

# Microwave Dielectric Properties of Low-Loss (1-x) $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-xSmAlO}_3$ Ceramics

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**Abstract:** A novel compositions in the (1-x)  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-xSmAlO}_3$  system were prepared via conventional mixed oxide route in order to modify the positive temperature coefficient of resonant frequency ( $\delta_f$ ) of  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3$ . The microwave dielectric properties and phase composition of this system ceramics were investigated. X-ray powder diffraction results showed that  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3$  and  $\text{SmAlO}_3$  formed a solid solution when  $0.05 \leq x \leq 0.20$ . Microstructures of the sintered ceramics were observed by SEM; dielectric properties of the samples were also measured. The  $\delta_f$  values showed a near linear decrease with increasing additions of  $\text{SmAlO}_3$ . A dielectric constant of 53.1,  $Qf$  value of 24,085GHz and  $\delta_f$  value of +13.3ppm/°C were obtained for 0.80 $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-0.20 SmAlO}_3$  ceramics sintered at 1450°C for 4h.

**Keywords:** Dielectric Ceramic, High Dielectric Constant, Zero Temperature Coefficient, Low Loss

## 1. Introduction

In recent years, increased attentions has been paid to develop dielectric materials with high quality factor ( $Q \times f$ ), high dielectric constant ( $\epsilon_r$ ) and zero temperature coefficient of resonant frequency ( $\tau_f$ ) as dielectric resonators and microwave device substrates [1]. High dielectric constant material can effectively reduce the size of resonators. 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. Small temperature coefficient of the resonant frequency is required to ensure the stability of the microwave components at different working temperatures. Numerous perovskite-type compounds and their solid solutions have been investigated and applied in microwave frequency devices [2–6]. However, in MW frequency range the number of reported dielectrics with high  $\epsilon_r$ ,  $\tau_f \sim 0$ , and low loss is relatively poor.

Research focused on discovering new compositions is still active as there is a great demand for various permittivities. Combining two compounds with negative and positive temperature coefficients is the most means of obtaining a near-zero temperature coefficient of resonant frequency. Since  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3$  has a high dielectric constant of 101,  $Q \times f$  of 14,000GHz and a large positive temperature

coefficient of resonant frequency of +220 ppm/°C [7]; rare-earth aluminates,  $\text{SmAlO}_3$  possesses microwave dielectric properties ( $\epsilon_r \sim 20.4$ ,  $Q \times f \sim 65,000\text{GHz}$ ,  $\tau_f \sim -74$  ppm/°C) [8]. So in the present work, to compensate the  $\tau_f$  value and improved the  $Q \times f$ ,  $\text{SmAlO}_3$  has been introduced to form the solid solution (1-x)  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-xSmAlO}_3$ .

## 2. Experimental Procedure

### 2.1. Sample Preparation

The samples were prepared by the conventional solid-state reaction technique. For the synthesis of (1-x)  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-xSmAlO}_3$  ( $x = 0.05\text{--}0.20$ ) powders, High purity  $\text{CaCO}_3$  (99.5%),  $\text{Sm}_2\text{O}_3$  (99.9%) and  $\text{TiO}_2$  (99.9%),  $\text{Al}_2\text{O}_3$  (99.5%) powders were used as raw materials. The starting materials were mixed according to the stoichiometries of  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3$  and  $\text{SmAlO}_3$  separately. Mixtures were ball-milled in a nylon jar with zirconia balls and ethanol for 12 h, and after drying these powders were calcined at 1050–1200°C for 2 h. Different amounts of  $\text{SmAlO}_3$  were added to the calcined  $\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3$  and the desired compositions prepared from these mixtures were grounded again in ethanol for 12h. Then, the dried powders added with 5 wt% polyvinyl alcohol solution as binder were passed through a mesh and pressed into cylindrical samples

with 15 mm in diameter and 7 mm in thickness under a pressure of 250 kg/cm<sup>2</sup>. At last, these compacts muffled with powder of the same composition were sintered at 1450°C for 4h.

