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Crystal structure and microwave dielectric properties of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions

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Abstract

The tungstenbronze-type-like $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions have been studied. Microwave dielectric properties of these solid solutions link to the substitution of large cations such as Ba ions by small Sr ions. In these solid solutions for $x = 0$, the quality factor ($Q{\cdot}f$) exibits extremely low due to the inner strain resulting by the occupation of large Ba ions at relatively small $A1$-sites. However, dielectric constant (ε_r) of this composition show a high value. In this paper, improvement of quality factor ($Q{\cdot}f$) by substituting small Sr ions for Ba ions in $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$, is reported. In addition, the relationship between crystal structure and microwave dielectric properties is discussed from the viewpoint of structural formula and occupational state of large cations such as Ba, Sr and Sm in $A1$-sites.

Keywords: Tungstenbronze-type-like structure; Dielectric properties; Powders-solid state reaction; X-ray methods

1. Introduction

Microwave dielectric materials have been used widespread for applications such as oscillators and filters in the microwave communications. The desirable properties in microwave dielectric materials are a high dielectric constant (ε_r), low dielectric loss ($\tan\delta$) (i.e. high quality factor ($Q{\cdot}f$)), and temperature coefficient of resonate frequency (τ_f) close to zero. Materials with a high dielectric constant are possible to reduce the size of microwave devices because the wavelength (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$ of the wavelength (λ_o). One of dielectric materials with high dielectric constant (ε_r) is tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions. Fig. 1 shows the crystal structure of tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions. The crystal data of R = Sm system with $x = 0.71$ is as follows: orthorhombic, *Pbnm* (No. 62), $a = 12.13$ (1), $b = 22.271$ (5), $c = 7.639$ (5) Å and $Z = 2$.[1] These solid solutions are constituted of Ti(1) – Ti(5) octahedral sites with Ti, $A2(1) - A2(2)$ pentagonal sites with Ba and $A1(1) - A1(5)$ rhombic sites with rare earth and Ba. These solid solutions have superlattice with doubled c-axis by tilting of TiO_6 octahedron (Fig. 2).[1] The relationship between these crystal structure and microwave dielectric properties has been discussed. Ohsato et al.[2] reported that the quality factor ($Q{\cdot}f$) of R = Sm system increases from 429 to 10548 GHz as increasing x value from 0.3 to 2/3. The structural formula of R = Sm system with $0 \le x \le 2/3$ is as follows: $[Ba_{2-3x}Sm_{8+2x}V_x]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ (V: Vacancy). Where $0 \le x < 2/3$, Ba ions occupy $A1$-sites that is slightly small for Ba ions, and create inner strain. This inner strain makes quality factor ($Q{\cdot}f$) decrease. On the other hand, quality factor ($Q{\cdot}f$), where $x = 2/3$, shows maximum value, which resulted from the lowest inner strain and the highest lattice stability. These behaviors are lead by rare earth ions and Ba ions occupying $A1$ and $A2$-sites, respectively. Imaeda et al.[3] studied $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ (BSST) solid solutions where $x = 0.6$ and $0 \le \alpha \le 0.2$. As according to this report, a quality factor ($Q{\cdot}f$) of these solid solutions was improved by increasing lattice stability, which resulted from substituting Sr ions with smaller ionic radius for Ba ions.

In this paper, the crystal structure of BSST solid solutions is demonstrated. Furthermore, microwave dielectric properties of BSST solid solutions, where $x = 0$ and $\alpha = 0$–1/3, are reported. Relationship between crystal structure and microwave dielectric

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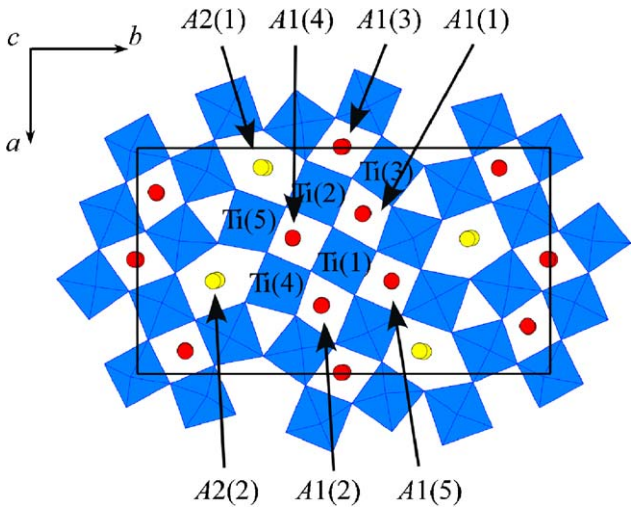

