Available online at www.sciencedirect.com
SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 1745–1748

www.elsevier.com/locate/jeurceramsoc

Relationships between Sr substitution for Ba and dielectric characteristics in Sm_2BaZnO_5 ceramics

Kenkichi Mori[a,*], Hirotaka Ogawa[a], Akinori Kan[a], Hitoshi Ohsato[b]

[a]*Faculty of Science and Technology, Meijo University, 1-501 Shiogamaguti, Tempaku-ku, Nagoya 468-8502, Japan*
[b]*Depertment of Materials Science and Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan*

Abstract

The effects of Sr substitution for Ba in $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ solid solutions on the crystal structure and microwave dielectric properties were investigated in this study. The ϵ_r values of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ are slightly increased with increasing x in the range $0 \leqslant x \leqslant 0.1$, and the $Q{\cdot}f$ values are extremely decreased from 35 505 to 8522 GHz. The variations in the $Q{\cdot}f$ values may depend on the differences in the crystal structure because a single phase of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with tetragonal structure was produced for $x \geqslant 0.1$ compositions instead of an orthorhombic structure. The highest $Q{\cdot}f$ value in $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with a tetragonal structure was 19 283 GHz at $x = 1$. The increase in the $Q{\cdot}f$ values of samples with $x \geqslant 0.1$ were attributed to the grain growth induced by the Sr substitution for Ba. In the sample at $x = 1$ many microcracks were observed. In order to remove these cracks, Co was substituted for Zn in Sm_2SrZnO_5, which improved the $Q{\cdot}f$ values.

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

1. Introduction

Several kinds of dielectric materials are used for microwave applications. The continued development of wireless communication technologies will rely upon the identification of new microwave dielectric materials with enhanced quality factor ($Q{\cdot}f$), a suitable dielectric constant (ϵ_r) and the zero temperature coefficient of resonant frequency (τ_f). Most studies to date of microwave dielectric properties have focused in particular on the complex perovskite materials, such as $Ba(Mg_{1/3}Ta_{2/3})O_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba[Zr_x(Zn_{1/3}Ta_{2/3})_{1-x}]O_3$.[1–3] The development of new compositions with better dielectric properties is now required for the microwave applications. Watanabe et al. reported a new non-perovskite material with an excellent $Q{\cdot}f$ value, higher than 100,000GHz, in the Y_2O_3–BaO–CuO–ZnO system.[4] Then, near-zero τ_f values and relatively high $Q{\cdot}f$ values in Sm_2O_3-BaO-ZnO system were also reported.[5] However, the effects on microwave dielectric properties of Sr substitution for Ba in Sm_2BaZnO_5 have not been reported, and it is important to clarify the relationships between microwave dielectric properties and crystal structure. Thus, $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ compositions were synthesized; the microwave dielectric properties and crystal structure studied. In addition, the effects of Co substitution for Zn on the microwave dielectric properties and microcracks in Sm_2SrZnO_5 were also investigated.

2. Experimental

$Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ($x = 0$–1) and $Sm_2Sr(Zn_{1-y}Co_y)O_5$ ($y = 0$–0.1) were prepared via the solid-state reaction method, using high-purity ($\geqslant 99.9\%$) Sm_2O_3, $BaCO_3$, $SrCO_3$ ZnO and CoO powders as the starting materials. In this study, the stoichiometric proportions of these powders were weighed, mixed in the mortar with acetone and calcined at 1050 °C for 20 h in air. After calcining, the powders were re-ground with an organic binder (polyvinyl alcohol), and then uniaxially pressed under the pressure of 100 MPa into pellets which were 12 mm in diameter and 6 mm in thickness. These pellets were sintered at various temperatures from 1200 to 1310 °C for 10 h in air, and then the sintered pellets were polished and subsequently annealed at 850 °C for 2 h in order to remove any strain. The phases of the synthesized materials were identified by X-ray diffraction

* Corresponding author. Tel.: +81-52-832-1151x5160; fax: +81-52-832-1253.
E-mail address: ogawah@ccmfs.meijo-u.ac.jp (H. Ogawa).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00539-9

(XRD), using CuK_α filtered through Ni foil. The lattice parameters and crystal structures of these oxides were refined by using the Rietveld analysis.[6,7] The microwave dielectric properties were measured by Hakki and Coleman's method.[8] The morphological changes in these samples were investigated by means of field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) analysis.

