

# The Sintering and Microwave Dielectric Characteristics

## of the $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$ Composite ( $0 \leq x \leq 0.5$ )

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The sintering and microwave dielectric characteristics of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  compositions ( $0 \leq x \leq 0.5$ ) are developed in the study. As the SrO content increases, the lattice constants (a, b, and c axis) first increase and then decrease. Sintered at 1350°C, only the  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  phase is exist in the  $\text{BaO-Sm}_2\text{O}_3\text{-4TiO}_2$  composite, but the  $0.9\text{BaO-0.1SrO-Sm}_2\text{O}_3\text{-4TiO}_2$ ,  $0.75\text{BaO-0.25SrO-Sm}_2\text{O}_3\text{-4TiO}_2$ , and  $0.5\text{BaO-0.5SrO-Sm}_2\text{O}_3\text{-4TiO}_2$  compositions reveal two phases:  $\text{Sm}_2\text{Ti}_2\text{O}_7$  and  $(\text{Ba,Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  coexist. The microwave dielectric characteristics of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics are influenced by SrO content. In the  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  compositions, the  $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramic reveals the optimum microwave dielectric characteristics:  $\epsilon_f=71.5$ ,  $Q \times f=8150$  GHz, and  $\tau_f=-2.83$  ppm/°C.

KEYWORDS:  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$ , two phase, microwave dielectric characteristic

### 1. Introduction

Microwave dielectric ceramics should possess extremely low losses (high quality factor, Q) and a small temperature coefficient of resonant frequency ( $\tau_f$ ) [1-3]. The  $\text{BaO-Re}_2\text{O}_3\text{-TiO}_2$  (Re=Sm, Nd, and Gd) ceramics, with a dielectric constant higher than 80, were developed to meet such requirements [4-7]. In the  $\text{BaO-Re}_2\text{O}_3\text{-TiO}_2$  system the ceramics composition was the most important parameter in tailoring of its microwave properties. Many ceramics dielectrics developed so far for microwave applications were prepared by the conventional solid-state reaction of mechanically mixed powders. The inevitable inhomogeneity, which was inherent in this technique, inhibited the compositional and microstructural homogeneity of fired products. Therefore, it was important to understand quantitatively the property-controlled factors to provide optimized and reproducible dielectric properties for a product.

In the  $\text{BaO-Re}_2\text{O}_3\text{-TiO}_2$  system the ceramics composition was the most important parameter in tailoring of its microwave properties, especially for Q and  $\tau_f$  values. In the  $\text{BaO-Sm}_2\text{O}_3\text{-TiO}_2$  system, Nishigaki et al. found that the compositions  $0.15(\text{Ba}_{1-x}\text{Sr}_x)\text{O-0.15Sm}_2\text{O}_3\text{-0.7TiO}_2$  system, which were composed of small amounts of two poorly dispersed second phases ( $\text{TiO}_2$  and

Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>), had a similarly crystal structure of BaO-Sm<sub>2</sub>O<sub>3</sub>-5TiO<sub>2</sub> [7]. They also found that  $\tau_f$  values could be changed by substitution of SrO for BaO and the composition 0.15(Ba<sub>0.95</sub>Sr<sub>0.05</sub>)O-0.15Sm<sub>2</sub>O<sub>3</sub>-0.7TiO<sub>2</sub> possessed a zero temperature coefficient of resonant frequency [7]. In this study, the (Ba,Sr)O-Sm<sub>2</sub>O<sub>3</sub>-4TiO<sub>2</sub> system were chosen as the main composition. The coprecipitation method, which we had established in the studies of the (Ba,Sr)O-Sm<sub>2</sub>O<sub>3</sub>-4TiO<sub>2</sub> system, was applicable to prepare single-phase powders with desired compositions in this system. We had studied this by varying the composition and calcination to obtain various crystalline phases, in order to contribute a better understanding the compositional deviation variation of (Ba<sub>1-x</sub>Sr<sub>x</sub>)Sm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> based ceramics.

