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Microwave dielectric properties of tungstenbronze type like $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd) solid solutions

Isao Kagomiya*, Masafumi Suzuki, Ken-ichi Kakimoto, Hitoshi Ohsato

Materials Science and Engineering, Nagoya Institute of Technology, Nagoya 466-8555, Japan

Abstract

Tungstenbronze type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm or Nd) dielectric ceramics reveal high quality factor $Q{\cdot}f$ as well as high dielectric constant ε_r. We have investigated the effect of Sr substitution for Ba ions on the microwave dielectric properties of the compounds. $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm or Nd) ceramics were prepared in the composition ranges of $x = 0$–0.2 and $\alpha = 0$–0.312 and the microwave dielectric properties were investigated. $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, where $x = 0.1$ and $\alpha = 0.298$, and $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, where $x = 0.2$, $\alpha = 0.296$ revealed remarkably higher $Q{\cdot}f$ value among the solid solutions, indicating that $Q{\cdot}f$ increased with substituting Sr ions into Ba ions at the rhombic $A1$-site. This fact suggests that relaxation of local distortions at the $A1$-sites is closely related to improvement of $Q{\cdot}f$.

Keyword: Microwave dielectrics; Quality factor; Tungstenbronze-type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$; $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$

1. Introduction

Three dielectric properties: (1) high dielectric constant ε_r, (2) high quality factor $Q{\cdot}f$ and (3) temperature coefficient of resonant frequency τ_f with nearly zero are of prime importance to develop miniaturized applications for high frequency wireless telecommunication. Tungstenbronze type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = La, Sm and Nd) is a possible candidate for the applications,[1–4] since this dense ceramics possesses high dielectric constant ε_r as well as high quality factor $Q{\cdot}f$.

As shown in Fig. 1, the crystal structure of the compounds belongs to orthorhombic (space group: *Pnma*). Five kinds of $Ti^{4+}O_6$ octahedral units connect each other throughout common sharing oxygen ions. Rhombic $A1$-site or pentagonal $A2$-site is surrounded by the octahedron network. The $A1$-site is preferentially occupied by Ba ions and the $A2$-site by R ions, since site volume of the $A1$-site is larger than that of the $A2$-site.

The $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd), where $x = 2/3$, has been found to be the highest $Q{\cdot}f$ value (10,548 GHz) in the Sm substituted solid solutions.[2] This composition sample completely separates Ba ions into $A1$-sites and R ions into $A2$-sites, suggesting that the local distortion of the $A1$- or the $A2$-site is strongly correlated to the quality factor $Q{\cdot}f$. In this study, we tried another substitution to investigate systematic influence of cation substitutions on microwave dielectric properties. Microwave dielectric properties of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ and $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ were investigated in the composition range of $x = 0$–0.2, $\alpha = 0$–0.316.

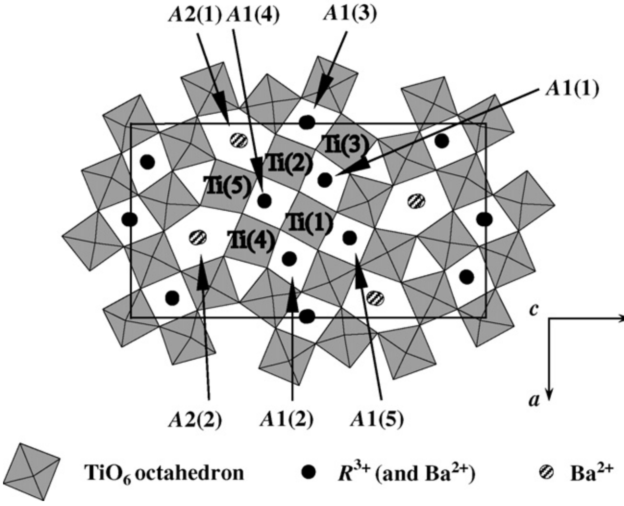

Fig. 1. Schematic illustration of crystal structure of tungstenbronze type like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm or Nd).

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[*] Corresponding author. Tel.: +81 52 735 7368; fax: +81 52 735 5284. *E-mail address:* kagomiya@nitech.ac.jp (I. Kagomiya).

