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Effects of CaO additives on the structure and properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ (x = 0.5) ceramics

Xu Wang[1,2] · **Juhua Luo**[1] · **Hao Guan**[1] · **Yue Xu**[2]

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Abstract The tungstenbronze-type-like Single-phase polycrystalline ceramics $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ (x = 0.5) doping with Ca ions had been prepared through the conventional solid-state reaction process. The phases and structure of the ceramics were analyzed through X-ray diffraction and scanning electron microscopy. The microwave dielectric properties of the ceramics were studied using a network analyzer. In this paper, the quality factor (Q × f) by substituting Ca ions for Ba ions in $(Ba_{1-\alpha}Ca_{\alpha})$ $Sm_2Ti_4O_{12}$ solid solutions in A1-sites was reported. In addition, the relationship between crystal structure and microwave dielectric properties was discussed from the viewpoint of structural formula and occupational state of large cations such as Ba, Ca ions in A1-sites.

1 Introduction

Microwave dielectric ceramic materials are rapidly developed in wireless communications, such as dielectric resonators in filters, phase shifters, and dielectric resonator antennae. Therefore, microwave dielectrics with high dielectric constant (ε_r) to enable device miniaturization, a low dielectric loss in the high-frequency region (i.e. high quality factor, Q × f) for good signal discrimination, and near-zero temperature coefficient (τ_f) of resonant frequency for temperature stability are of significant importance for these applications [1–4]. One of dielectric materials with high dielectric constant (ε_r) is tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions. The crystal structure of tungstenbronze-type-like $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ solid solutions was showed in these articles [5, 6].

Tungsten bronze-type like solid solutions with a formula of $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ feature excellent microwave properties; thus they have been employed in mobile phones and other microwave devices. Bolton et al. found that the compositions from $BaO–Sm_2O_3–TiO_2$ ternary system have good capacitance temperature stability; thus, they are suitable for temperature compensating ceramic capacitors [7]. Kolar et al. [8] and Nishigaki et al. [9] proposed $BaO–Nd_2O_3–TiO_2$ and $BaO–Sm_2O_3–TiO_2$ for ceramic filters due to their good dielectric properties.

The compounds $BaO–Sm_2O_3–TiO_2$ were appreciably developed and attracted the interest of both research and industry because they featured good microwave properties, high permittivity, and a high quality factor respectively. However their large negative or positive temperature coefficients of the resonant frequency (τ_f) values are far beyond the requirement of the microwave devices [10–15].

Compositional modification, such as partial substitution or formation of a solid solution is suggested to optimize the dielectric properties of microwave dielectric ceramics. Imaeda et al. [16, 17] studied $(Ba_{1-\alpha}Sr_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions where x = 0.6 and $0 \leq \alpha \leq 0.2$. As according to this report, a quality factor (Q × f) of these solid solutions was improved by increasing lattice stability, which resulted from substituting Sr ions with smaller ionic radius for Ba ions. However the relative permittivity decreased sharply and the temperature coefficient of resonant frequency (τ_f) were still far above the 0 ppm/°C.

✉ Xu Wang
wangxu@ycit.cn

[1] School of Materials Engineering, Yancheng Institute of Technology, 9 Yingbin Street, Yancheng 224051, People's Republic of China

[2] College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, 29 Yudao Street, Nanjing 210016, People's Republic of China

In this paper, the crystal structure of $(Ba_{1-\alpha}Ca_{\alpha})$ $Sm_2Ti_4O_{12}$ (BCST)solid solutions were demonstrated i.e. $(Ba_{1-\alpha}Ca_{\alpha})_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ where x = 0.5. Furthermore, microwave dielectric properties of $(Ba_{1-\alpha}Ca_{\alpha})Sm_2Ti_4O_{12}$ solid solutions, and α = 0.01, 0.03, 0.05 and 0.07, were reported. Relationship between crystal structure and microwave dielectric properties was discussed from the viewpoint of structural formula and occupational state of large cations such as Ba, Ca ions in A1-sites.

2 Experimental procedure

$(Ba_{1-\alpha}Ca_{\alpha})$ $Sm_2Ti_4O_{12}$ ceramic samples with α = 0.01, 0.03, 0.05, 0.07 were fabricated by conventional solid-state reaction process from the starting materials including Sm_2O_3 (99.9%), $CaCO_3$ (99.8%), $BaCO_3$ (99.7%), TiO_2 (99.9%).The raw materials were dried and weighed according to the above formalism and milled with ZrO_2 balls in ethanol for 24 h. The wet mixed powders were dried and calcined at the temperature about 1000 °C for 2 h in an alumina crucible. The calcined powders were reground for 24 h, dried, mixed with 7 mol% PVA as binder and granulated. The granulated powders were uniaxially pressed into compacts with 15 mm in diameter and 6–8 mm in height under the pressure of 100 MPa. The compacts were sintered at optimum temperature for 4 h. In order to prevent the evaporation loss, the compacts were muffled with powder of the same composition. The cooling rate of 100 °C/h was executed till room temperature.