## 2.2. Characterization

The phase composition was identified by X-ray diffraction (XRD) using CuK $\alpha$  radiation (Bruker D8 advanced X). The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM) (Model Hitachi-SU8010, Hitachi Ltd., Japan). All samples were polished and thermally etched at a temperature which was about 100°C -150°C lower than its sintering temperature. The dielectric characteristics at microwave frequencies were measured by the Hakki-Coleman dielectric resonator method in the TE<sub>011</sub> mode [9] using a network analyzer (Advantest R3767C, Tokyo, Japan) and parallel conductor boards. The  $\tau_f$  value was determined from the difference between the resonant frequencies obtained at -35°C and 85°C.

## 3. Results and Discussion

Fig. 1 denoted the powder XRD patterns of (1-x) Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub>-xSmAlO<sub>3</sub> (x = 0.05–0.20) ceramics sintered at 1450°C for 4 h. All the four XRD peaks can be assigned to the orthorhombic perovskite type compounds (JCPDS-PDF#42-0423) with increasing addition of SmAlO<sub>3</sub>, extrapeaks were not observed even at the highest concentration when x=0.20. The X-ray diffraction study showed that Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> and SmAlO<sub>3</sub> can form a solid solution across the range (0.05 ≤ x ≤ 0.20) because of the similar ionic radii between Ca (1.34Å) and Sm (1.24Å) and between Ti (0.605Å) and Al (0.535Å) [10, 11]. It can be deduced that the most probable mechanism for solid solution formation is the substitution of Sm on the A (Ca) site and B (Ti) site in the perovskite structure.

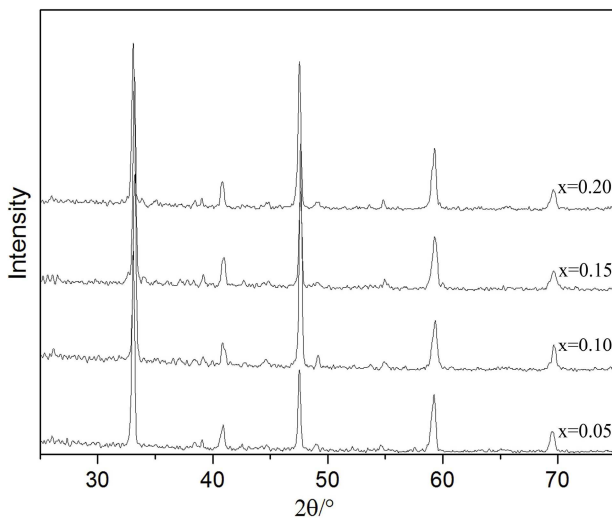


Fig. 1. X-ray diffraction patterns of (1-x) Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub>-xSmAlO<sub>3</sub> (x = 0.05–0.20) ceramics calcined at 1450°C.

Fig. 2 showed typical hexagonal grain morphology usually can be observed in perovskite structure ceramics. With increasing content of SmAlO<sub>3</sub> additions the grain sizes tended to become smaller as SmAlO<sub>3</sub> additions suppressed the grain growth and enhanced the densification process, which was analogy with the report by the researchers [12,13]. No significant amount of porosity is observed even at higher concentrations of SmAlO<sub>3</sub>. No evidence of second phases were observed in the SEM micrographs too.

