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Microstructures and Microwave Dielectric Characteristics of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ Solid Solutions ($x = 2/3$ and 0.75)

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Abstract. $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ solid solutions were prepared and characterized. For $x = 2/3$, tungsten bronze type solid solutions were observed in the entire range of $y = 0$–1. While, La substitution for Sm will change the phase constitution in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics with $x = 0.75$. Though the single phase solid solutions were observed for the compositions at the vicinity of the end-members, $La_4Ti_9O_{24}$ secondary phase was detected for the compositions of $y = 0.3$–0.8. For $x = 2/3$, the dielectric constant increased continuously with increasing y, and the $Q \cdot f$ value increased slightly at first then decreased. The dielectric constant had more complex change with increasing y for the situation of $x = 0.75$ where $Q \cdot f$ value decreased continuously. In both cases, the temperature coefficient of resonant frequency varied from negative to positive with increasing y.

Keywords: microwave dielectric ceramics, microstructures, solid solution, tungsten bronze structure

1. Introduction

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ and $Ba_{6-3x}La_{8+2x}Ti_{18}O_{54}$ are both the important microwave dielectric ceramics in $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$(Ln = La, Nd and Sm) solid solution family, which have received much scientific and commercial interest as the key materials for microwave dielectric resonators and filters in microwave communication systems [1–4]. The former has the highest quality factor (evaluated in the form of $Q \cdot f$, where Q is the quality factor and f is the resonant frequency) combined with a small negative temperature coefficient of resonant frequency (τ_f), but a relatively lower dielectric constant (ε). Meanwhile, the latter has the highest dielectric constant but a lower quality factor and a relatively larger temperature coefficient of resonant frequency. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics have the typical microwave dielectric properties for the composition of $x = 2/3$: $\varepsilon = 81$, $Q \cdot f = 9{,}600$ GHz, $\tau_f = -14$ ppm/°C [4] and the microwave dielectric properties for the same composition in $Ba_{6-3x}La_{8+2x}Ti_{18}O_{54}$ are reported as: $\varepsilon = 110$, $Q \cdot f = 2300$ GHz, $\tau_f > 400$ ppm/°C [3].

So far, many efforts have been taken to modify the microwave dielectric characteristics through substitution in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics [4–7]. The most popular approach was substituting Nd for Sm to achieve higher dielectric constant and near zero temperature coefficient of resonant frequency [4–6], and the authors have proposed and investigated a co-substitution approach for synergistic modification of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics, through which a higher $Q \cdot f$ value can be obtained [7]. The $Ba_{6-3x}(Sm, La)_{8+2x}Ti_{18}O_{54}$ solid solution system has been investigated for a special base composition of $x = 0.6$ [8]. However, there is little systematic work dealing with this solid solution system for the base compositions such as $x = 2/3$ and $x = 0.75$.

In the present paper, the $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ solid solution ceramics are prepared and characterized for the two compositions: $x = 2/3$ and 0.75. The different trends in phase constitution for the solid solutions with different base compositions is emphasized together with their microwave dielectric characteristics.

2. Experiments

$Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$ and 0.75) ceramics with $y = 0$, 0.1, 0.2, 0.3, 0.5, 0.8 and 1.0 were prepared by a routine solid state reaction process where the reagent grade $BaCO_3$ (99.93%), La_2O_3 (99.99%), Sm_2O_3 (99.5%) and TiO_2 (99.8%) powders were used as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in ethanol for 24 h, and then were calcined at 1200°C in air for 3 h after drying. The calcined powders with additions of 8 wt% of PVA were pressed into discs with dimensions of 12 mm in diameter and 2 to 6 mm in height, and then sintered at 1300°C to 1370°C in air for 3 h. After cooling from the sintering temperature to 1100°C at a rate of 2°C min^{-1}, the ceramics were subsequently furnace cooled.

