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Effects of Sm substitution on microwave dielectric properties of $Ba_4La_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics

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ABSTRACT

Sm substitution for La was investigated for the modification of $Ba_4La_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics. A single-phase solid solution with tungstenbronze-like structure formed in the whole range of y values in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics. As Sm content increased, there was a constriction of the *b*-axis and *c*-axis, and decrease in the cell volume. The *Qf* value did not obey the mixing rules and it varied nonlinearly with composition y. Small levels of Sm substitution improved the *Qf* value with a decrease of dielectric constant. The temperature coefficient of resonant frequency varied from positive to negative and decreased continuously with the increase of Sm content. A near zero τ_f value ($-2.38 \times 10^{-6}/^\circ C$) was obtained at the composition of $y = 0.7$.

1. Introduction

Microwave dielectric materials play a key role in our global society with a wide range of applications, from terrestrial and satellite communication including GPS and DBS TV to environmental monitoring via satellite. The desirable properties in microwave dielectric resonators are high dielectric constant (ε_r), which can reduce the dimension of resonators, low dielectric loss (or high Q value, usually reported in terms of *Qf*, where f is the resonant frequency) and near zero temperature coefficient of resonant frequency (τ_f). In the line of the available microwave dielectric materials, $BaO–R_2O_3–TiO_2$ (R: rare earth) systems are widely used in communication devices because of their high dielectric constants in the range of 80–110, good quality factors (*Qf* = 1800–10,000 GHz), and a low temperature coefficient [1]. Although many compounds have been reported in this system, the general phase with excellent microwave dielectric properties is now accepted as a solid solution of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ with the tungstenbronze-like structure [2]. The structure of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ compounds has been investigated by many researchers [3–5]. The basic structure of such compounds includes elements of the tungstenbronze framework in which corner sharing TiO_6 octahedra form networks of pentagonal, rhombic and triangular channels. The *Qf* exhibits the largest value at $x = 2/3$ in which Ba and R ions occupy separately pentagonal and rhombic channels, respectively [6].

$Ba_{6-3x}La_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramic has the highest ε_r of 110 in the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ family, but it has not been so much focused in for the relatively low *Qf* value (∼1800 GHz) and the large positive τ_f (∼300 ppm/°C) [7]. At present, many studies mainly focus on improving dielectric properties by ionic substitution [7–9] as well as doping [10–12]. A number of efforts are being made to reduce the τ_f of dielectric resonators by combing two materials with positive and negative τ_f [13,14]. A near zero τ_f value has be obtained by adjusting the Ba/Sm ratio in $Ba_{2-x}Sm_{4+2x/3}Ti_9O_{26}$ ceramics [15]. Combining different rare earth cations R^{3+} under the formation of solid solutions in the single-phase state of the $Ba_{6-3x}(La_{1-y}R_y)_{8+2x}Ti_{18}O_{54}$ compounds is also a possible solution to the limitation of the low *Qf* value and poor temperature stability. Sm substitution for La has been found effective on improving *Qf* value and reducing τ_f in $Ba_{6-3x}La_{8+2x}Ti_{18}O_{54}$ ceramics [7,16]. A significant improvement of *Qf* value can achieved by incorporation of small levels of Zr into $Ba_4La_{9.33}Ti_{18}O_{54}$ ceramics. The influence of ionic substitution for rare earth ions on the dielectric properties of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ systems ceramics has been widely investigated, however, until now there is no report dealing with the effects of Sm/Zr co-substitution upon the microstructures and microwave properties of $Ba_4La_{9.33}Ti_{18}O_{54}$ solid solutions.

In this study, ceramics with $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ compositions were prepared via solid-state route. We tried to adjust the microwave dielectric properties by substitution of Sm for La in $Ba_4La_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics and obtain ceramics with good temperature stability. A systematic investigation on the phase constitution, microstructures, and microwave dielec-

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tric properties of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics has been performed.