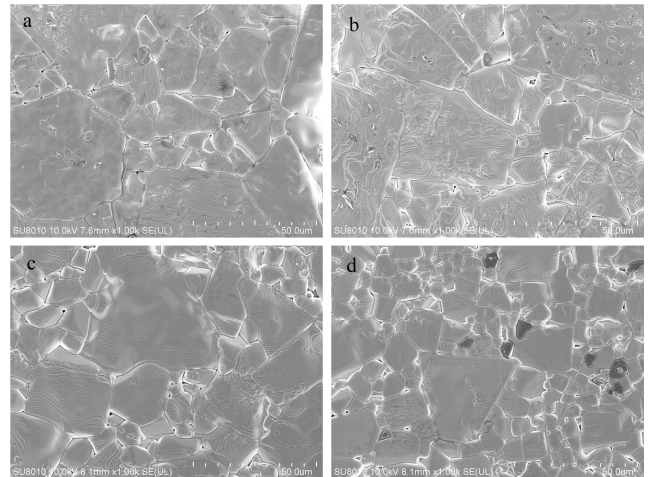
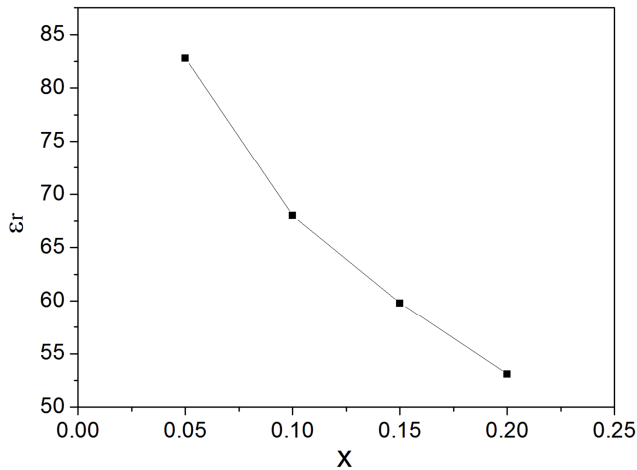
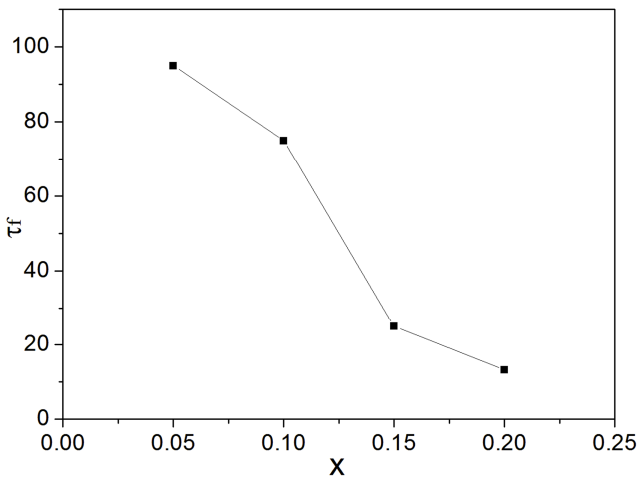


Fig. 2. SEM photographs of (1-x) Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub>-xSmAlO<sub>3</sub> (x = 0.05–0.20) ceramics with (a) x = 0.05, (b) x = 0.10, (c) x = 0.15, (d) x = 0.20.