The crystalline phases of the sintered samples were identified by X-ray powder diffraction using Cu K_α radiation and the microstructures were characterized by scanning electron microscopy (SEM) on the polished and thermal-etched surfaces. The lattice parameters were calculated by least-squares refinement of the angular positions of the reflections obtained in the 2θ range 10–70°. The microwave dielectric properties were evaluated at 4 to 5 GHz by the Hakki and Coleman's resonator method [9], and the temperature coefficient of resonant frequency was calculated from the equation

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

where, α is the linear expansion coefficient (~10 ppm/°C) [10], τ_ε is the temperature coefficient of dielectric constant evaluated at 1 MHz by an LCR meter (HP4284A) equipped with a thermostat.

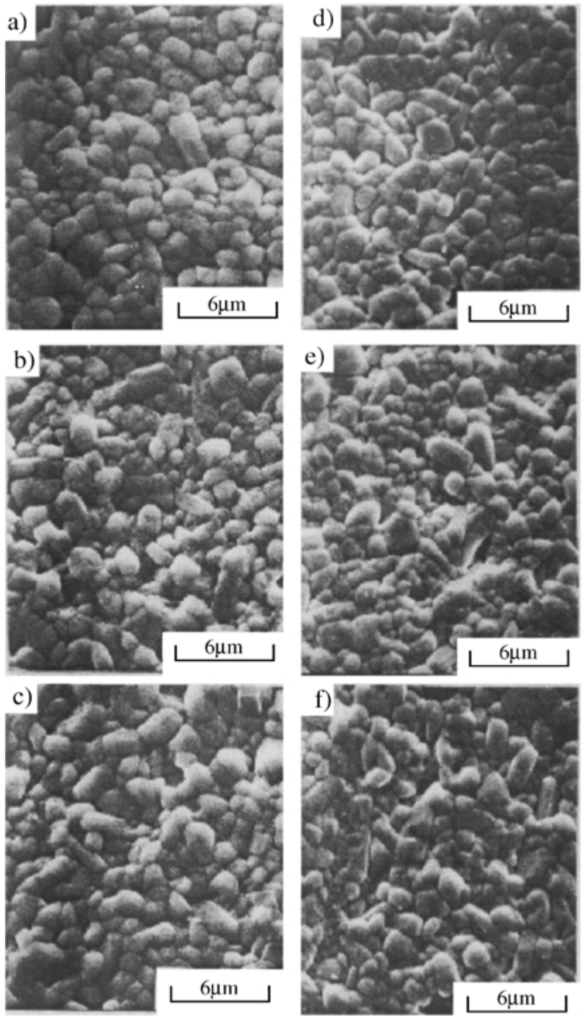

Fig. 1. SEM micrographs for polished and thermal etched surfaces of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics. (a) $x = 2/3$, $y = 0.1$; (b) $x = 2/3$, $y = 0.3$; (c) $x = 2/3$, $y = 0.5$; (d) $x = 0.75$, $y = 0.1$; (e) $x = 0.75$, $y = 0.3$; and (f) $x = 0.75$, $y = 0.5$.

3. Results and Discussion

Dense $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ ceramics can be obtained by sintering at 1320–1350°C in air for 3 h, and the homogenous microstructures are observed in the dense ceramics (see Fig. 1). No obvious difference is observed in the grain morphology and grain size for different compositions.

XRD patterns of specimens with $x = 2/3$ and 0.75 are shown in Figs. 2 and 3, respectively. For $x = 2/3$, all peaks are assigned to the tungsten bronze phase, and this allows us to conclude that the tungsten bronze solid solution forms in the entire range of $y = 0$–1. Meanwhile, when $x = 0.75$, though there is no obvious secondary phase observed for the compositions in vicinity of the end-members, a secondary phase, $La_4Ti_9O_{24}$ is detected for $y = 0.3$–0.8 since the three strongest peaks for (404), (440) and (442) planes of $La_4Ti_9O_{24}$ are observed at $d = 0.335$ nm, 0.326 nm and 0.298 nm, respectively, and the intensities for such peaks increase with increasing y. This difference is also reflected in the variation of unit cell volume of the tungsten bronze phase with y (Fig. 4). Figure 4(a) indicates the continuous change of lattice parameters in the solid solution of $Ba_{6-3x}(Sm, La)_{8+2x}Ti_{18}O_{54}$ in the case of $x = 2/3$. While, Fig. 4(b) suggests the more complex phase relations in the case of $x = 0.75$.

