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Preparation and microwave dielectric properties of the $BaO \cdot (Sm_{1-x}La_x)_2O_3 \cdot 5TiO_2$ ceramic system

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Abstract

The microwave dielectric properties of the $BaO \cdot (Sm_{1-x}La_x)_2O_3 \cdot 5TiO_2$ ceramic system were studied for developing high quality microwave dielectric ceramics. In this system, the substitution of La for Sm is effective for dielectric constant ε_r, but not effective for Q value. We found high quality resonator materials which show high ε_r of 90.7, $Q \cdot f$ products of 8900 GHz and temperature coefficient of resonant frequency $\tau_f = 4.2$ ppm/°C at the composition of $x = 0.1$.

Keywords: $BaO \cdot Sm_2O_3 \cdot 5TiO_2$; Dielectric properties; Microwave properties; Resonator materials

1. Introduction

Recently, high quality microwave dielectric ceramics, which enable miniaturization of the dimensions of resonators, have received much attention due to the rapid progress in microwave telecommunications, for example in car telephone systems, portable telephones and satellite broadcasting receivers. The dielectric characteristics requisite for microwave resonator materials are as follows. The first one is high dielectric constant (ε_r) for reducing the size of resonators, because the wave length (λ) in dielectrics is inversely proportional to $\sqrt{\varepsilon_r}$of the wavelength (λ_0) in vacuum ($\lambda = \lambda_0\sqrt{\varepsilon_r}$). Secondly, the inverse of the dielectric loss ($Q = 1/\tan\delta$) is required to be high for achieving prominent frequency selectivity and stability in microwave transmitter components. As the third characteristic, the temperature coefficient of the resonant frequency (τ_f) is required to be as close to 0 ppm/°C as possible.[1]

Since the first report on high-quality resonator materials with excellent microwave dielectric properties in the TiO_2 rich region of the BaO–R_2O_3–TiO_2 (R = rare earth) ternary system, many studies concerning this have been conducted.[2–5] The ternary component was estimated to be $BaO \cdot R_2O_3 \cdot 5TiO_2$ based on single crystals by Kolar et al.[2] However, it has recently been demonstrated that the component of this compound was $BaO \cdot R_2O_3 \cdot 4TiO_2$ (R = La, Nd and Sm) using TEM, X-ray powder diffractometry and Raman spectroscopy.[6,7]

On the other hand, Ohsato et al.[8] studied two kinds of tungsten bronze type solid solution, $Ba_{6-3x}(Sm_{1-y},R_y)_{8+2x}Ti_{18}O_{54}$ ($x = 0.6$, R = Nd and La). In the Sm–La series,the optimum one is $y = 0.1$. The materials exhibited high values of $\varepsilon_r = 84$ and $Q \cdot f = 9000$ GHz.

In this work, La_2O_3 substituted $BaO \cdot Sm_2O_3 \cdot 5TiO_2$ ceramic system was studied for improving microwave dielectric properties.

2. Experimental

Reagent-grade $BaCO_3$, TiO_2, Sm_2O_3 and La_2O_3 with 99.9% purity was used as raw materials. The examined composition system is nominally expressed as $BaO \cdot (Sm_{1-x} La_x)_2O_3 \cdot 5TiO_2$ ($1.0 \geqslant x \geqslant 0$). The mixtures were ground for 24 h by a ball mill with ethanol, dried and calcined for 2 h in air at 1200 °C. The calcined powder, which was reground in an alumina mortar, was mixed with an organic binder of 3 wt.% PVA passed through a 50 mesh screen for turning out in granular powder, and pressed into a disk at a pressure of 1 t/cm^2. The disks were sintered at 1300–1350 °C in air for 4 h. The apparent densities of the sintered samples were measured by Archimedes' method.

The relative densities were obtained from the apparent densities and the calculated ones. The crystalline phases of the sintered samples were identified by X-ray powder diffraction patterns, using CuK_α radiation. The dielectric constants at microwave frequencies were cal-

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culated using the size of the fired disk and Coleman's method[9]. The temperature coefficient of the resonant frequency, τ_f was measured between 25 and 85 °C.

3. Results and discussion

The sintering temperatures are determined based on the apparent densities of the solid solutions, which are shown as a function of sintering temperatures in Fig. 1. Fig. 2 shows the densities of specimens sintered at various temperatures as a function of La content.