2. Experimental

$Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics were prepared by the conventional solid-state reaction. High purity (>99.0%) $BaCO_3$, La_2O_3, Sm_2O_3, ZrO_2 and TiO_2 powders were weighed on the basis of the stoichiometric composition. Sm composition y varied from 0 to 1. The mixtures were ground for 6 h in a polyethylene bottle with alcohol and zirconia balls. The wet slurries were dried and calcined at 1200 °C in air for 2 h. Then the powders added with PVA organic binder (8 wt%) were palletized into cylindrical compacts of 12 mm in diameter and 5–6 mm in thickness. The green compacts were firstly heated at 600 °C in air for 2 h to expel the organic binder, and subsequently sintered at 1350–1500 °C in air for 2 h.

The density of the samples was measured using Archimedes' method. The phase constitutions were studied by X-ray diffraction analysis (XRD, ARL X'TRA) using Cu Kα radiation. The polished samples were thermally etched at a temperature 100 °C below that of sintering temperature and the surface morphology was studied by taking scanning electron microscopic (SEM, LEO 1530 VP) pictures. Element composition of the samples was obtained through an energy dispersive analysis of X-rays (EDAX) technique. The EDAX patterns were taken on the LEO 1530 VP scanning electron microscope, operated at 20 keV. The microwave dielectric properties were evaluated at 3–5 GHz by Hakki and Coleman's resonator method [17]. The temperature coefficient of resonant frequency (τ_f) was calculated from the equation:

$$\tau_f = (-1/2\tau_\varepsilon) - \alpha \qquad (1)$$

where α is the linear expansion coefficient ($10 \times 10^{-6}/°C$) [18], τ_ε is the temperature coefficient of dielectric constant evaluated at 1 MHz by an LCR meter (HP4294A) equipped with a thermostat in a temperature range from −20 to 80 °C.

3. Results and discussion

The bulk densities of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics versus sintering temperature are plotted in Fig. 1. The Sm-free ceramics reach their maximum densities for a sintering temperature of 1400 °C, and the densification temperature tends to increase with increasing Sm^{3+} content, and settled on 1450 °C for $y = 0.1$ and $y = 0.3$, 1500 °C for $y = 0.5$, 0.7 and $y = 1$.

The XRD patterns of dense $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics are shown in Fig. 2. These patterns are similar and match with tungstenbronze-like solid solution. All of the peaks are indexed which suggests that $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ($y = 0.1$–1) system forms into a single-phase solid solution in the whole range of y values. It seems that incorporation of Sm does not alter the tungstenbronze-like phase. Moreover, the XRD peaks slightly shift towards higher angles with the increase of Sm content, which suggests the decrease in the cell parameters based on Bragg formula since the Shannon's effective ionic radii of Sm^{3+} (0.124 nm) is smaller than that of La^{3+} (0.136 nm).

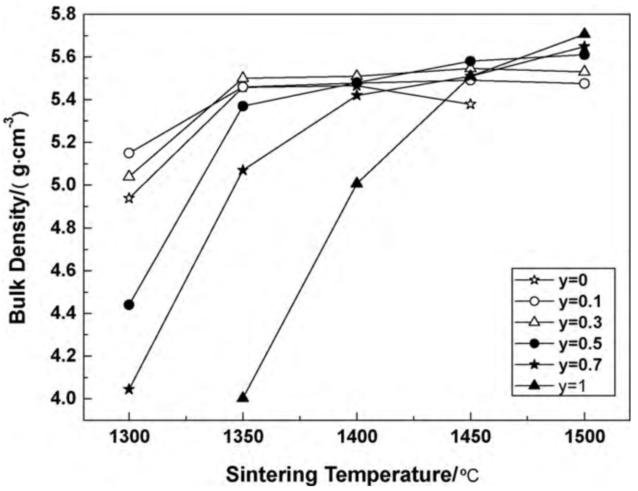

Fig. 1. Relationship between the bulk densities of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics and sintering temperatures.

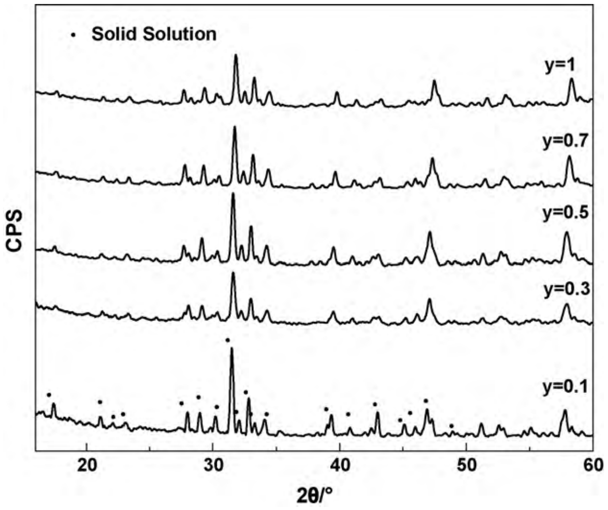

Fig. 2. XRD patterns of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics.