The phase constituents of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered CuKa radiation (40 KV and 40 mA, Model advanced D8 Bruker). Bulk densities of the sintered specimens were identified by the Archimedes' method. The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM) (Model Hitachi S-4800, Hitachi Ltd., Japan). All samples were polished and thermally etched at the temperature which was 150 °C lower than its sintering temperature. Microwave dielectric properties of the sintered samples were measured about 3.6 GHz using a network analyzer(Advantest R3767C, Tokyo, Japan). The ε_r was measured according to the Hakki–Coleman method using the TE011 resonant mode, and the τ_f was measured using invar cavity in the temperature range from 20 to 80 °C.

3 Results and discussion

3.1 Crystalline structure and microstructure

The $(Ba_{1-\alpha}Ca_{\alpha})$ $Sm_2Ti_4O_{12}$ ceramic with α = 0.01, 0.03, 0.05, 0.07 samples with faint yellow color, no cracks after sintering meant well sintered. Their linear shrinkage (i.e. from the green body to the sintered specimens) was approximately 15%. The X-ray diffractograms of the sintered BCST ceramics with different amounts of Ca ions addition (1–7 mol%) are plotted in Fig. 1a and the expanded graph in the region (2θ of 31.2°–32.2°) is presented in Fig. 1b. The end of sample's name about BCST-1, BCST-3,BCST-5,BCST-7 means the (Ba1−αCaα) $Sm_2Ti_4O_{12}$ with different amount of CaO addition (in mol%) of the samples.

The patterns of the samples matched well with the orthorhombic tungsten bronze structure of the $BaSm_2Ti_4O_{12}$ samples (PDFNO.43–0235). The strongest diffraction peaks appeared at 2θ = 31.7° should be attributed to the (151) plans of $BaSm_2Ti_4O_{12}$. No other characteristic peaks from other crystalline forms were detected, indicating that no obvious secondary phases were present.

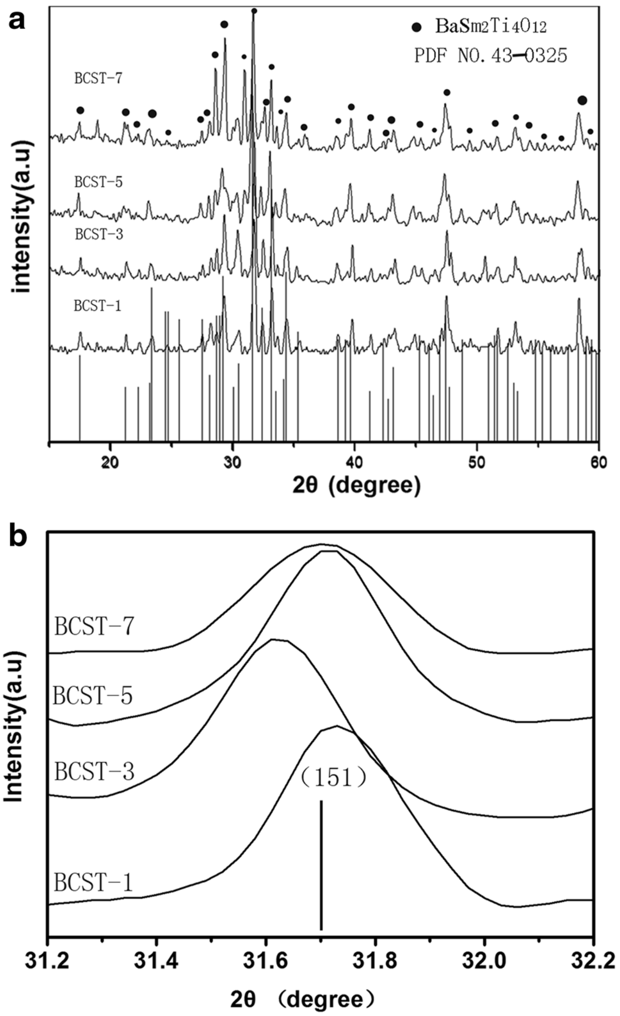

Fig. 1 **a** X-ray diffractograms of the sintered ceramics BCST with different amounts of Ca ions addition(at the *bottom* of the figure used for matching the XRD peaks refer to the PDFNo. 43–0235), **b** Expanded XRD patterns in the 2θ range of 31.2°–32.2°