## 2. Experimental procedures

Samples were prepared from reagent-grade BaCO<sub>3</sub>, SrCO<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>. The powders were weighted according to the ratio BaO:SrO:Sm<sub>2</sub>O<sub>3</sub>:TiO<sub>2</sub> = 1-x:x:1:4, which was equivalent to a composition of (Ba<sub>1-x</sub>Sr<sub>x</sub>)-Sm<sub>2</sub>O<sub>3</sub>-4TiO<sub>2</sub>, where x=0, 0.1, 0.25, and 0.5, respectively. The powders were milled in a plastic jar with deionized water for 4h, then the powders were dried and ground to force through a 250-mesh sieve. These powders were then calcining for 4h from 850°C to 1300°C at a step of 50°C. After crushing and grinding, the crystalline phases of calcining powders were determined by X-ray powder diffraction. The densification behaviors of the BaSm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> ceramics as a function of sintering temperature were evaluated by determining the bulk density using the Archimedes method. Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method [8], which was improved by Courtney [9]. An HP8720ET network analyzer was used for the microwave characteristic measurements. The dielectric constant can be accurately determined by measuring the resonant frequency of the TE<sub>011</sub> mode and verified by the TE<sub>01δ</sub> resonant mode. For convenience, the Q×f-factor was used for evaluating the loss quality, where f is the resonant frequency and Q is the quality factor. The temperature change of the resonant frequency  $\Delta f_0/f_0$  and temperature coefficient of resonant frequency  $\tau_f$  are defined as:

$$\Delta f_0/f_0 = (f_T - f_0) / f_0, \quad (6)$$

$$\text{and} \quad \tau_f = \Delta f_0 / (f_0 \times \Delta T) \quad (7)$$

where  $f_T$  and  $f_0$  are the resonant frequency at T°C and 20°C, respectively.

## 3. Results and discussion

The X-ray powder diffraction (XRD) patterns of (Ba<sub>1-x</sub>Sr<sub>x</sub>)O-Sm<sub>2</sub>O<sub>3</sub>-4TiO<sub>2</sub> ceramics for x=0, 0.1, 0.25, and 0.5 and calcined at 1100°C are shown in Fig. 1. The BSST system calcining at the same temperatures show the similarly crystal phase. Using 1100°C as the calcining temperatures, the BaSm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> (or (Ba,Sr)Sm<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub>) phase was formed accompanying the existence of intermediate

phases  $\text{Sm}_2\text{Ti}_2\text{O}_7$  and  $\text{BaTi}_4\text{O}_9$  and source material  $\text{Sm}_2\text{O}_3$  as minor crystal phase.

The results of x-ray powder diffraction of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{O}-\text{Sm}_2\text{O}_3-4\text{TiO}_2$  ceramics for  $x=0, 0.1, 0.25,$  and  $0.5$  and sintered at  $1350^\circ\text{C}$  are shown in Fig. 2. For  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  sintered at  $1350^\circ\text{C}$ , the source material  $\text{Sm}_2\text{O}_3$  and the intermediate phases  $\text{Sm}_2\text{Ti}_2\text{O}_7$  and  $\text{BaTi}_4\text{O}_9$  are consumed. For  $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{Sm}_2\text{Ti}_4\text{O}_{12}, (\text{Ba}_{0.75}\text{Sr}_{0.25})\text{Sm}_2\text{Ti}_4\text{O}_{12},$  and  $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  and sintered at  $1350^\circ\text{C}$ , the source material  $\text{Sm}_2\text{O}_3$  and the intermediate phase  $\text{BaTi}_4\text{O}_9$  are also consumed, but the intermediate phase  $\text{Sm}_2\text{Ti}_2\text{O}_7$  is residual. Because the mainly crystal phase shown in Fig. 2(a)-(d) is the  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  (or  $(\text{Ba},\text{Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$ ). These results suggest that in the  $(\text{Ba}_{1-x}\text{Sr}_x)\text{O}-\text{Sm}_2\text{O}_3-4\text{TiO}_2$  system, the BaO site could be substituted by the SrO, completely.

Figure 3 shows the lattice constants of a, b, and c axis of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{O}-\text{Sm}_2\text{O}_3-4\text{TiO}_2$  system. As the SrO content increases, the lattice constants a and b increase, reach a maximum at  $x=0.1$ , then decrease linearly; The lattice constant c first increases, and almost unchanged as for  $0.25 \geq x \geq 0.1$ , and then decrease as  $x \geq 0.25$ . For that, the influence of SrO content on the density values of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics will be predicted.

The density of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics are investigated as a function of SrO content, and the results are shown in Fig. 4. The density values of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  system decreases with the increase of x value. The density of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  system increase with the increase of sintering temperatures and reach a maximum at  $1350^\circ\text{C}$  (not shown here). In the  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  system, the density decrease with the increase of SrO content. In this time, the theoretical density for each composition is obtained from the lattice parameter calculated from XRD data. The relative densities of all  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  compositions exhibit a value higher than 97.2% at a sintering temperature of  $1350^\circ\text{C}$ . The implies that the SrO has a beneficial influence on the density of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$ .