The cell parameters and cell volume of the orthorhombic tungstenbronze-like phase in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics, which are calculated from the main diffraction peaks with the least square refinement, are showed in Fig. 3. As Sm content increases, there is a constriction of the *b*-axis and *c*-axis and decrease in the cell volume. A decrease in volume reflects the incorporation of the smaller Sm^{3+} ions in place of the larger La^{3+} ions.

SEM micrographs taken on thermally etched surfaces of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics are shown in Fig. 4. The microstructures do not show detectable chemical contrast, which also suggests that these ceramics are single phase. It is noticeable that columnar grains in random orientation are observed in both compositions and the average grain size decreases with increasing content of Sm. The grains shorten

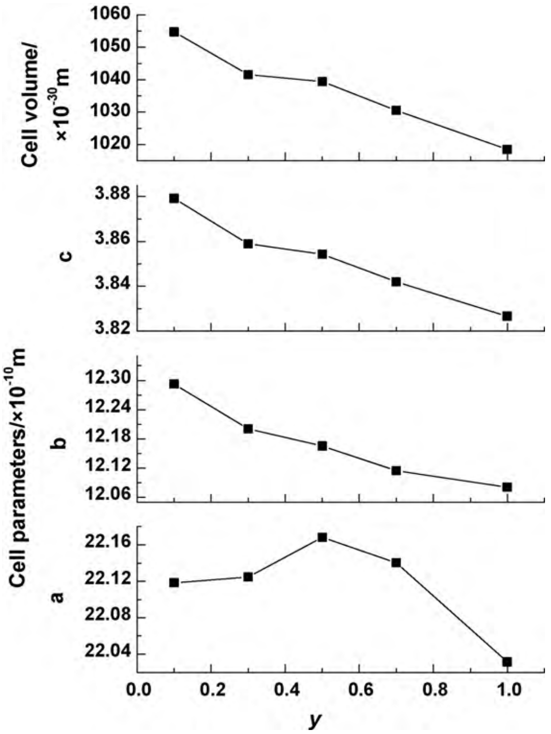

Fig. 3. Cell parameters and cell volume of the tungstenbronze-like phase in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics.