3. Results and discussion

The XRD profiles of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ series are shown in Fig. 1. The structure of Sm_2BaZnO_5 is orthorhombic, a single phase of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with tetragonal structure is produced for $x \geqslant 0.1$. In addition, this structure has the same crystallography as the Nd_2BaZnO_5 reported by Taibi et al.[9] The orthorhombic and tetragonal phases coexist at lower levels of the Sr substitution ($0 < x < 0.1$) in $Sm_2(Ba_{1-x}Sr_x)ZnO_5$. Moreover, the peak positions of the XRD profiles in the compositions ranging from 0.1 to 1 is shifted to higher 2θ angles with the Sr substitution for Ba. Systematic shifts of the peaks to the higher 2θ angles indicate a decrease in the lattice parameters with increasing the composition x. In order to clarify the influence of the ionic radii difference between Ba and Sr on the crystal structure, the lattice parameters of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ compounds were determined; the results are shown in Fig. 2. The reliability factor of weighed patterns (R_{wp}), the reliability factor of the pattern (R_p) and goodness of fit indicator (s) range from 4.43 to 6.92%, 3.29 to 4.91% and 1.32 to 1.74, respectively. The lattice parameters of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with the tetragonal structure remain almost constant in the compositions ranging from 0.05 to 0.1. On the other hand, the lattice parameters of the samples for which $x \geqslant 0.1$ linearly decrease with the increasing composition x. From these results, the decreases of the lattice parameter are attributed to the decreases of volume in the MO_{10} (M = Ba and/or Sr) polyhedra induced by the differences of ionic radii between Ba and Sr, because the ionic radius of Sr^{2+} (1.36 Å) is smaller than that of Ba^{2+} (1.52Å) when the coordination number is ten.[10] Therefore, the interatomic distances in MO_{10} polyhedra, such as M–O(1) and M–O(2), were determined in order to clarify the interrelationships between the variations in the lattice parameters and the Sr substitution for Ba. The decreases of interatomic distances, M–O(1) and M–O(2), in the MO_{10} polyhedra are recognized as shown in Fig. 3. Since the variation in the interatomic distances of MO_{10} polyhedra as described above agrees with the results of those in the lattice parameters of the samples, the variation in the lattice parameters are considered to be caused by the variation in the interatomic distances of MO_{10} polyhedra.

The microwave dielectric properties of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ are listed in Table 1. The ϵ_r values of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ are slightly increased in the compositions ranging from 0 to 0.1, while these $Q{\cdot}f$ values are extremely decreased from 35 505 to 8522 GHz. Thus, the variations in $Q{\cdot}f$ values of the

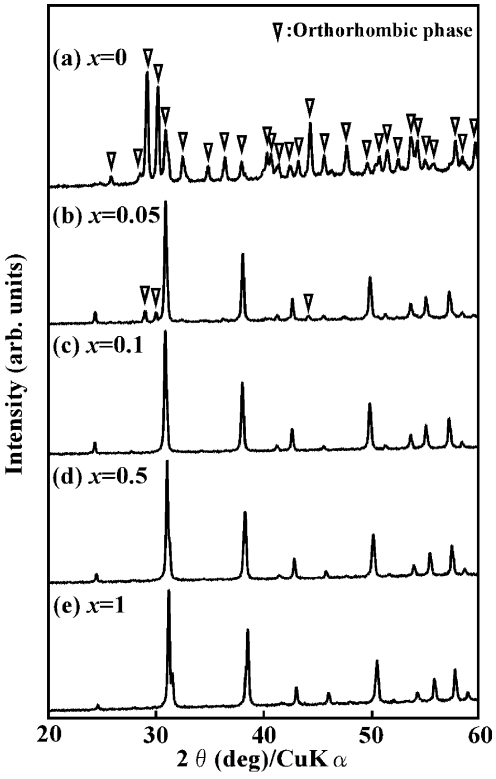

Fig. 1. XRD patterns of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ceramics.