The dielectric constants ( $\epsilon_r$  values) of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  system are investigated as a function of SrO content and sintered at  $1350^\circ\text{C}$ , and the results are also shown in Fig. 4. At first, as sintering temperatures increase, the  $\epsilon_r$  values of all  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics increase and saturate at about  $1350^\circ\text{C}$  independent of SrO content (not shown here). The saturated  $\epsilon_r$  values of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics decrease from 82.2 to 66.3 linearly as x is changed from 0 to 0.5. The implies that the SrO has an apparent influence on the  $\epsilon_r$  values of  $1350^\circ\text{C}$ -sintered  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.

The  $Q \times f$  values of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics are measured under a sintering temperature of  $1350^\circ\text{C}$ , and the results are shown in Fig. 5. As the SrO content increases, the  $Q \times f$  values first increase, reach a maximum for  $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics, and then decrease slightly with the further increase of SrO content. Although good densification process of  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  ceramics are obtained at  $1350^\circ\text{C}$ , the maximum  $Q \times f$  values are lower than  $(\text{Ba}_{0.9}\text{Sr}_{0.1})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.

Figure 5 also shows the  $\tau_f$  values of the  $1350^\circ\text{C}$ -sintered ceramics. As the SrO content changes

from 0 to 0.1mol, the  $\tau_f$  values change from  $-22.1 \text{ ppm}/^\circ\text{C}$  to  $-2.83 \text{ ppm}/^\circ\text{C}$  apparently. As the SrO content changes from 0.1 to 0.25mol, the  $\tau_f$  values change from  $-2.83 \text{ ppm}/^\circ\text{C}$  to  $-14.7 \text{ ppm}/^\circ\text{C}$ . Further increase the SrO content from 0.25 to 0.5mol, the  $\tau_f$  values show no apparent change with the increase of SrO content. According to the X-ray patterns, for  $x \leq 0.1$  the crystal phases of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics are only the two phases of  $(\text{Ba,Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  and  $\text{Sm}_2\text{Ti}_2\text{O}_7$ . If the  $(\text{Ba,Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$ - $\text{Sm}_2\text{Ti}_2\text{O}_7$  ceramics are thought as heterogeneous phases, the unapparent change of  $\tau_f$  values of the  $(\text{Ba,Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics could be thought as the influence of  $\text{Sm}_2\text{Ti}_2\text{O}_7$  phase.

#### 4. Conclusion

(a)  $1100^\circ\text{C}$  is enough for  $\text{BaO-Sm}_2\text{O}_3\text{-}4\text{TiO}_2$  powder to form  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  phase.

(b) Sintered at  $1350^\circ\text{C}$ , only the single  $\text{BaSm}_2\text{Ti}_4\text{O}_{12}$  phase is revealed in the sintered  $\text{BaO-Sm}_2\text{O}_3\text{-}4\text{TiO}_2$  ceramics; But two phases,  $(\text{Ba,Sr})\text{Sm}_2\text{Ti}_4\text{O}_{12}$  and  $\text{Sm}_2\text{Ti}_2\text{O}_7$ , coexist in the  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics,  $x=0.1, 0.25, \text{ and } 0.5$ .

(c) The density and the microwave characteristics (dielectric constants, quality values, and  $\tau_f$  values) of  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics will saturate at about  $1350^\circ\text{C}$ .

#### References

- [1] T.Jaakola, A.Uusimaki, R.Rautioaho, and S.Leppavuori: *J.Am.Ceram.Soc.* **69** (1986) c-234.
- [2] A.Yamada, Y.Utsumi, and H.Watarai: *Jpn.J.Appl.Phys.* **30** (1991) 2350.
- [3] M.Valant, D.Suvorov, and D.Kolar: *Jpn.J.Appl.Phys.* **35** (1996) 144.
- [4] P.Laffez, G.Desgardin, and B.Raveau: *J.Mater.Sic.* **30** (1995) 267.
- [5] H.Ohsato, S.Nishigaki, and T.Okuda: *Jpn.J.Appl.Phys.* **31** (1992) 3136.
- [6] S.Nishigaki, H.Kato, S.Yano, and R.Kamimura: *Am.Ceram.Soc.Bull.* **66** (1987) 1405.
- [7] R.B.Waterhouse: *Electron.Lett.* **31** (1995) 604.
- [8] B. W. Hakki and P. D. Coleman: *IRE. Trans. MTT* **8** (1960) 402.
- [9] W. E. Courtney: *IRE. Trans. MTT* **18** (1985) 476.