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2. Experimental methods

$(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm or Nd) solid solutions, where $x = 0$–0.2, $\alpha = 0$–(1/3), were prepared by conventional solid-state reaction method. The desired amounts of $BaCO_3$ (98.74% purity), $SrCO_3$ (99.5% purity), TiO_2 (99.8% purity) and R_2O_3 (99.9% purity) were ball-milled with ethanol for 24 h. After drying, the ground powder was calcined in air at 1250 °C for 2 h. The obtained powder with an organic binder was uniaxially pressed into a disk shape with diameter of 12 mm and then sintered in air at 1300 °C for 2 h.

The crystal phases of the solid solutions were characterized by powder X-ray diffraction using Cu *Kα* radiation (Philips: X'pert MPD). The microwave dielectric properties of the samples were investigated by the Hakki and Coleman method[5] in the TE_{011} mode using a network analyzer (Agilent Technology: HP 8757).

3. Results and discussion

3.1. X-ray characterization of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions

X-ray diffraction patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd) solid solutions, where $x = 0$, $\alpha = 0$–(1/3), are illustrated in Figs. 2 and 3. Bragg peaks corresponding to the tungstenbronze type like crystal structure were observed as main phase. An additional phase of (Ba, Sr)TiO_3 solid solutions was also observed in the full α range, indicating that no single phase can be obtained in the case of $x = 0$. Peak positions of the secondary phase shifted to higher angle with increasing the composition α, suggesting that Ba ions ($r_{12CN} = 1.61$ Å) in $BaTiO_3$ were substituted into smaller Sr ions ($r_{12CN} = 1.44$ Å) with increasing the composition α.[6]

XRD patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, where $x = 0.1$, $\alpha = 0$–0.316, and $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, where $x = 0.2$, $\alpha = 0$–0.296, are illustrated in Figs. 4 and 5. A tungstenbronze type like oxide was observed as main phase in the all α compositions. Amount of secondary phase of (Ba, Sr)TiO_3 decreases with increasing the composition α. No secondary phase was observed in the α range of higher than 0.2 for $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.1$), and higher than 0 for $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 0.2$).

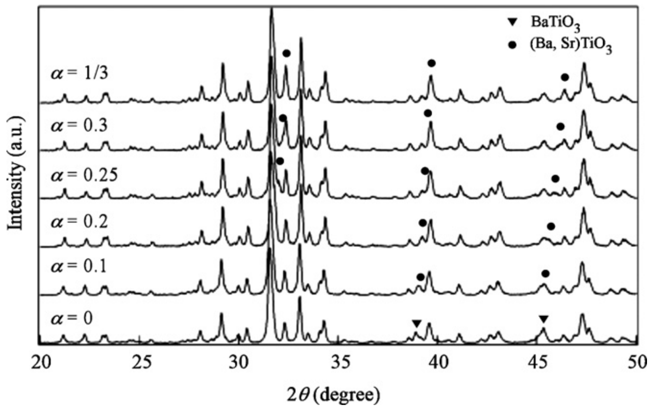

Fig. 2. XRD patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$ and $\alpha = 0$–(1/3).

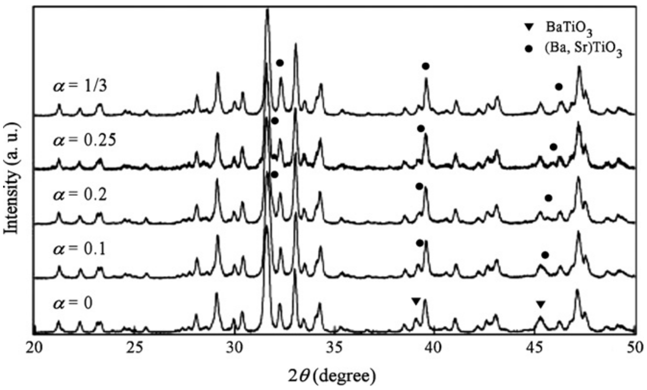

Fig. 3. XRD patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$ and $\alpha = 0$–(1/3).