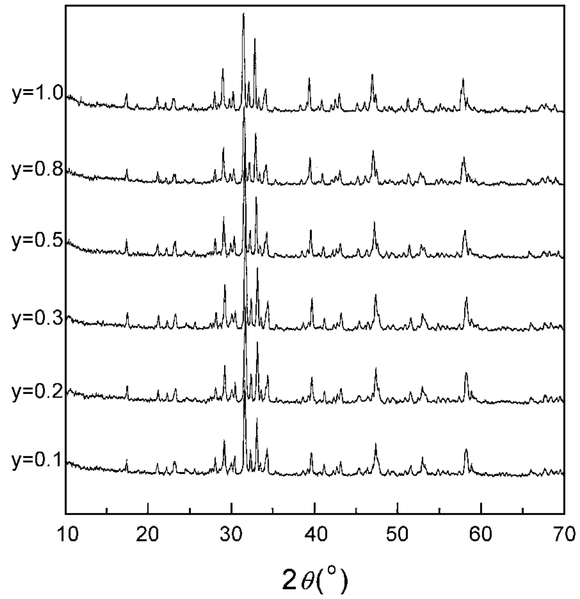

Fig. 2. XRD patterns for $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics with $x = 2/3$.

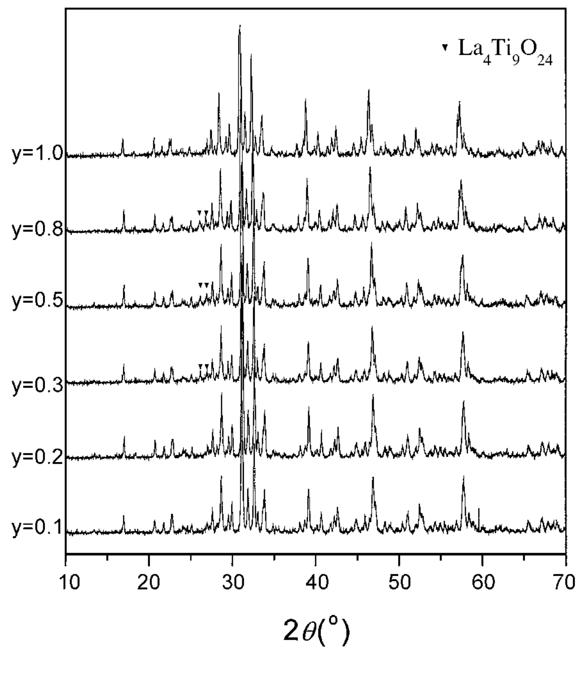

Fig. 3. XRD patterns for $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics with $x = 0.75$.