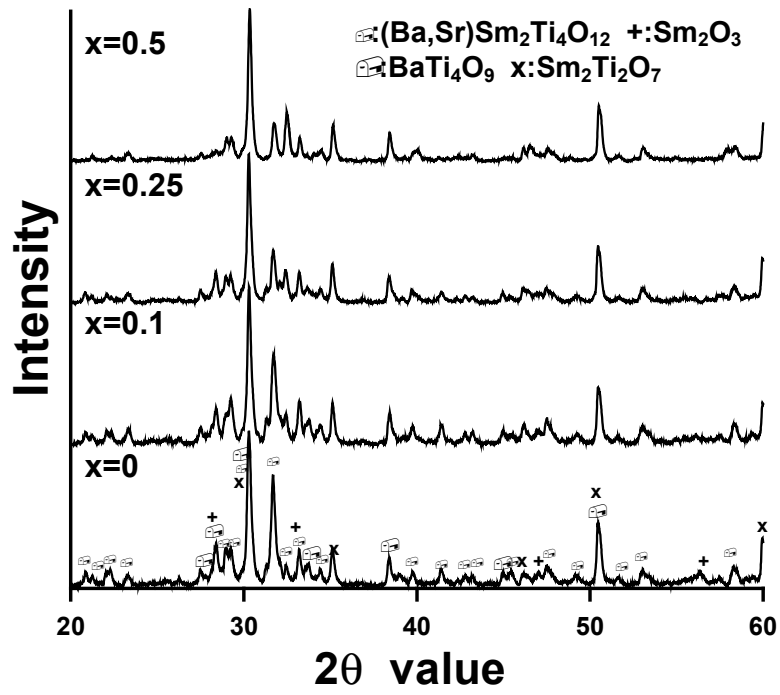


Fig. 1 The X-ray patterns of 1100°C-calcined  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  powders.

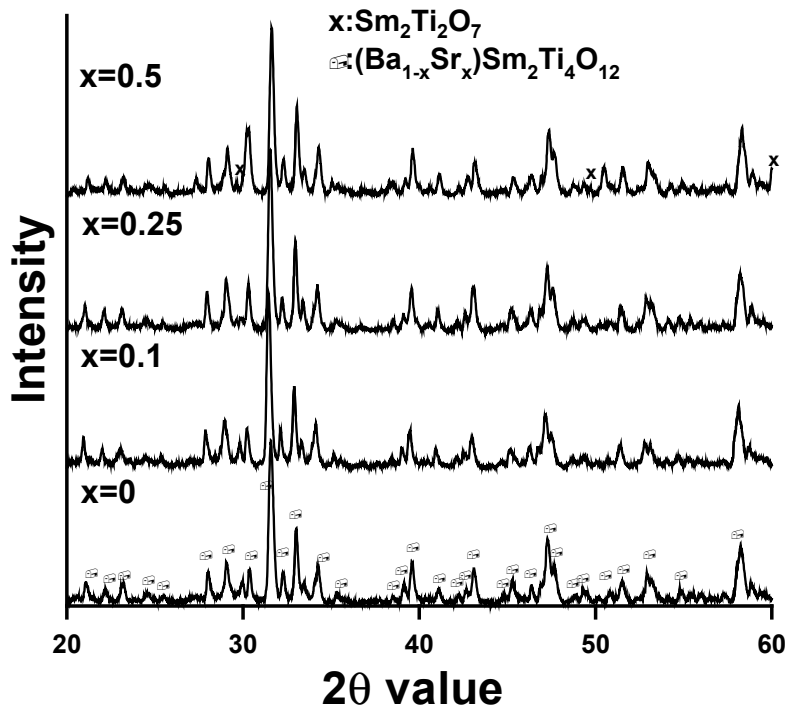


Fig. 2 The X-ray patterns of 1350°C-sintered  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.

