fig. 4. Variation in the position of Sr and Ca ions inside the BaO_{10} polyhedron along the *c*-axis.

are shifted as represented in Fig. 4. The variations in the atomic distances between the Ba^{2+} ions and oxygen atoms in the BaO_{10} polyhedra are shown in Table 2 along with those for the ZnO_4 tetrahedra of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides. The atomic distance between Ba^{2+} ion and O(1) atom which is parallel in the direction of *c*-axis and those between Ba^{2+} ion and O(2) atom are decreased, resulting in a decease of volume in the BaO_{10} polyhedron in this study. Therefore, the decreases of the lattice parameters as mentioned above are considered to be caused by the variations in atomic distances of the BaO_{10} polyhedra. In addition, with these variations in the BaO_{10} polyhedra, the volume of the ZnO_4 tetrahedron is increased in comparison with that of Nd_2BaZnO_5. Namely, the atomic distances between Zn and O(2) are increased by Sr and/or Ca substitution for Ba. Regarding the NdO_8 polyhedron, it is suggested that the Nd^{3+} ion located inside the capped prism is suppressed by the variations in the atomic distances between that ion and the oxygen atoms, decreasing the volume of the polyhedron.

The valences of cations, i.e. Nd^{3+}, Ba^{2+}, Sr^{2+}, Ca^{2+} and Zn^{2+} ions, were estimated by using the bond valence sum reported by Brown and Altermatt[6] in order to clarify the valences of cations with the variations in atomic distances as described above and to evaluate the stability of the crystal structures in which Sr and/or Ca are substituted for Ba. Thus, the estimates of the valence in the cations and evaluations of the stability in the crystal structures were analyzed in terms of bond valence, *s*, which is related to the following equations:

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

Table 2
Atomic distances of BaO_{10} polyhedron and ZnO_4 tetrahedron for Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$

Samples	Atomic distance	Å
Nd_2BaZnO_5	Ba-O(1)×2	2.886(7)
	Ba-O(2)×8	2.878(3)
	Zn-O(2)×4	2.016(1)
$Nd_2Ba_{0.5}Sr_{0.5}BaZnO_5$	Ba-O(1)×2	2.864(8)
	Ba-O(2)×8	2.835(4)
	Zn-O(2)×4	2.079(2)
$Nd_2Ba_{0.5}Ca_{0.5}BaZnO_5$	Ba-O(1)×2	2.864(9)
	Ba-O(2)×8	2.841(9)
	Zn-O(2)×4	2.061(1)

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

Eq. (1) is the empirical relationships between the valence (s_{ij}) and the atomic distances (R_{ij}) where *i* and *j* represent the number of atoms in a unit cell. Moreover, R_0 is a constant value which is tabulated for most known types of bond.[6] Then, Eq. (2) is the bond valence sum rule which satisfies the rule that the sum of the valence of the bonds formed by each atom is equal to its atomic valence. The atomic valences of cations of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ were listed in Table 3. The valences of Ba and Nd atoms in Nd_2BaZnO_5 are larger than those of $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$, whereas the atomic valences of Zn in $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ are decreased in comparison with the atomic valence of Nd_2BaZnO_5. To increase the volume of the ZnO_4 tetrahedron, the atomic valence of Zn is decreased by Sr or Ca substitution for Ba. In this way, the increase of the atomic valences of Nd and Ba are induced by the decreases of the volume in the NdO_8 and BaO_{10} polyhedra. This, therefore, suggests that these variations in atomic valence occurring through Sr or Ca substitutions for Ba are closely related to polyhedra volume variation. Moreover, since the difference of the atomic valence between Ba and Sr or Ca are remarkable, as listed in Table 3, this tendency suggests that the instability of the crystal structure is induced by Sr or Ca substitution for Ba.

Table 3
Atomic valence of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$

Samples	Atoms	Valence
Nd_2BaZnO_5	Ba	2.00
	Nd	2.86
	Zn	1.72
$Nd_2Ba_{0.5}Sr_{0.5}BaZnO_5$	Ba	2.23
	Sr	1.69
	Nd	3.17
	Zn	1.45
$Nd_2Ba_{0.5}Ca_{0.5}BaZnO_5$	Ba	2.37
	Ca	1.16
	Nd	3.10
	Zn	1.52

The microwave dielectric properties of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ are listed in Table 4. The dielectric constants of these oxides are 22.4, 25.5 and 26.4, respectively, and are suitable for the high frequency microwave applications. It is considered that the increments of ε_r in comparison with those of Nd_2BaZnO_5 oxide depend on the variations of the polyhedra in the unit cell because the significant variations of the relative densities (D_r) were not recognized. Here, the decreases of the valence of Zn caused by Sr and/or Ca substitution are decreased because the bond valence sum equation depends on the atomic distances between cations and oxygen atoms, as mentioned above. The temperature coefficient of the resonant frequency, τ_f, increase from 4.6 to 26.0 ppm/°C. The $Q{\cdot}f$ values of these oxides are 12,541, 6185 and 6210 GHz, respectively, and the values in Sr and Ca substituted samples are decreased as listed in Table 3. In this manner, the variations in the $Q{\cdot}f$ values were evaluated on the basis on the stability of the crystal structure as mentioned above. As listed in Table 4, the valences of Ba and Sr and/or Ca ions are remarkably different and the variations in the atomic distances between the cations and the oxygen atoms induce the instability of the crystal structure. Therefore, these decreases of the $Q{\cdot}f$ values may be attributed to the instability of the crystal structure in $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ related to the difference of the atomic valence between Ba and Sr and/or Ca determined by using bond valence sum.

Table 4
Microwave dielectric properties of Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$

Samples	Nd_2BaZnO_5	$Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$	$Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$
D_r (%)[a]	95.5	96.1	96.4
f (GHz)[b]	8.987	8.687	8.553
ε_r[c]	22.6	25.5	26.4
τ_f (ppm/°C)[e]	4.6	26.0	24.0
$Q{\cdot}f$ (GHz)[d]	12,451	6120	6185

[a] D_r: relative density.

[b] f: Resonant frequency.

[c] ε_r: Dielectric constant.

[d] $Q{\cdot}f$: Quality factor.

[e] τ_f: Temperature coefficient of the resonant frequency.

4. Conclusion

Nd_2BaZnO_5, $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ were prepared by the solid-state reaction method, and the formations of the single phase for each sample were observed from the result of XRPD analysis. In addition, the lattice parameters of $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ were decreased in comparison with those of Nd_2BaZnO_5, resulting in the decrease of the volume for BaO_{10} and NdO_8 polyhedra, and an increase of the volume for ZnO_4 tetrahedra. The variations in the volume of these polyhedra in the unit cell were closely related to the variations in the atomic valence of cation ions obtained by bond valence sum calculations. Thus, it was suggested that the differences of atomic valence between Ba and Sr and/or Ca in $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ induce the instability of the crystal structure. $Q{\cdot}f$ values of $Nd_2Ba_{0.5}Sr_{0.5}ZnO_5$ and $Nd_2Ba_{0.5}Ca_{0.5}ZnO_5$ oxides are lower than those of Nd_2BaZnO_5 oxide. Therefore, it is considered that the decreases of these values are caused by the instability of the crystal structure induced by the Sr or Ca substitution for Ba.

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