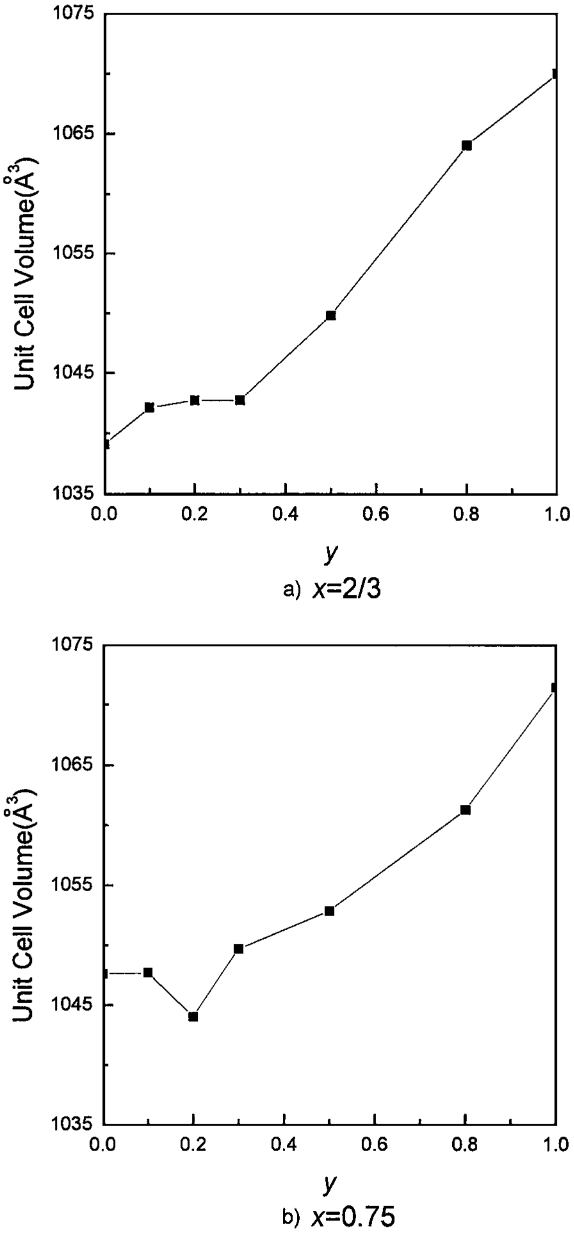

Fig. 4. Unit cell volume of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ as function of composition y. (a) $x = 2/3$; and (b) $x = 0.75$.

Corresponding to the variation of phase constitution, the compositions of $x = 2/3$ and $x = 0.75$ have different dependencies in dielectric constant and $Q \cdot f$ value with y (Figs. 5 and 6). For the former, the dielectric constant increases from 81 to 106.5 continuously, and the $Q \cdot f$ value increases slightly at first, and reaches a maximum 9,510 GHz at $y = 0.1$ then decreases with increasing y. In the case of $x = 0.75$, though the dielectric constant generally increases with increasing y, there is some obvious tortuosity in the vicinity of $y = 0.2$ and 0.3, corresponding