Figure 1 showed all samples doped with different amounts of Ca ions have the same main diffraction patterns except the position of diffraction peaks little difference. It meant doping Ca ions did not have great influence on the BCST crystal structure till the content of the doped ca^{2+} increased to 3%. This was due to the solubility of CaO in the lattice without additional phase when the content of addition was small. As the Ca content (α) increased to 0.03 in BCST, the diffraction peaks of the BCST powders shifted towards to a lower angle, which indicated that the volume of unit cell increased and the results agreed well with Table 1. It was also worth noting that the full-width-at-half-maximum(FWHM) of the diffraction peak varies remarkably with the Ca content, which should be correlated with the magnitude of grain size.

Table 1 Cell volume of the produced $(Ba_{1-\alpha}Ca_{\alpha})\ Sm_2Ti_4O_{12}$ (BCST) ceramics with different amounts of Ca ions (represented in the number at the end of samples' name)

Sample	Density (g/cm^3)	Refined volume (Å^3)
BCST-1	5.559	1032.8
BCST-3	5.546	1037.3
BCST-5	5.525	1033.3
BCST-7	5.568	1034.1

Figure 2 demonstrates microstructures of thermally etched BCST (α = 0.01, 0.03, 0.05 and 0.07) ceramics after sintering at their optimal sintering temperatures. Dense and homogenous microstructures were observed in all samples. No apparent grains of a secondary phase were observed in the Ca ions doped BCST ceramics. The results matched X-ray analysis (Fig. 1a) fairly well.

The grains are mostly typical hexagonal grain morphology sized for undoped $BaSm_2Ti_4O_{12}$. With increasing CaO content the difference between the larger grains and the smaller grains became more pronounced and irregular in shape Fig. 2c, d. Obviously, addition of small amounts of dopants i.e. 0.01 and 0.03 mol CaO enhances the grain size. A small amount of porosity can be observed at α = 0.03. Moreover, the general grain size of ceramics with α = 0.07 was much smaller than the others, which is in good accordance with the variation of FWHM shown in Fig. 1b.

Generally, with increasing CaO doping level, an enlarged grain size should be expected as more liquid phase would