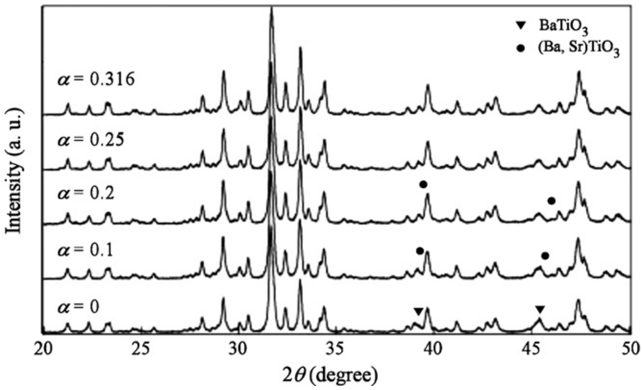

Fig. 4. XRD patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0.1$ and $\alpha = 0$–0.316.

3.2. Microwave dielectric properties of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$

Microwave dielectric properties of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd) are shown in Figs. 6 and 7. Dielectric constant ε_r of the $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}R_{8+2x}Ti_{18}O_{54}$ ($x = 0$) was

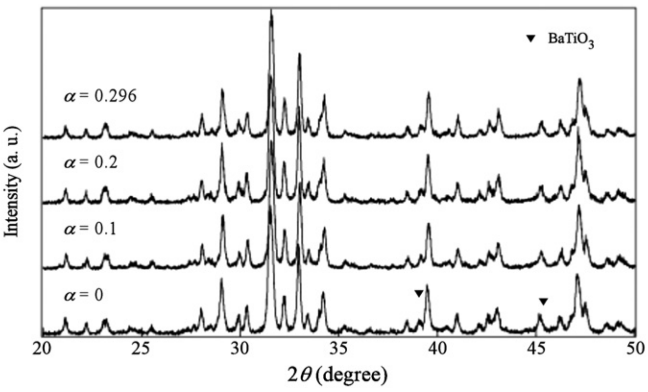

Fig. 5. XRD patterns of $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0.2$ and $\alpha = 0$–0.296.

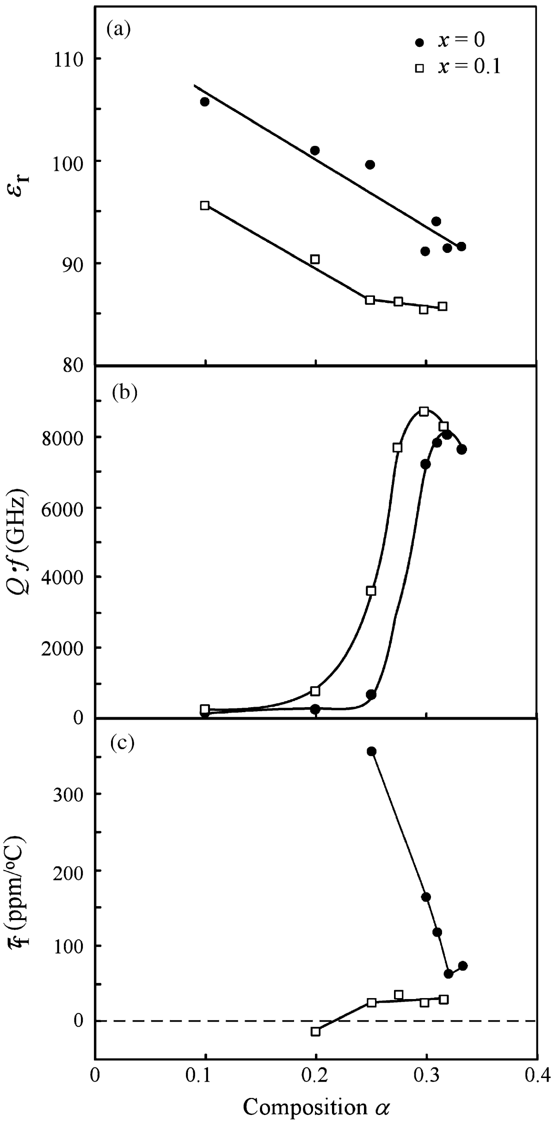

Fig. 6. Dielectric constant ε_r (a), quality factor $Q{\cdot}f$ (b) and temperature coefficient of resonant frequency τ_f (c) of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$, $\alpha = 0$–(1/3) or $x = 0.1$, $\alpha = 0$–0.316.