Fig. 1. The tungstenbronze-type-like structure of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions.

properties is discussed from the viewpoint of structural formula and occupational state of large cations such as Ba, Sr and Sm in $A1$-sites.

2. Experimental

Single crystal of BSST solid solutions was synthesized by cooling method from the liquid phase. High purity $BaCO_3$, $SrCO_3$, Sm_2O_3 and TiO_2 were weighed out composition $x = 0$ and $\alpha = 1/3$. After mixing for 24 h in ethanol, the dried mixture was calcined in air at 1000 °C for 2 h. The calcined powder was melted at 1650 °C for 5 h and cooled 2 °C/h for 1650–1400 °C, 4 °C/h for 1400–1300 °C, 1 °C/min for 1300–1050 °C, and 5 °C/min for 1050 °C to room temperature. The X-ray diffraction data were obtained by a single crystal diffractometer with imaging plate (Rigaku; R-AXIS RAPID). The structural parameters were refined by a full-matrix least-squares method that is termed RADY (S. Sasaki, 1982).[4]

Ceramics resonators of BSST solid solutions, where $x = 0$ and $\alpha = 0$–1/3, were synthesized conventional solid-state reaction method. High purity $BaCO_3$, $SrCO_3$, Sm_2O_3 and TiO_2 were weighed out various α values from 0 to 1/3 and ball-milled for 24 h in ethanol. The mixture was dried and calcined in air at 1250 °C for 2 h. The calcined powders with organic binder were mixed using alumina mortar and pressed into discs 12 mm in diameter. These discs were sintered in air at 1300 °C for 2 h. Sintered discs were polished and annealed in air at 1000 °C for 2 h. Microwave dielectric properties were measured by the Hakki & Coleman method.[5] The crystalline phase of samples were identified by X-ray diffraction using Cu Kα with Ni filter (Phillips; X'Pert MPD).

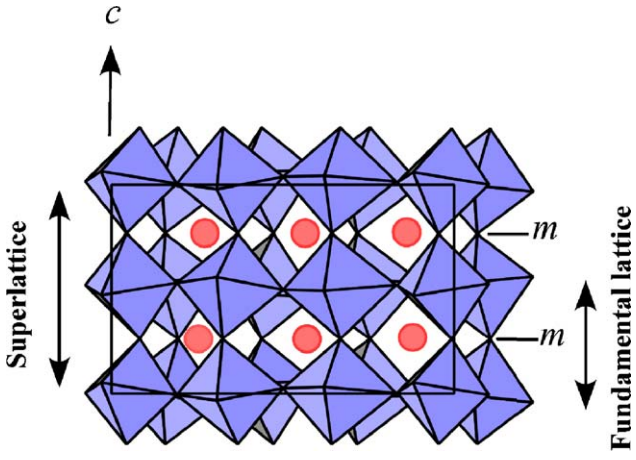

Fig. 2. Superlattice and fundamental lattice of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions.[1]

3. Results and discussion

Crystal data of BSST solid solutions with superlattice were as follows: orthorhombic, *Pbnm* (No. 62), $a = 12.174$ (4), $b = 22.378$ (9), $c = 7.670$ (2) Å and $Z = 2$. The structural parameters were refined with compositions which were fixed at $x = 0$ and $\alpha = 1/3$. According to the refined results, R-factor and weighted R-factor were 4.01 and 5.14%, respectively. Structural parameters of BSST ($x = 0$, $\alpha = 1/3$) solid solutions are listed in Table 1. All Sr ions occupied $A1$-sites. Especially, $A1(1)$ and $A1(3)$-sites had more amount of Sr ions as compared with another $A1$-sites.