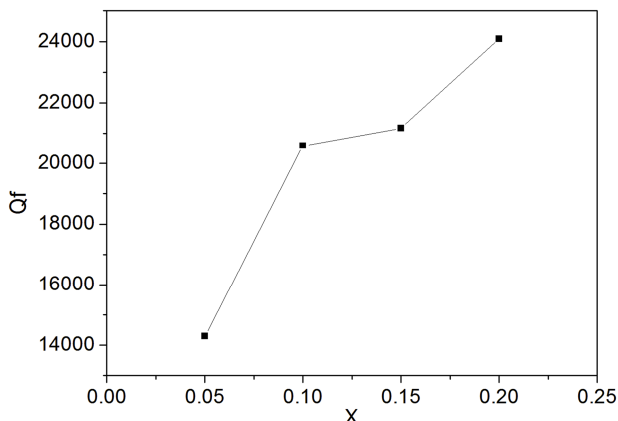
Fig. 3 demonstrated the dielectric constant of Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> ceramics with increasing additions of SmAlO<sub>3</sub> sintered at 1450°C for 4h. In all the compositions, additions of rare earth aluminates deteriorate the dielectric constant obviously. The observed change in permittivities is attributed to the low permittivities of the dopants SmAlO<sub>3</sub>. In a similar to the variation in permittivity in Fig. 3, as Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> and SmAlO<sub>3</sub> exhibit positive and negative temperature dependencies of permittivity respectively, a linear decrease with increasing content of the additives of the  $\tau_f$  values was shown in Fig. 4. SmAlO<sub>3</sub> decreased the  $\tau_f$  of (1-x)Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub>-xSmAlO<sub>3</sub> from +95ppm/°C to +13.3ppm/°C for samples with 5-20% additions. It is known that the temperature coefficient of composite ceramic was derived from the rule [14]:  $\tau_f = \nu / \tau_{f1} + \nu / \tau_{f2}$ , where the  $\tau_{f1}$  and  $\tau_{f2}$  are the  $\tau_f$  values of the Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> and SmAlO<sub>3</sub> phase, respectively. In all the compositions it is apparent that the  $\tau_f$  values of perovskite structured Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> ceramics can be tuned to near zero with suitable additions of SmAlO<sub>3</sub>. Fig. 5 showed a notable variation in Q×f values of Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> with various additions of SmAlO<sub>3</sub> ceramics. The entire range of compositions investigated exhibited a significant increase in the Q×f values with x=0.20 additions of SmAlO<sub>3</sub>. The high Q×f values of SmAlO<sub>3</sub> attributes to the increase in the Q×f values of Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub> under the condition of good densification. Q×f values as high as 24,085GHz were achieved with addition of x=0.20 to (1-x) Ca<sub>0.6</sub>Sm<sub>0.267</sub>TiO<sub>3</sub>-xSmAlO<sub>3</sub>.



**Fig. 3.** Variations of the relative permittivities of  $(1-x)\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}x\text{SmAlO}_3$  ( $x = 0.05\text{--}0.20$ ) ceramics with  $x$ .



**Fig. 4.** Change of  $\tau_f$  value with  $x$  for  $(1-x)\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}x\text{SmAlO}_3$  ( $x = 0.05\text{--}0.20$ ) ceramics.



**Fig. 5.** Quality factor ( $Qxf$ ) of  $(1-x)\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}x\text{SmAlO}_3$  ( $x = 0.05\text{--}0.20$ ) sintered at  $1450\text{ }^\circ\text{C}$  for 2 h as a function of the content of  $\text{SmAlO}_3$ .

## 4. Conclusion

$(1-x)\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}x\text{SmAlO}_3$  ( $x = 0.05\text{--}0.20$ ) microwave ceramics were prepared by solid-state reaction route at  $1450\text{ }^\circ\text{C}$  for 4h for the purpose of investigating effect of  $\text{SmAlO}_3$  ratio on the sintering behavior and microwave

dielectric properties. As the content of  $\text{SmAlO}_3$

increased from 0.05 to 0.20, no secondary phase appeared.

All samples of the  $(1-x)\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}x\text{SmAlO}_3$  ceramics exhibited formed perovskite phase system only. And furthermore,  $\text{SmAlO}_3$  functioned as sintering aids, which promoted the densification and suppressed the grain growth and thus, influenced the microwave dielectric properties. When the ratio of  $\text{SmAlO}_3$  was increased, the dielectric constant decreased monotonically,  $\tau_f$  values decreased continuously and  $Q \times f$  values increased. Ceramics with composition  $0.80\text{Ca}_{0.6}\text{Sm}_{0.267}\text{TiO}_3\text{-}0.20\text{SmAlO}_3$  sintered at  $1450\text{ }^\circ\text{C}$  for 4h had compact and possessed excellent microwave dielectric properties: relative permittivities constant  $\epsilon_r = 53.1$ ,  $Q \times f = 24,085\text{GHz}$  and the temperature coefficient of resonant frequency  $\tau_f = 13.3\text{ ppm}/^\circ\text{C}$ .

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