The X-ray powder diffraction patterns of this system, shown in Fig. 3, are mostly identified with tungsten bronze type compounds.[10] The lattice parameters are determined using the main peaks and linearly increasing with increase as the amount of La. The increase of the lattice parameters is based on the difference of the ionic radii between Sm and La. Shannon et al.[11] reported the effective ionic radii for 12 coordination are 1.24 and 1.34 A for Sm and La, respectively.

Dielectric properties such as dielectric constant (ε_r), $Q{\cdot}f$ values and temperature coefficients (τ_f) are shown as a function of composition (x) in Fig. 4. As has been reported[8], the τ_f of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=0.6$) solid solution is negative value of −12.8 ppm/°C. According to the amount of substitution of La for our system, the τ_f changed linearly from negative to positive as shown in Fig. 4. The composition at which the τ_f becomes 0 ppm/°C is around $x=0.1$. At the composition of $x=0.1$ with $\tau_f=4.2$ ppm/°C, the $Q{\cdot}f$ value is 8900 GHz. As is the characteristics of the tungsten bronze type structure, the dielectric constant increases as a function of the lattice parameter as shown in Fig. 4.

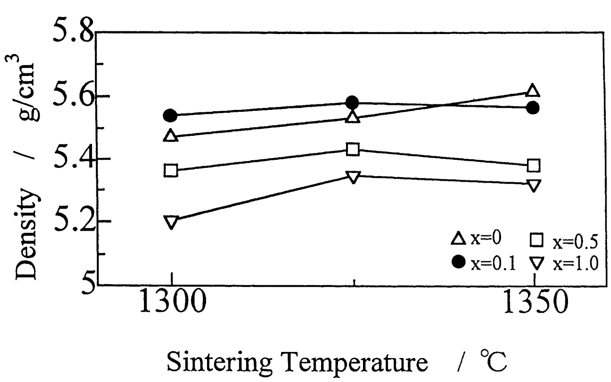

Fig. 1. The apparent densities as a function of sintering temperatures.

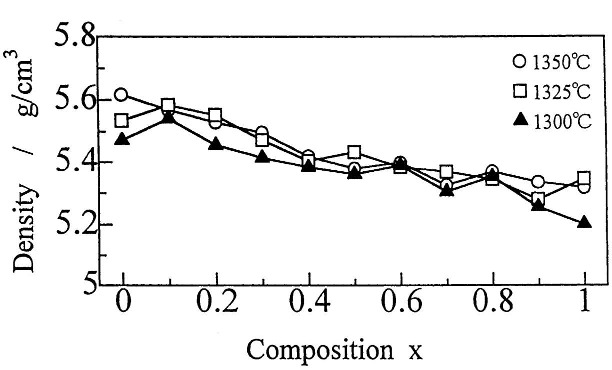

Fig. 2. The densities of specimens sintered at various temperatures as a function of La content.