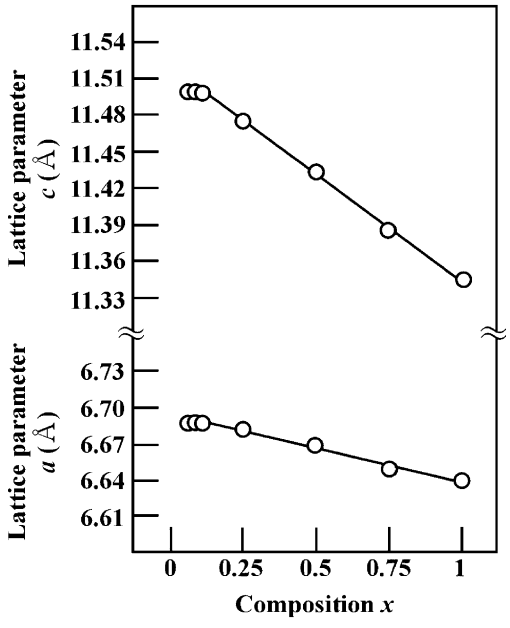

Fig. 2. Lattice parameters and unit cell volumes of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ceramics as a function of composition x.

$Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ($0 \leqslant x \leqslant 0.1$), which were very sensitive to the Sr substitution for Ba, were considered to depend on the differences in the crystal structure between an orthorhombic and tetragonal structures as mentioned above. In addition, the remarkable decreases in the $Q{\cdot}f$ values may depend on the instability of the crystal structure induced by the Sr substitution for Ba, because the valence of Ba and Sr ions at $x = 0.1$ obtained by bond valence sum[11] are remarkably different from that of Ba ions at $x = 0$ as listed in Table 2. Moreover, the difference of the atomic valence between Ba and Sr ions at $x = 0.1$ is remarkable, suggesting that the instability of the crystal structure is induced by Sr substitution for Ba. Therefore, the decrease of $Q{\cdot}f$ values in the compositions ranging from 0 to 0.1 may be attributed to the relative instability of the tetragonal crystal structure in $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ due to the difference of the atomic valence between Ba and Sr. The τ_f values of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ($x \geqslant 0.1$) decrease with increasing x. In these samples, it is possible to obtain a low τ_f by controlling the amounts of Sr substitution for Ba. The near-zero τ_f value of 2.6 ppm/°C was obtained at $x = 0.85$. Moreover, the $Q{\cdot}f$ values of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ increased from 8522 to 19 283 GHz in the compositions ranging from 0.1 to 1. As a result, the highest $Q{\cdot}f$ value in $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with tetragonal structure was 19 283 GHz at $x = 1$. In general, the $Q{\cdot}f$ values are known to be affected by the concentration of defects, impurities, grain size and porosity, and that the large grain size of ceramics results in low dielectric loss materials.[12,13] Consequently, the microstructure of the samples was observed by using FE-SEM; Fig. 4 shows the surface micrographs of the $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ at $x = 0.1$ and 1, respectively. The

Table 1
Dielectric properties of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ceramics-

x	f (GHz)	ϵ_r	$Q{\cdot}f$ (GHz)	τ_f (ppm/°C)
0	9.479	18.5	35 505	−6.4
0.05	8.609	22.1	10 053	30.3
0.1	8.424	23.0	8522	36.1
0.25	8.167	24.3	8671	30.2
0.5	8.097	25.3	10 074	29.6
0.75	8.171	25.1	11 904	18.0
0.85	8.193	24.4	12 132	2.6
0.9	8.229	24.5	14 950	−35.5
0.95	8.204	24.6	18 694	−81.5
1	8.134	24.1	19 283	−97.1

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

Table 2
Atomic valence of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ at $x = 0$, 0.15 and 1