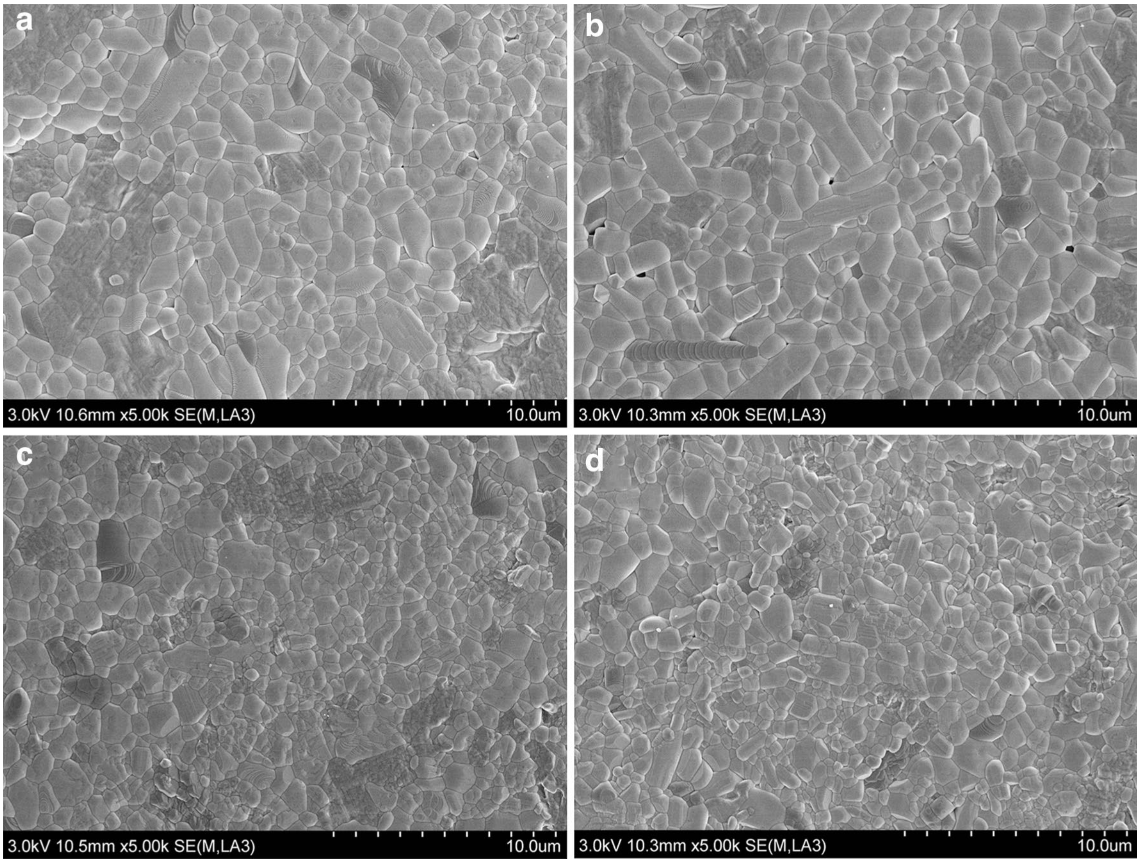

Fig. 2 Microstructure (observed by SEM) of BCST ceramics with different amounts of Ca ions: **a** 1%, **b** 3%, **c** 5%, **d** 7%

form to promote the grain growth [18]. Nevertheless, rare earth oxide often plays a role of grain growth inhibitor in many ceramics [19], which should be responsible for the unexpected decline of grain size in Fig. 2(c, d).

3.2 Densification

The influence of the amount of Ca ions added on the values of the relative density of the sintered BCST ceramics was plotted in the curve of Fig. 3. In BCST ceramics, the relative density decreased with α increase as a small amount of porosity can be observed. However when α up to 7% the densification increased to 94.7% of the theoretical density.

3.3 Microwave dielectric properties

The Q×*f* values and dielectric constant of BCST ceramics with different amounts of Ca ions sintered at their optimal sintering temperatures for 4 h were shown in Fig. 4.

The Q×*f* of undoped $BaSm_2Ti_4O_{12}$ ceramics is about 10,000 GHz [11]. The Q×*f* of BCST ceramics decreased obviously when α up to 3%, meanwhile the ε_r varied slightly according with the relative density (seen from Fig. 3).

Q×f value is generally affected by crystallizability, oxygen vacancy, long-range ordering degree of cations, inner stress of the crystals and phase constitution. In the present situation, Ca substitution for Ba leaded to alter the crystal cell volume (seen from Table1) and decrease the reduced mass which increases the Q×f value according the following equation:

$$Q\times f = \frac{\beta - \frac{(Ze)^2}{3V\varepsilon}}{2\pi\gamma m} \tag{1}$$

where V is the crystal cell volume in Å^3, γ is damping constants, m is reduced mass, Z is charge valences; However the γ was greatly influenced by grain boundaries、porosity, so decline of grain size increased the grain boundaries and the amount of porosity can decreased Q×f value greatly.

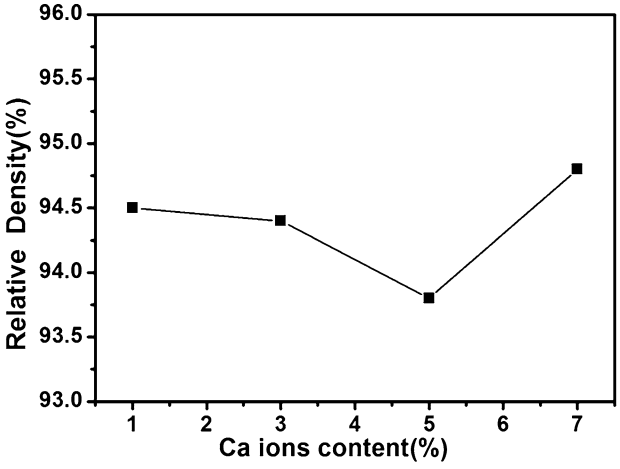

Fig. 3 Influence of the relative density of the sintered BCST ceramics on the amount of Ca ions