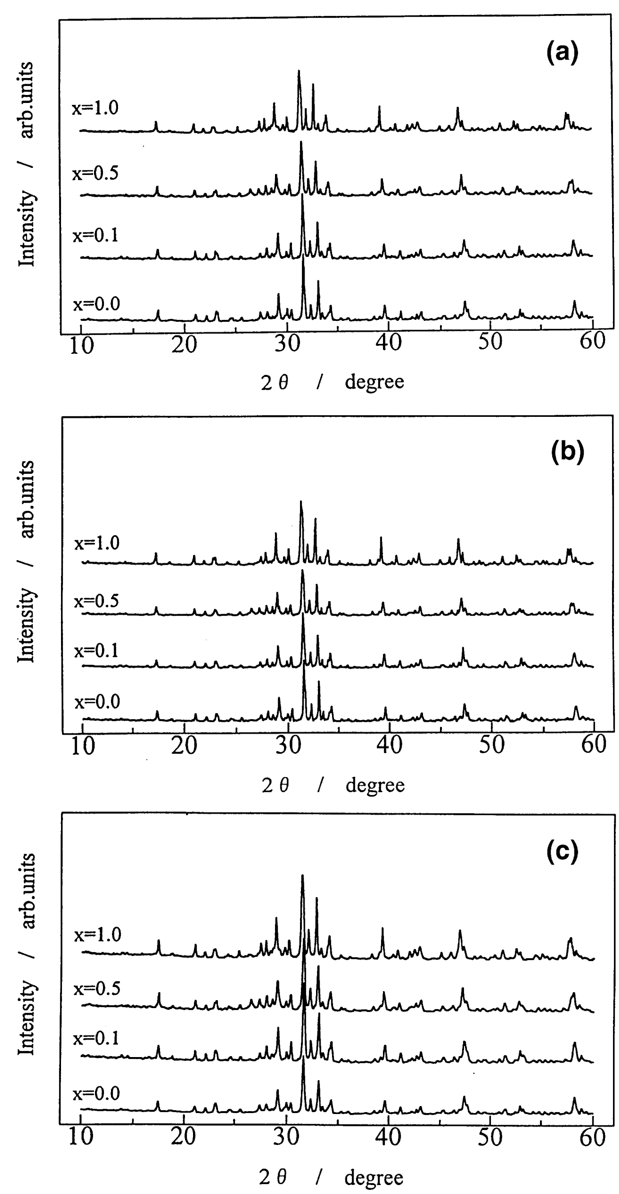

Fig. 3. X-ray diffraction patterns of $BaO{\cdot}(Sm_{1-x}La_x)_2O_3{\cdot}5TiO_2$ ceramics sintered at various temperatures for 4h: (a) 1300 °C; (b) 1325 °C; (c) 1350 °C.

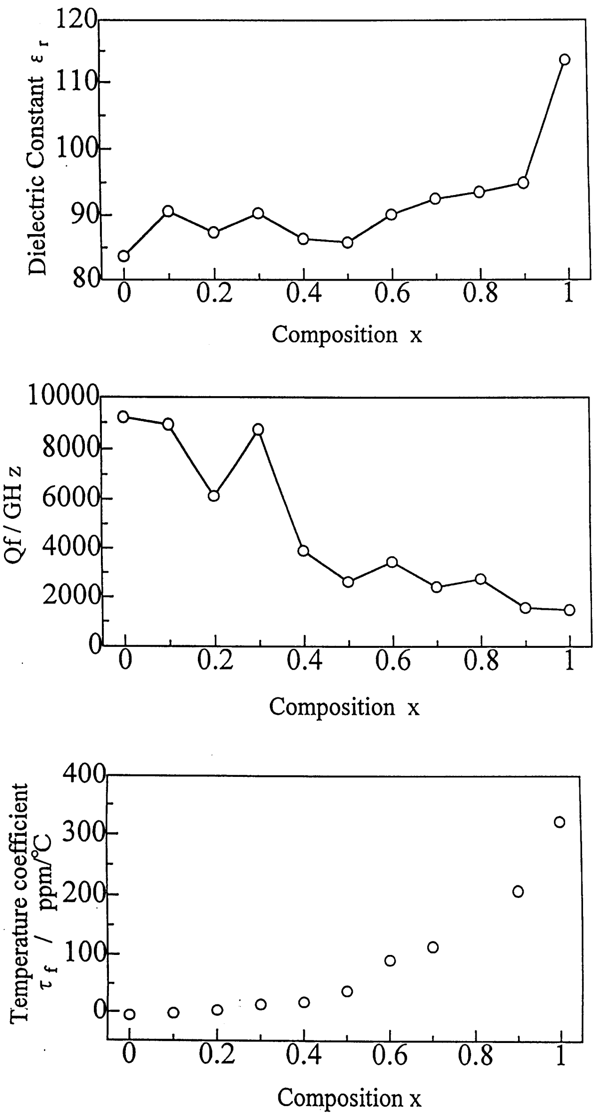

Fig. 4. Dielectric constants, $Q{\cdot}f$ values and temperature coefficients of resonant frequency as a function of composition for $BaO{\cdot}(Sm_{1-x}La_x)_2O_3{\cdot}5TiO_2$ sintered at 1325 °C for 4 h.

4. Conclusions

1. For the $BaO{\cdot}(Sm_{1-x}La_x)_2O_3{\cdot}5TiO_2$ ceramic system, tungsten bronze type phases are mostly formed in the whole range examined. The lattice parameters are linearly increasing with increase as the amount of La, which is due to the difference of the ionic radii between Sm and La.
2. At the composition of $x=0.1$, the materials exhibited high value of $\varepsilon_r = 90.7$ and $Q{\cdot}f = 8900$ GHz with $\tau_f = 4.2$ppm/°C.

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