The XRD patterns of sintered ceramics, where $0 \leq \alpha \leq 1/3$, are shown in Fig. 3. Ohsato et al.[6] reported that the domain of solid solutions is limited by the composition, where $0.3 \leq x \leq 0.7$, in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions. Therefore, BSST solid solutions, where $x = 0.3$, were obtained in the case of the starting composition that was weighed out as $x = 0$. As a result, Ba and Sr were surplus and formed secondly phases such as (Ba, Sr)TiO_3 solid solutions with all composition α.

Microwave dielectric properties of BSST solid solutions, where $x = 0$ and $\alpha = 0$–1/3, are shown in Fig. 4. Quality factor ($Q{\cdot}f$) of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$, shows extremely low values.[1] However, quality factor ($Q{\cdot}f$) of BSST solid solution, where $x = 0$, was improved with increasing α. The aforesaid remarked that BSST solid solutions, where $x = 0.3$, are obtained in the case of the starting composition that is weighed out as $x = 0$. Structural formula of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0.3$, is as follows: $[Ba_{1.1}Sm_{8.6}V_{0.3}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ (V: Vacancy). When Ba ions are substituted by Sr ions, at first Ba ions in

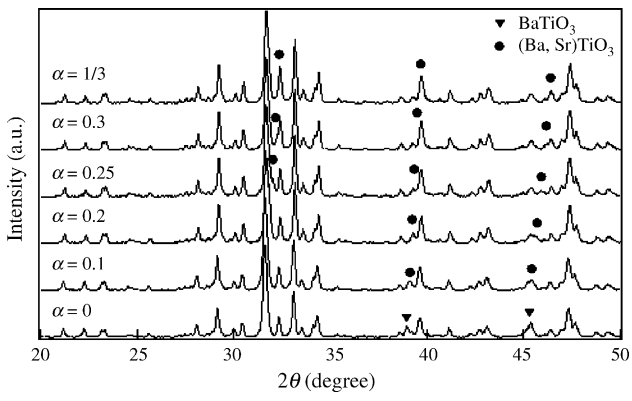

Fig. 3. XRD patterns of BSST solid solutions where $x = 0$ and $\alpha = 0$ to 1/3.

Table 1
Structural parameters of BSST solid solutions where $x = 0$ and $\alpha = 1/3$