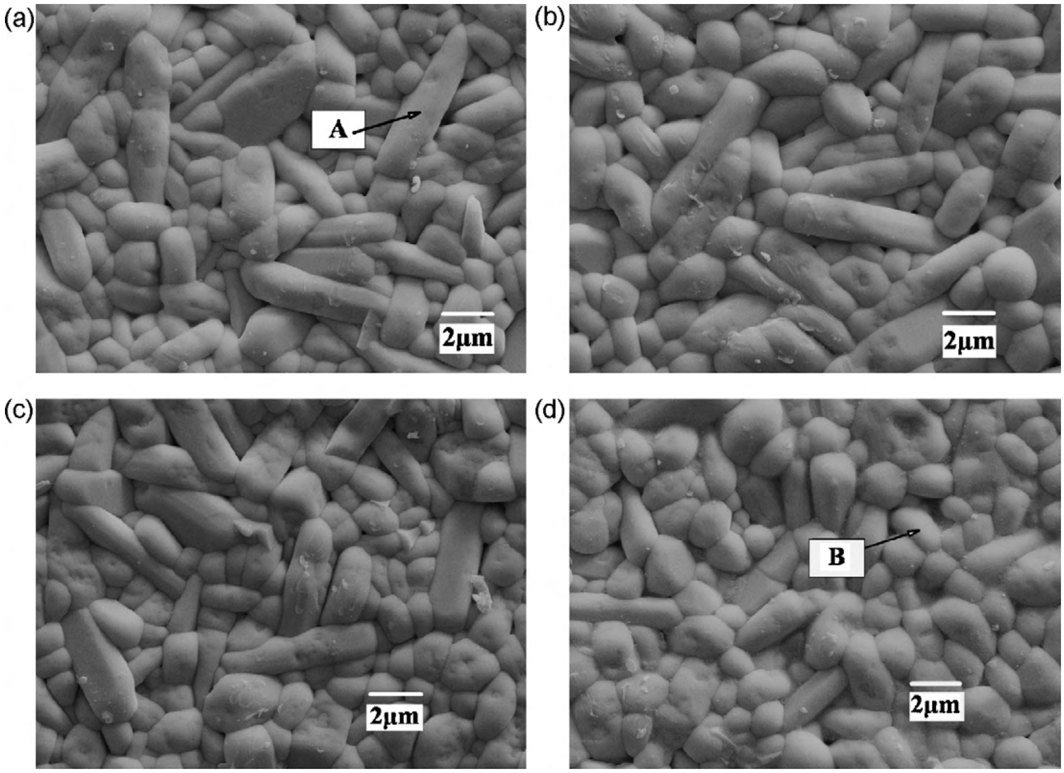

Fig. 4. SEM micrographs taken on thermally etched surfaces of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics: (a) $y = 0.1$, sintered at 1450 °C, (b) $y = 0.3$, sintered at 1450 °C, (c) $y = 0.7$, sintered at 1500 °C and (d) $y = 1$, sintered at 1500 °C.

in length and the packed grains are in the length range of 5–6 μm for $Ba_4(La_{0.9}Sm_{0.1})_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramic (Fig. 4(a)) and 2–3 μm for $Ba_4Sm_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramic(Fig. 4(d)). Element composition of the samples is obtained by EDAX technique. The EDAX pattern of Fig. 5(a) displays five essential constituents such as Ba, La, Sm, Ti, Zr when $y = 0.1$ and the elements contents are near to the stoichiometric composition of $Ba_4(La_{0.9}Sm_{0.1})_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$. On the other hand, when $y = 1$, La is not detected as shown in Fig. 5(b) and the elements contents are near to the stoichiometric composition of $Ba_4Sm_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$.

The microwave dielectric properties of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics are summarized in Figs. 6 and 7. The dielectric constant decreases with increasing Sm content y, which has a similar trend with that of the cell volume. It varies from 86.8 to 74.9 as y increasing from 0 to 1. The Qf value varies nonlinearly with composition y. As for $y = 0.1$, the most attractive microwave dielectric properties of high Qf value is obtained in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics. The maximum value of Qf is 6353 GHz while ε_r is 86.1. And then it decreases to 3037 GHz with the composition up to $y = 1$. The temperature

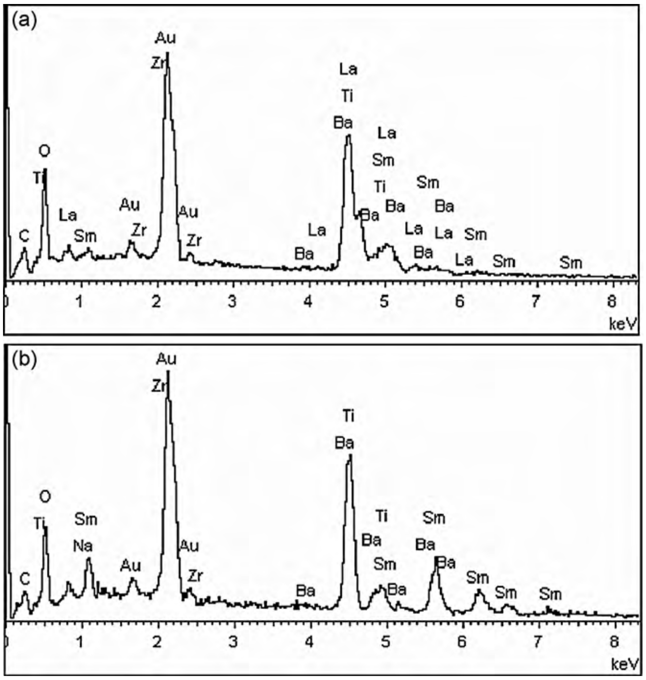

Fig. 5. EDAX of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics: (a) EDAX of A and (b) EDAX of B.