Composition	Crystal structure	Atoms	Valence
$x = 0$	Orthorhoinbic	Sm(1)	3.08
		Sm(2)	2.90
		Ba	1.76
		Zn	1.80
$x = 0.1$	Tetragonal	Sm	2.70
		Ba	1.89
		Sr	1.18
		Zn	2.53
$x = 1$	Tetragonal	Sm	2.70
		Sr	1.51
		Zn	2.42

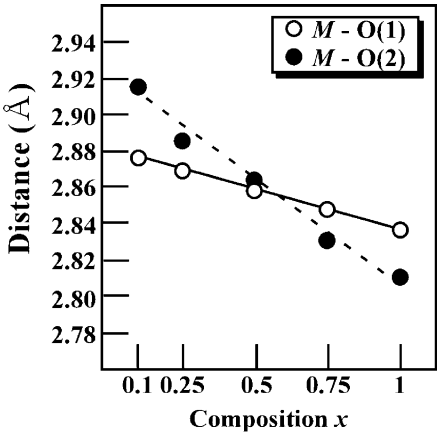

Fig. 3. Atomic distances of MO_{10} (M = Ba and Sr) polyhedra as a function of composition x.

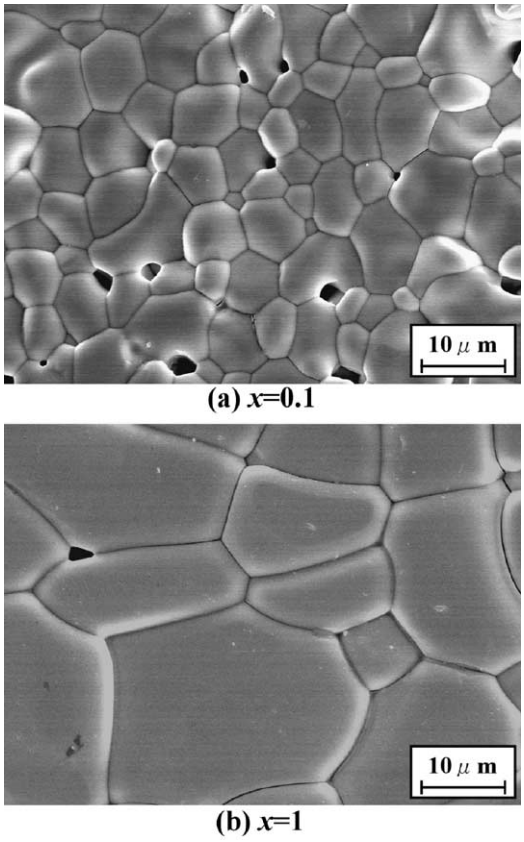

Fig. 4. FE-SEM micrographs of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ ceramics at $x = 0.1$ and 1.

low-$Q{\cdot}f$ value of the sample for which $x=0.1$ has the small grain size, whereas grains growth are sufficiently observed for samples with the composition $x=1$. These results suggest that the increase in $Q{\cdot}f$ values of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ may be attributed to the grain growth of the samples caused by the Sr substitution for Ba.

On the other hand, the formation of microcracks were observed in the sample at $x=1$, and this was considered to be closely related to the deterioration of $Q{\cdot}f$ values.[14] Thus, $Sm_2Sr(Zn_{1-y}Co_y)O_5$ samples were synthesized because the ionic radius of Co (0.58Å) is close to that of Zn (0.6Å),[10] and the effects of the Co substitution for Zn on the microwave dielectric properties and microcracks were investigated. The XRD results of the $Sm_2Sr(Zn_{1-y}Co_y)O_5$ showed a single phase in the composition range from 0 to 0.025. In addition, crack-free samples were obtained with small amounts of the Co substitution ($y \geqslant 0.01$). The $Q{\cdot}f$ values of $Sm_2Sr(Zn_{1-y}Co_y)O_5$ samples are increased with Co substitution up to $y=0.01$, where the highest $Q{\cdot}f$ value of 22 301 GHz was obtained, suggesting that a small amount of Co substitution for Zn is effective in eliminating microcracks in this system and improving $Q{\cdot}f$ values.