	Site	*g*	*x*	*y*	*z*	*Beq*/Å
Ti(1)	4*a*	0.5	0	0	0	0.66 (3)
Ti(2)	8*d*	1.0	0.19926 (25)	0.43528 (25)	−0.00024 (57)	0.65 (2)
Ti(3)	8*d*	1.0	0.39884 (24)	0.10731 (14)	0.00473 (54)	0.69 (2)
Ti(4)	8*d*	1.0	0.11621 (24)	0.16446 (14)	0.00150 (56)	0.67 (2)
Ti(5)	8*d*	1.0	0.33724 (24)	0.26068 (14)	0.00172 (59)	0.71 (2)
*A*2(1)-Ba	4*c*	0.5	0.08784 (17)	0.30085 (9)	0.25	1.30 (1)
*A*2(2)-Ba	4*c*	0.5	0.59695 (16)	0.18602 (9)	0.25	1.36 (1)
*A*1(1)-Sm	4*c*	0.335	0.19400 (15)	0.04544 (8)	0.25	0.81 (1)
*A*1(1)-Sr	4*c*	0.161	0.19400	0.04544	0.25	0.81
*A*1(2)-Sm	4*c*	0.430 (3)	0.70529 (14)	0.44809 (7)	0.25	0.82 (1)
*A*1(2)-Sr	4*c*	0.078 (6)	0.70529	0.44809	0.25	0.82
*A*1(3)-Sm	4*c*	0.387 (3)	0.99951 (16)	0.49466 (8)	0.25	0.80 (1)
*A*1(3)-Sr	4*c*	0.118 (5)	0.99951	0.49466	0.25	0.80
*A*1(4)-Sm	4*c*	0.414 (3)	0.40392 (14)	0.37743 (7)	0.25	0.77 (1)
*A*1(4)-Sr	4*c*	0.082 (6)	0.40392	0.37743	0.25	0.77
*A*1(5)-Sm	4*c*	0.435 (3)	0.91056 (14)	0.12439 (7)	0.25	0.85 (1)
*A*1(5)-Sr	4*c*	0.061 (6)	0.91056	0.12439	0.25	0.85
O(1)	4*c*	0.5	0.0974 (16)	0.1716 (9)	0.25	1.16 (14)
O(2)	4*c*	0.5	0.6049 (16)	0.3588 (10)	0.25	1.32 (15)
O(3)	8*d*	1.0	0.4190 (10)	0.1929 (6)	0.0053 (24)	1.47 (10)
O(4)	8*d*	1.0	0.6828 (10)	0.2627 (5)	0.0221 (21)	0.93 (10)
O(5)	4*c*	0.5	0.3123 (16)	0.2758 (11)	0.25	1.36 (16)
O(6)	4*c*	0.5	0.8416 (15)	0.2251 (9)	0.25	1.02 (15)
O(7)	8*d*	1.0	0.3749 (10)	0.0191 (6)	0.0167 (23)	1.62 (11)
O(8)	4*c*	0.5	0.2315 (17)	0.4440 (10)	0.25	1.38 (15)
O(9)	4*c*	0.5	0.6742 (18)	0.0550 (10)	0.25	1.55 (16)
O(10)	8*d*	1.0	0.2429 (10)	0.1130 (6)	0.0214 (21)	1.46 (11)
O(11)	4*c*	0.5	0.4840 (16)	0.4797 (9)	0.25	1.09 (14)
O(12)	8*d*	1.0	0.0389 (11)	0.0795 (6)	0.0516 (20)	1.40 (11)
O(13)	8*d*	1.0	0.7662 (11)	0.1372 (5)	0.0169 (21)	1.37 (11)
O(14)	8*d*	1.0	0.8419 (10)	0.0197(6)	0.0383 (18)	1.16 (11)
O(15)	8*d*	1.0	0.0562 (11)	0.4052 (7)	0.0449 (18)	1.33 (10)
O(16)	8*d*	1.0	0.4654 (11)	0.3125 (6)	0.0228 (21)	1.41 (11)
O(17)	4*c*	0.5	0.4238 (16)	0.1006 (9)	0.25	0.82 (14)
O(18)	4*c*	0.5	0.8810 (15)	0.4047 (9)	0.25	1.14 (15)

*A*1-sites are substituted by Sr ions. Structural formula becomes $[Ba_{1.1-5.1\alpha}Sr_{5.1\alpha}Sm_{8.6}V_{0.3}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ at this point. After all Ba ions in *A*1-sites are substituted by Sr ions, Ba ions in *A*2-sites are substituted by Sr ions and vacancies in *A*1-sites are filled by Sr ions. Therefore, structural formula becomes $[Sr_{5.1\alpha}Sm_{8.6}V_{0.3-5.1(\alpha-0.216)}]_{A1}[Ba_{4-5.1(\alpha-0.216)}V_{5.1(\alpha-0.216)}]_{A2}Ti_{18}O_{54}$. All Ba ions in *A*1-sites are substituted by Sr, where $\alpha \approx 0.216$, and all vacancies in *A*1-sites are filled by Sr ions, where $\alpha \approx 0.275$. As a result, decreasing of inner strain and increasing of lattice stability by substitution made quality factor ($Q{\cdot}f$) increase significantly up to 7189 GHz at α value ranging between 0.2 and 0.3.

Dielectric constant (ε_r) decreased linearly in the range from 105 to 91 with increasing α. Ba ions are substituted by Sr ions with increasing α. Dielectric constant (ε_r) is affected by ionic polarizability,[7] where Ba ion and Sr ion have 6.40 and 4.24, respectively. Ohsato[1] reported that dielectric constant (ε_r) of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions is affected by TiO_6 octahedral volume. In the perovskite structure, the polarity of the Ti ions in the TiO_6 octahedron is produced as a result of the large octahedral volume. Diffraction peaks in Fig. 3 shifted to high 2θ—angle with increasing α. Decrease of dielectric constant (ε_r) with increasing α in BSST solid solutions, where $x = 0$, is also affected by decreasing of TiO_6 octahedral volume as following lattice contraction.