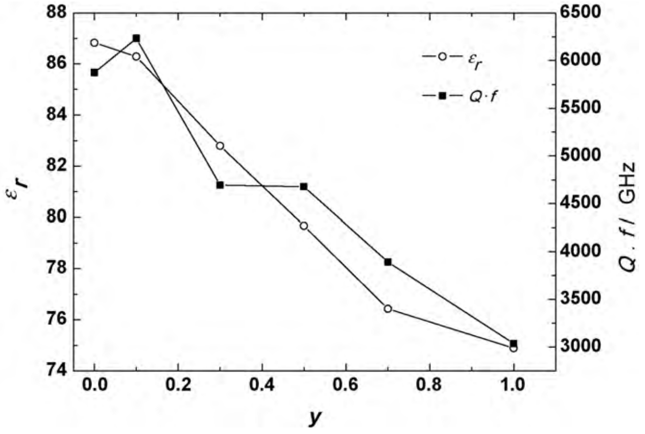

Fig. 6. ε_r and Qf of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics as a function of Sm composition y.

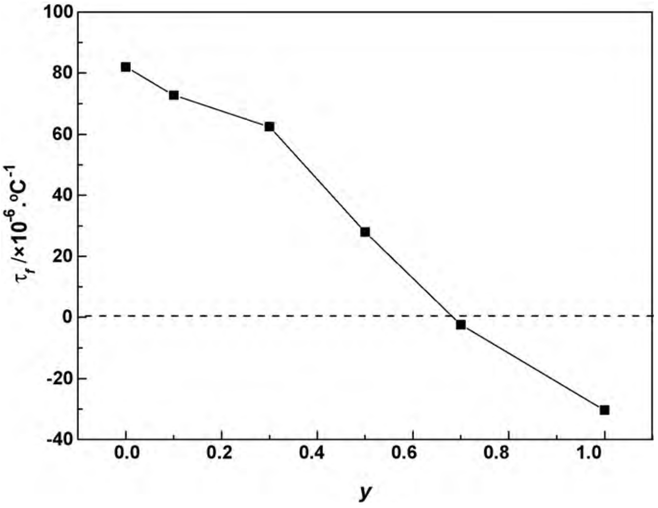

Fig. 7. τ_f of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics as a function of Sm composition *y*.

coefficient of resonant frequency τ_f varies from positive to negative and decreases continuously with increasing *y*, as shown in Fig. 7. The composition at which τ_f becomes $0 \times 10^{-6}/°C$ is around $y = 0.7$. At the composition of $y = 0.7$ with $\tau_f = -2.38 \times 10^{-6}/°C$, the *Qf* value is 3891 GHz. The optimal microwave dielectric characteristics of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics are $\varepsilon_r = 86.1$, $Qf = 6353$ GHz, $\tau_f = 72.7 \times 10^{-6}/°C$ for $y = 0.1$. While in $Ba_4La_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics, $\varepsilon_r = 86.8$, $Qf = 5875$ GHz, $\tau_f = 81.99 \times 10^{-6}/°C$. The *Qf* value and τ_f are improved by small levels of Sm substitution for La, with dielectric constant (ε_r) almost unchanged.

In the microwave region, ε_r was mainly determined by the total dielectric polarizability (α_D) per molar volume (V_m) according to Clausius-Mossotti equation [19]:

$$\varepsilon_r = \frac{1 + 2b\alpha_D/V_m}{1 - b\alpha_D/V_m} \tag{2}$$

where *b* is assumed to $4/3\pi$. The dielectric constant increases with increasing total dielectric polarizability α_D and decreasing per molar volume. However α_D in one primitive cell decreases with increasing Sm content due to the fact that the ionic polarizability of Sm^{3+} is much lower than that of La^{3+} (α_{La}: 6.07 Å^3 and α_{Sm}: 4.74 Å^3) [19]. Meanwhile, the smaller Sm^{3+} decreases the cell volume and leads to the constriction of the octahedral B site occupied by Ti/Zr ions, which in turn, decreases the allowed displacement of Ti/Zr in the TiO_6 octahedron and reduces the ionic polarizability and the dielectric constant [1,6].