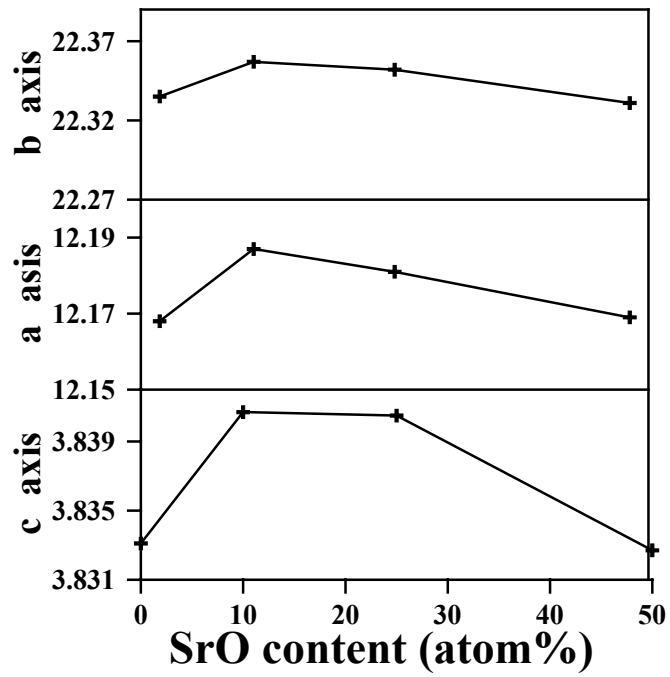


Fig. 3 The lattice constants of 1350°C-sintered  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.

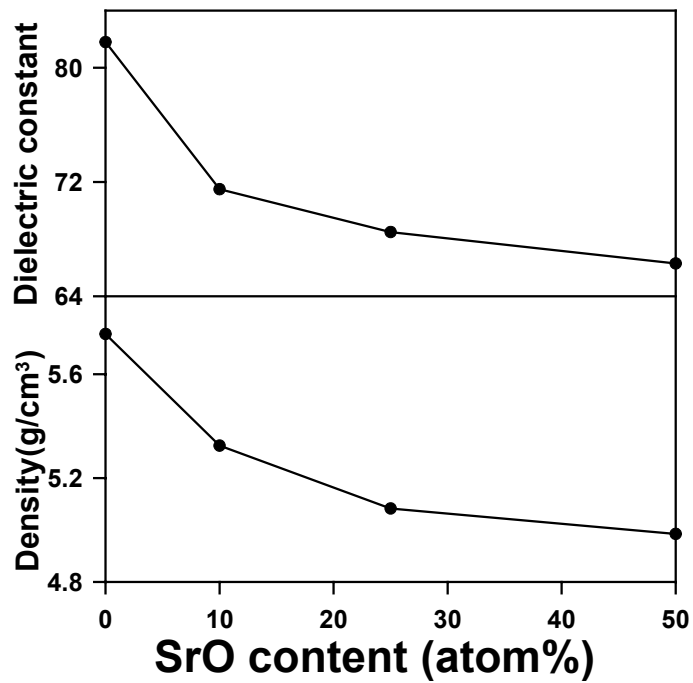


Fig. 4 The density and the dielectric constants of 1350°C-sintered  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.

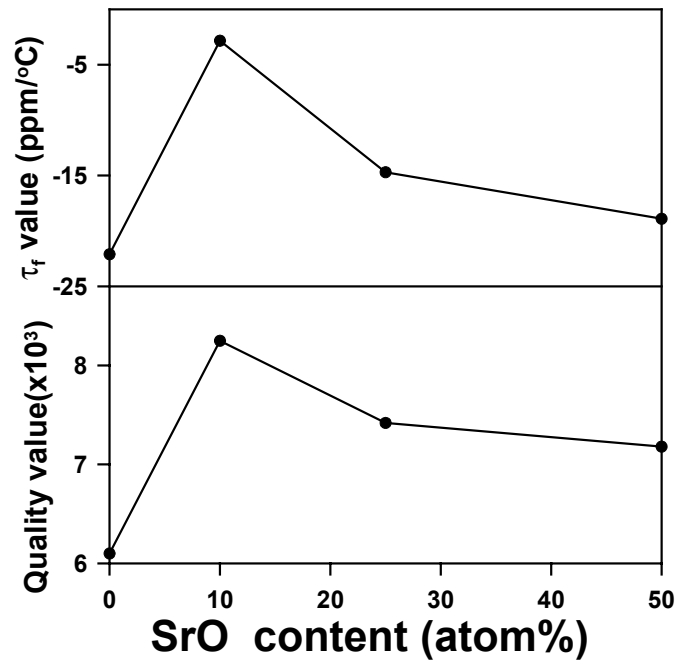


Fig. 5 The quality values and the temperature coefficients of resonant frequency of 1350°C-sintered  $(\text{Ba}_{1-x}\text{Sr}_x)\text{Sm}_2\text{Ti}_4\text{O}_{12}$  ceramics.