Temperature coefficient of resonant frequency (τ_f) decreased significantly in the range from 355 to 61 ppm/°C at α value ranging between 0.25 and 0.32. Imaeda et al.[3] reported that temperature coefficient of resonant frequency (τ_f) of BSST solid solutions with no secondly phases, where $x = 0.6$ and $0 \leq \alpha \leq 0.2$, shows values between −16.7 and 0.4 ppm/°C. Therefore, significant change of the temperature coefficient of resonant frequency (τ_f) in BSST solid solutions, where $x = 0$, should be affected by secondly phases such as (Ba, Sr)TiO_3 solid solutions.

4. Conclusions

Crystal structure of BSST solid solutions has been investigated. All Sr ions occupied *A*1-sites. Especially, *A*1(1) and *A*1(3)-sites had more amount of Sr ions as compared with another *A*1-sites. The effects of substituting Sr ions for Ba ions

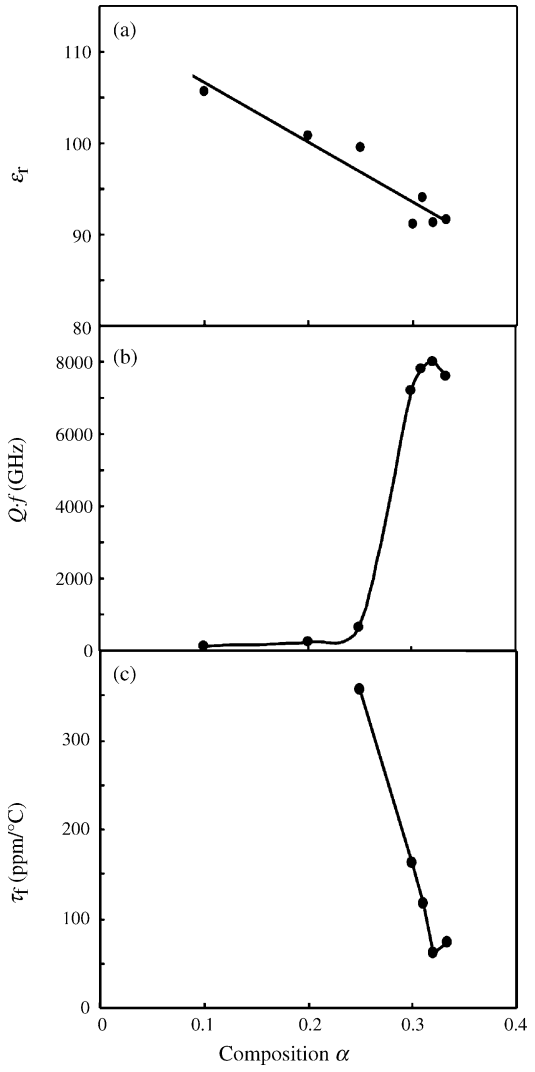

Fig. 4. Microwave dielectric properties of BSST solid solutions where $x = 0$ and $\alpha = 0$ to 1/3. (a) Dielectric constant (ε_r); (b) quality factor ($Q{\cdot}f$); (c) temperature coefficient of resonant frequency (τ_f).

in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions have been studied in terms of microwave dielectric properties, structural formula and occupational state in $A1$-sites. Behavior of quality factor ($Q{\cdot}f$) is related with the strain in the crystal structure due to substitute Sr ions for Ba ions. Under the condition, where $x = 0.3$, structural formula of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions is as follows: $[Ba_{1.1-5.1\alpha}Sr_{5.1\alpha}Sm_{8.6}V_{0.3}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$. $A1$-sites have Ba ions and vacancies. Substituting Sr ions for Ba ions and filling vacancies in $A1$-sites makes relax inner strain and increase lattice stability. As consequences, quality factor ($Q{\cdot}f$) is increased. Dielectric constant (ε_r) is affected by TiO_6 octahedral volume and ionic polarizability of Ba ions and Sr ions. Temperature coefficient of resonant frequency (τ_f) of BSST solid solutions, where $x = 0$, is affected by secondly phases.

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