Generally, there are two kinds of dielectric loss: one is intrinsic loss, which is controlled by the model of crystal lattice liberation. The other is extrinsic loss, which is influenced by many factors such as oxygen vacancy, ordering degree of cations, internal stress of the crystals and phase constitution [5]. It is reported [7,20] that the *Qf* value increased slightly at first then decreased in the $Ba_4(Sm_{1-y}La_y)_{9.33}Ti_{18}O_{54}$ system. However, the reason has not been discussed in their paper. In this study, the *Qf* value also varies nonlinearly with composition *y* in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics. Small levels of Sm substitution improve the *Qf* value. The reason lies in the fact that the crystal structure is maintained by the size difference of large cations such as Ba and La/Sm. It is revealed that the crystal structure with the largest size difference between Ba and R shows excellent quality factor, as it has low internal strain [21]. The *Qf* value decreases dramatically as Sm content increases from $y = 0.1$ to $y = 1$, which is mainly due to the decrease of A1-site ordering. It is reported [22] that *Qf* value is improved with ordering of cations distribution. In the present situation, the large Ba ions occupies the pentagonal sites, while La/Sm ions occupy the rhombic sites, and Ti/Zr ions occupy the B-sites [5], as shown in the structural formula $[Sm_{9.33y}La_{9.33(1-y)}V_{0.67}]_{A1}[Ba_4]_{A2}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$. Here, *V* means vacancy. La/Sm ions and Ba ions are ordering in both the rhombic sites (A1) having medium size and pentagonal sites (A2) having the largest size, respectively. While there are five different locations in A1-site [23], Sm substitution for La leads to a change of the ordering of A1-site. Disordering of cations in A1-site produces many different polars between cations and oxygen ions which reduces the *Qf* value [24]. At the same time, incorporation of smaller Sm into the structure leads to the tilting and distortion of TiO_6 octahedron which increases the internal stress. The internal stress increases corresponding to the substitution of Sm for La, which in turn increases the extrinsic loss and decreases the *Qf* value, as shown in Fig. 6.

The mechanism in controlling τ_f has not been understood up to now. In generally speaking, the τ_f value is related to the composition and the existed phases in ceramics and suggests to obey the mixing rules [25]. $Ba_4Sm_{9.33}Ti_{18}O_{54}$ has a negative τ_f while $Ba_4La_{9.33}Ti_{18}O_{54}$ has a positive τ_f, by adjusting the ratio of La/Sm can obtain a zero τ_f value. According to Sm substitution for La in $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$, τ_f changes linearly from positive to negative with the increasing Sm content (Fig. 7), which was consistent with the variation of the cell volume. As considered by Kim et al. [26], the temperature coefficient of resonant frequency of tungsten bronze-type structure depends on the extent of the tilting and distortion of the octahedron and perovskite ceramics with small A-site cations tend to have near zero or positive τ_ε. $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ with a decreasing average radius of A1-site ions have more severely tilted octahedron. Therefore, τ_f changes to negative value with the substitution of small atoms on A1-site in $Ba_4La_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_5$ ceramics. Systematic analysis is necessary to reveal the relationship between τ_f and the tilting of TiO_6 octahedron.

4. Conclusions

$Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics have been prepared by the conventional solid-state ceramic route. A single-phase solid solution containing tungstenbronze-like structure formed in the whole range of *y* values. And the second phase was not found in all composition of the ceramics. Incorporation of Sm into the structure led to a decrease in the dielectric constant, from 86.8 to 74.9. The τ_f value of $Ba_4(La_{1-y}Sm_y)_{9.33}(Ti_{0.95}Zr_{0.05})_{18}O_{54}$ ceramics was adjusted from positive ($81.99 \times 10^{-6}/°C$ for $y = 0$) to negative ($-30.44 \times 10^{-6}/°C$ for $y = 1$). Ceramics with near zero τ_f ($-2.38 \times 10^{-6}/°C$) were achieved at compositions of $y = 0.7$. The *Qf* value did not obey the mixing rules. Small levels of Sm substitution improved the *Qf* value. With Sm content further increasing, the *Qf* value decreased dramatically. It was mainly due to the decrease of A1-site ordering. Further work is needed to investigate this behavior deeply.

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