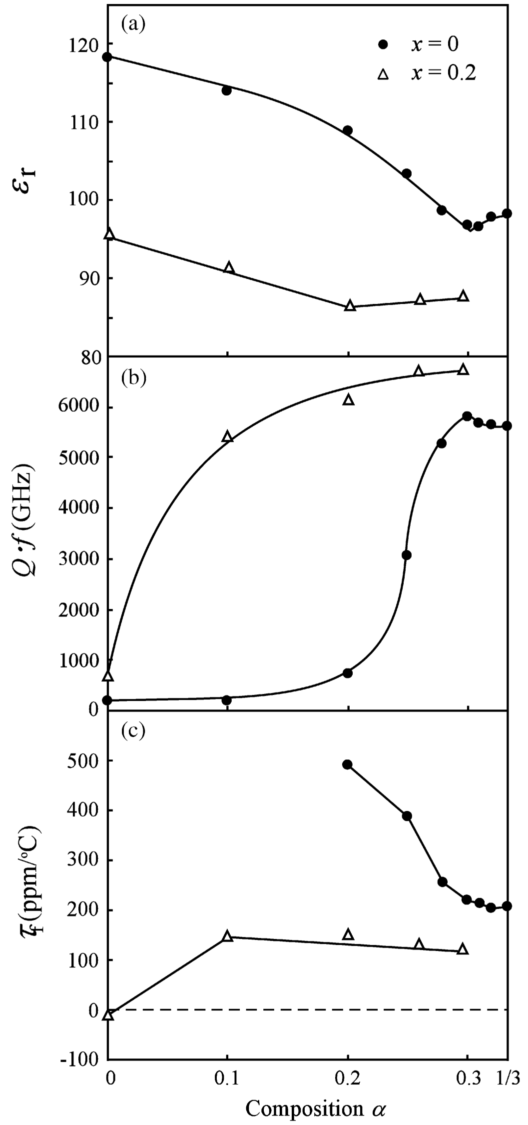

Fig. 7. Dielectric constant ε_r (a), quality factor $Q{\cdot}f$ (b) and temperature coefficient of resonant frequency τ_f (c) of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0$, $\alpha = 0 - 1/3$ or $x = 0.2$, $\alpha = 0$–0.296.

higher than that of the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ ($x \neq 0$). ε_r of the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.1$) varies more abruptly in the range of $\alpha = 0.1$–0.225, compared to the α of higher than 0.225. These results suggest that ε_r of the $(Ba_{1-\alpha}Sr_\alpha)_6R_8Ti_{18}O_{54}$ ceramics are affected by dielectric constant of the secondary phase (Ba, Sr)TiO_3. In fact, the (Ba, Sr)TiO_3 solid solutions possess higher dielectric constant than the tungstenbronze type like $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$. The ε_r of the (Ba, Sr)TiO_3 solid solutions abruptly decrease with substituting Ba into Sr ions. On the other hand, ε_r of the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, where $x = 0.1$, $\alpha \geq 0.25$, as well as $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, where $x = 0.2$, $\alpha \geq 0.1$, is considered to be intrinsic one, because no secondary phase (Ba, Sr)TiO_3, was observed as described in Section 3.1.

The quality factor $Q{\cdot}f$ of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ was improved by increasing the composition α (Figs. 6 and 7). At $\alpha = 0.298$, the maximum of $Q{\cdot}f$, 8706 GHz, was obtained in the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.1$) (Fig. 6(b)). $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ solid solutions, where $x = 0.2$, $\alpha = 0.296$, reveals the highest $Q{\cdot}f$ value (6736 GHz) in the Nd solid solutions (Fig. 7(b)). It is suggested that the improvement of the $Q{\cdot}f$ is closely related to the crystal structure.