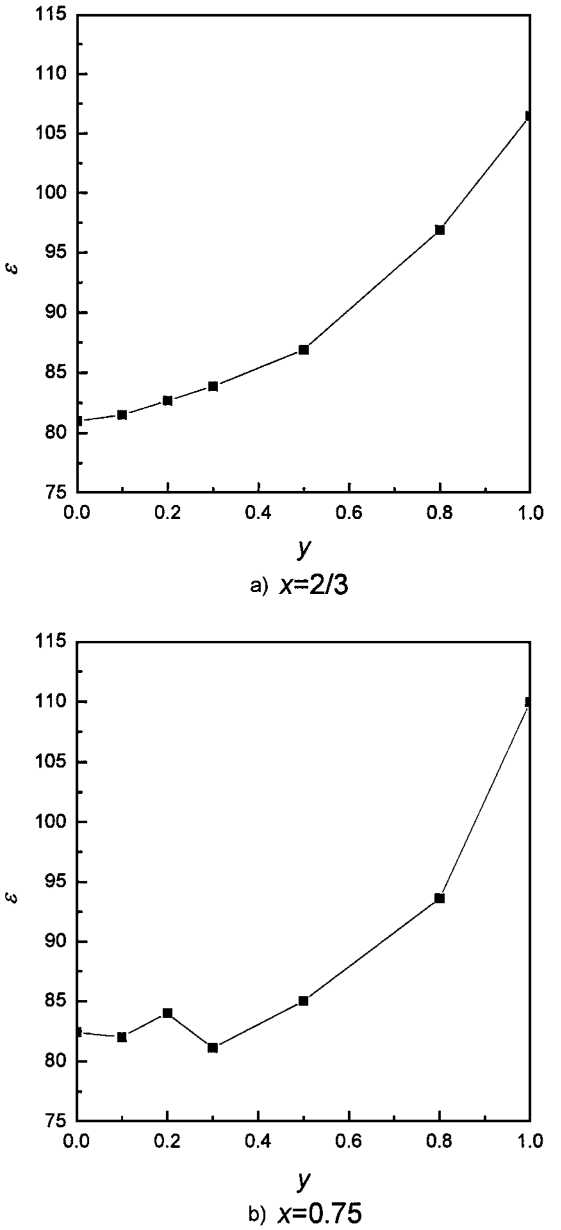

Fig. 5. Dielectric constant of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics as function of composition y. (a) $x = 2/3$ and (b) $x = 0.75$.

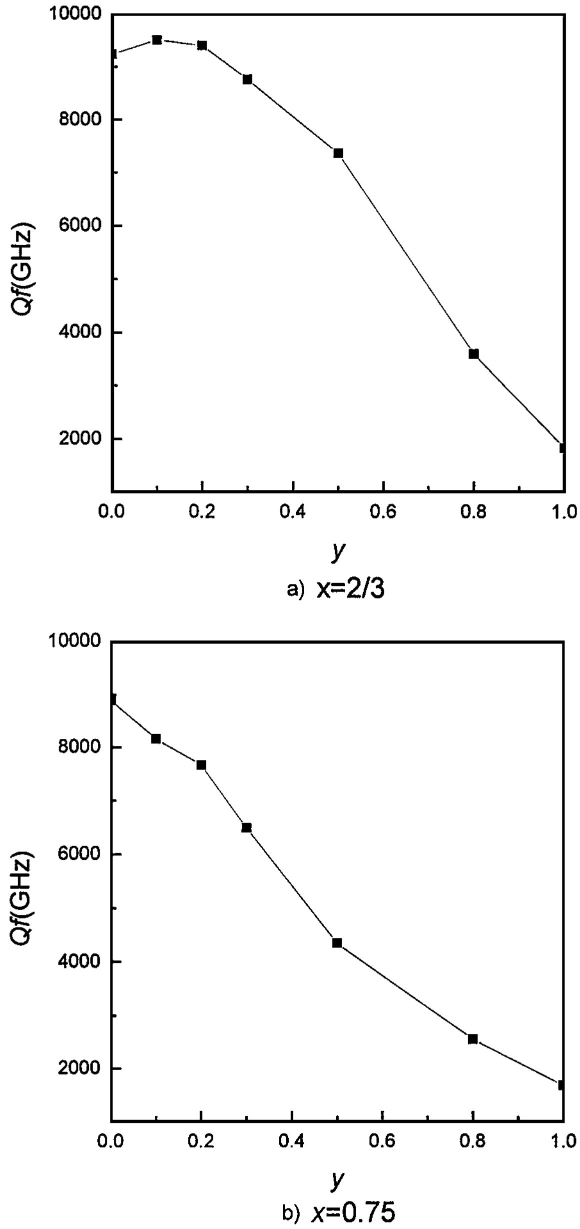

Fig. 6. $Q \cdot f$ of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics as function of composition y. (a) $x = 2/3$ and (b) $x = 0.75$.

to the appearance of a small amount of $La_4Ti_9O_{24}$ ($\varepsilon = 37$, $Q{\cdot}f = 24{,}800$ GHz, $\tau_f = +15$ ppm/°C [11]) at $y = 0.3$. The $Q{\cdot}f$ value decreases continuously in the case of $x = 0.75$.