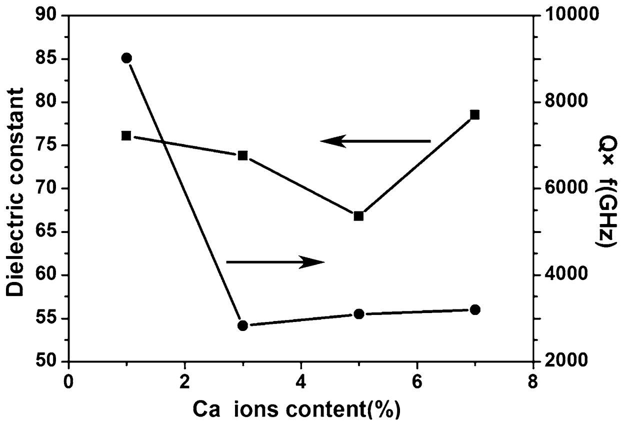

Fig. 4 Influence of the Q×f values and dielectric constant of the BCST ceramics on the amount of Ca ions

The Clausius–Mosotti equation shows explicitly how dielectric constant depends on composition and crystal structure through polarizability and molar volume as following:

$$\varepsilon = \frac{3V + 8\pi\chi}{3V - 4\pi\chi} \tag{2}$$

where *V* is the crystal cell volume in Å^3, χ is the cell polarization. The polarizability of Ca^{2+} 3.16 Å^3 is lower than that of Ba^{2+}(6.40 Å^3) [20, 21] and consequently the total polarizabilities reduced significantly with increasing α due to the substitution of Ca^{2+} for Ba^{2+}, which leads to the decrease of ε_r. Although the increase of crystal cell volume resulted in the increase of ε_r; but it was relatively not so much. On the other hand, the influence of relative density on the dielectric constant was more significant. Therefore, there was a decrease of ε_r with α which matched well with the relative density.

The temperature coefficient of the resonant frequency τ_f correlated with the structural and compositional characteristics of a material.

From Fig. 5, the BCST ceramics approached to zero value τ_f with 1.0 mol% Ca ions additions. The value of τ_f can be adjusted by Ca ions additions with changing the tolerance factor (t). The tolerance factor can be calculated by the following equation:

$$t = \frac{[(\frac{4}{5} + \frac{x}{5})R_{Sm^{3+}} + (\frac{1}{5} - \frac{x}{5})R_{Ba^{2+}}] + R_{O^{2-}}}{\sqrt{2}(R_{Ti^{4+}} + R_{O^{2-}})} \tag{3}$$

where *R* is the ionic radius in Å, in the $(Ba_{1-\alpha}Ca_\alpha)_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ systems (in this paper x=0.5). This structural formula can be represented as

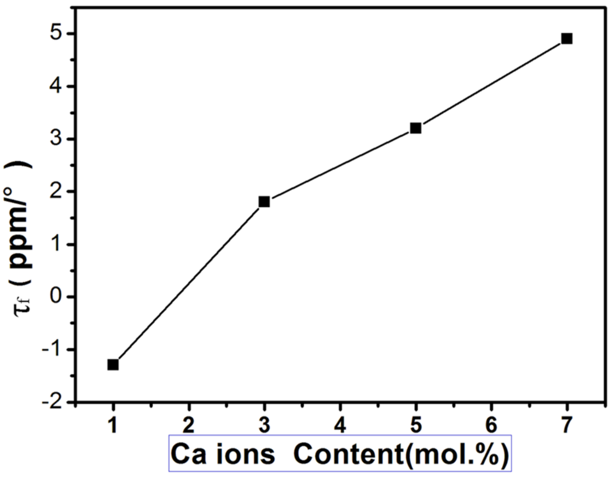

Fig. 5 Influence of temperature coefficient of resonant frequency (τ_f) of the BCST ceramics on the amount of Ca ions

$[Ba_{0.5-\alpha}Ca_{\alpha}Sm_9V_{0.5}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ [22]. Some Ba ions in A1-sites are substituted by Ca ions. As a result, the *t* decreased, the τ_f move toward to the positive value. So the τ_f value increases almost linearly and changes from negative to positive in the region of $0.01 \leq \alpha \leq 0.07$.

4 Conclusion

Single-phase ceramics can be prepared by the Ca substitution of $BaSm_2Ti_4O_{12}$, resulting in the formation of $(Ba_{1-\alpha}Ca_{\alpha})$ $Sm_2Ti_4O_{12}$ based solid solutions for determined sintering conditions. The addition of Ca ions, tested up to 7 mol%, did not alter the main orthorhombic tungsten bronze structure of the crystalline phase. The values of ε_r and τ_f can be influenced by varying the amount Ca ions. The values of Q×f exhibited a non-monotonous behavior and deteriorated greatly with the increase of Ca ions addition. For the BCST ceramics, the best values of the dielectric properties were obtained with 1.0 mol% Ca ions addition as $\varepsilon_r = 76.1$, $Q\times f = 9000$ GHz, and $\tau_f = -1.3$ ppm/°C.

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