The structural formula of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ ($x = 0.1$) is classified into two parts as follows:

$$0 \leq \alpha < 0.298: \ [Ba_{1.7-5.7\alpha}Sr_{5.7\alpha}Sm_{8.2}V_{0.1}]_{A1}[Ba_4]_{A2} Ti_{18}O_{54} \ (V: \ \text{vacancy}) \quad (1)$$

$$0.298 \leq \alpha \leq 0.316: \ [Sr_{5.7\alpha}Sm_{8.2}V_{0.1-5.7(\alpha-0.298)}]_{A1} [Ba_{4-5.7(\alpha-0.298)}V_{5.7(\alpha-0.298)}]_{A2}Ti_{18}O_{54} \quad (2)$$

According to single crystal X-ray diffraction analysis,[7] Sr^{2+} ions of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ are preferably substituted into the $A1$-sites in the range of $0 \leq \alpha < 0.298$. Then, the $A1$-sites are occupied by only Sr ions at $\alpha = 0.298$, resulting in following structure formula: $[Sr_{1.7}Sm_{8.2}V_{0.1}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$. No vacancies at the $A2$-sites are present in this composition. With further Sr substitution, $A2$-sites of Ba ions were replaced into Sr ions. Quality factor $Q{\cdot}f$ of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$, where $x = 0.1$, $\alpha = 0.298$, indicates the maximum value of 8706 GHz, supposing that the local lattice distortion was relaxed by substituting larger Ba ions of the $A1$-site into smaller Sr ions. In addition, crystal structure of $\alpha = 0.298$ possesses no vacancies at $A2$-sites. It is also related to improvement of the quality factor. When α is more than 0.298, vacancies appear at $A2$-sites, suggesting that the vacancies cause a decrease of quality factor. Quality factor of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 0.2$) can be explained by the same consideration, though there is a difference between the two. $Q{\cdot}f$ of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ abruptly varied in the range of $0.25 \leq \alpha \leq 0.316$. In contrast, $Q{\cdot}f$ of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x = 0.2$) varied more slowly in the range of $0.25 \leq \alpha \leq 0.316$. The abrupt decrease of $Q{\cdot}f$ in the Sm solid solutions is possibly due to the ionic radius of ions substituted for Ba ions. Ionic radii of Sm, Nd and Ba are as follows: $Sm^{3+}{}_{12CN}$ (=1.24 Å) $\leq$ $Nd^{3+}{}_{12CN}$ (=1.27 Å) $\leq$ $Ba^{2+}{}_{12CN}$ (=1.61 Å).[6] Thus, difference in the ionic radius between Sm^{3+} and Ba^{2+} is larger than that between Nd^{3+} and Ba^{2+}. We suppose that the larger difference contributes to larger local distortion at $A1$-site, resulting in abrupt variation of $Q{\cdot}f$ in the Sm solid solutions.

Temperature coefficient of resonant frequency of τ_f for $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd), where $x = 0$, was characterized by larger value than that of $x \neq 0$ and varied remarkably with increasing the composition α. τ_f of the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}R_{8+2x}Ti_{18}O_{54}$ ($x = 0$) ceramics was possibly affected by slight amount of the secondary phase (Ba, Sr)TiO_3, since $BaTiO_3$ possesses higher τ_f (1650 ppm/°C). On the other hand, intrinsic τ_f value might be obtained in the $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.1, \alpha = 0.25$–0.316) and the $(Ba_{1-\alpha}Nd_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.2$, $\alpha = 0.1$–0.296).

4. Conclusion

Microwave dielectric properties of $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, where $x = 0$, 0.1, and $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, where $x = 0$, 0.2, were investigated in the composition range of $\alpha = 0$–(1/3). Dielectric constant ε_r or temperature coefficient of resonant frequency τ_f was significantly affected by the secondary phase (Ba, Sr)TiO_3. Quality factor $Q{\cdot}f$ of the solid solutions increased with substituting Sr ions for Ba ions. $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, where $x = 0.1$, $\alpha = 0.298$, reveals the highest $Q{\cdot}f$ value (8706 GHz) in the Sm solid solutions. On the other hand, $(Ba_{1-\alpha}Sr_\alpha)_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$, where $x = 0.2$, $\alpha = 0.296$, reveals the highest $Q{\cdot}f$ value (6736 GHz) in the Nd solid solutions. This improvement infers to be due to the relaxation of local distortions at $A1$-sites caused by substituting smaller Sr ions for Ba ions.

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