Figure 7 shows the variation of temperature coefficient of resonant frequency τ_f with y. For both $x = 2/3$ and 0.75, τ_f varies from negative to positive and increases continuously with increasing y. For $x = 2/3$, τ_f changed from -12 ppm/°C to $+297$ ppm/°C, and varies from -7 ppm/°C to $+314$ ppm/°C for $x = 0.75$. It should be noted here that the presence of the secondary phase $La_4Ti_9O_{24}$ has no significant influence on the temperature coefficient of resonant frequency though it obviously affects the dielectric constant.

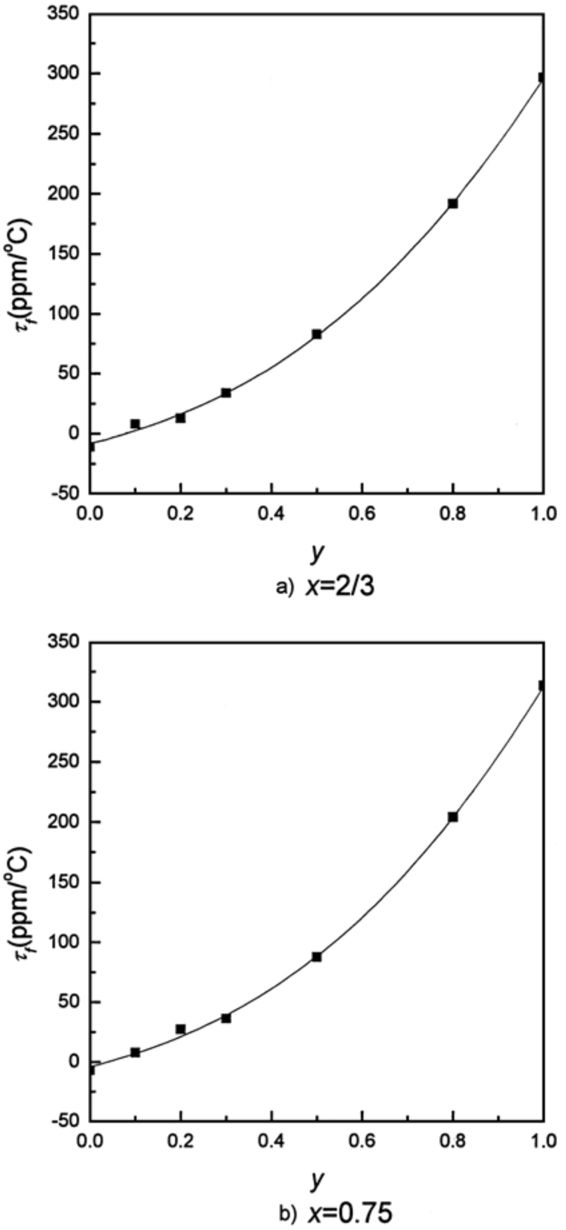

Fig. 7. Temperature coefficient of resonant frequency of $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ dense ceramics as function of composition y. (a) $x = 2/3$ and (b) $x = 0.75$.

4. Conclusions

Different phase constitution and microwave dielectric characteristic trends were observed in the $Ba_{6-3x}(Sm_{1-y}La_y)_{8+2x}Ti_{18}O_{54}$ system. The tungsten bronze type solid solution formed in the entire range of $y = 0$–1 for $x = 2/3$, while the $La_4Ti_9O_{24}$ secondary phase was detected for the compositions of $y = 0.3$–0.8 for $x = 0.75$. For $x = 2/3$, the dielectric constant increased continuously with increasing y, and the $Q \cdot f$ value increased slightly at first then decreased. The dielectric constant had more complex dependence with increasing y for $x = 0.75$ where $Q \cdot f$ decreased continuously. In both cases, the temperature coefficient of resonant frequency varied from negative to positive with increasing y. Excellent microwave dielectric properties were obtained: $\varepsilon = 81.5$, $Q \cdot f = 9{,}510$ GHz, $\tau_f = 8$ ppm/°C for $x = 2/3$, $y = 0.1$.

Acknowledgments

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