4. Conclusion

$Sm_2(Ba_{1-x}Sr_x)ZnO_5$ solid solutions were synthesized by the solid-state reaction method, and the crystal structure and microwave dielectric properties of these compounds were evaluated in this study. While Sm_2BaZnO_5 is orthorhombic, it is clear from XRD results that these compounds showed the presence of $Sm_2(Ba_{1-x}Sr_x)ZnO_5$ with a tetragonal structure for $x \geqslant 0$. The lattice parameters, a and c, of samples linearly decrease with increasing composition x; the variations in these are considered to be closely related to the differences in the ionic radii of Sr and Ba. As for the microwave dielectric properties, the $Q{\cdot}f$ and τ_f values are significantly changed by small amounts of Sr substitution ($0 < x < 0.1$), which were attributed to the difference between the orthorhombic and tetragonal structures. The increases in the $Q{\cdot}f$ values in the compositions ranging from 0.1 to 1 may be attributed to the grain growth of the samples induced by the Sr substitution. In addition, the Co substitution for Zn in $Sm_2Sr(Zn_{1-y}Co_y)O_5$ is effective in eliminating microcracks and improving $Q{\cdot}f$ values in this system.

References

1. Nomura, S., Toyama, K. and Kaneta, K., $Ba(Mg_{1/3}Ta_{2/3})O_3$ ceramics with temperature-stable high dielectric constant and low microwave loss. *Jpn. J. Appl. Phys.*, 1982, **21**, L624–L626.
2. Wakino, K., Murata, M. and Tamura, H., Far infrared reflection spectra of Ba(Zn, Ta)O_3-$BaZrO_3$ dielectric resonator material. *J. Am. Ceram. Soc.*, 1986, **69**, 34–37.
3. Venkatesh, J., Sivasubramanian, V., Subramanian, V. and Murthy, V. R. K., Far-IR reflectance study on B-site disordered $Ba(Zn_{1/3}Ta_{2/3})O_3$ dielectric resonator. *Mater. Res. Bull.*, 2000, **35**, 1325–1332.
4. Watanabe, M., Ogawa, H., Ohsato, H. and Humphreys, C., Microwave dielectric properties of $Y_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions. *Jpn. J. Appl. Phys.*, 1998, **37**, 5360–5363.
5. Kan, A., Ogawa, O., Watanabe, M., Hatanaka, S. and Ohsato, H., Microwave dielectric properties of $Sm_2Ba(Cu_{1-x}Zn_x)O_5$ solid solutions. *Jpn. J. Appl. Phys.*, 1999, **38**, 5629–5632.
6. Rietveld, H. M., A profile refinement method for nucear and magnetic structures. *J. Appl. Crystallogr.*, 1969, **2**, 65–71.
7. Izumi, F., In *Rietveld Method*, ed. R. A. Young. Oxford University Press, Oxford, 1993
8. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive capacities in the millimeter range. *IRE Trans: Microwave Theory & Tech.*, 1960, **MTT-8**, 402–410.
9. Taibi, M., Aride, J., Darriet, J., Moqine, A. and Boukhari, A., Structure crystalline de 1′ oxyde Nd_2BaZnO_5. *J. Solid State Chem.*, 1990, **86**, 233–237.
10. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta. Cryst.*, 1976, **A32**, 751–767.
11. Brown, I. D. and Altermatt, D., Bond-valence parameters from a systematic analysis of the inorganic crystal structure database. *Acta Crystallogr.*, 1985, **B41**, 244–247.
12. Matsumoto, H., Tamura, H. and Wakino, K., Ba(Mg, Ta)O_3-$BaSnO_3$ high-Q dielectric resonator. *Jpn. J. Appl. Phys.*, 1991, **30**, 2347–2349.
13. Tzou, W. C., Yang, C. F., Chen, Y. C. and Cheng, P. S., Improvements in the sintering and microwave properties of $BiNbO_4$ microwave ceramics by V_2O_5 addition. *J. Eur. Ceram. Soc.*, 2000, **20**, 991–996.
14. Kim, H. T., Byun, J. D. and Kim, Y., Microstructure and microwave dielectric properties of modified zinc. *Mater. Res. Bull.*, 1998, **33**, 975–986.