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Short communication

Microstructure and dielectric tunable properties of $SrO(Sr_{1-x}Ba_xTiO_3)_n$ microwave ceramics

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Abstract

Microstructure and dielectric tunable properties of $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0$ and 0.5, $n = 1$–4) microwave ceramics prepared through solid-state reactions have been investigated. For $SrO(SrTiO_3)_n$ series, Sr_2TiO_4 can be isolated as single phase in $n = 1$ product and $Sr_4Ti_3O_{10}$ appears in the $n \geq 2$ cases as either a major phase ($n = 3$, 4) or a second phase ($n = 2$). Ba^{2+} substitution for Sr^{2+} causes the formation of $SrTiO_3$ and $Ba_xSr_{2-x}TiO_4$. $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($n = 1$, 2) have no dielectric non-linear behavior in the temperature range of −165 to 50 °C. As n increases, the tunability increases. As a result, Ba^{2+} substitution for Sr^{2+} results in an increase in permittivity and tunability, but a decrease in Q value.

Keywords: Layered perovskite structure; Tunability; Microwave properties

1. Introduction

$SrO(SrTiO_3)_n$ (n = integer) series represents the prototype of a huge family of layered oxides described by Ruddlesden and Popper [1,2], consisting of alternate stacks of SrO layers and perovskite $(SrTiO_3)_n$ block layers along the c-axis. The upper member of $SrO(SrTiO_3)_n$ is the well-known $SrTiO_3$ ($n = \infty$), which has been commonly used in grain boundary barrier-layer capacitors [3], resistive oxygen gas-sensors [4], solar cells [5], solid oxide electronic devices [6,7], substrates for perovskite films [8], and efficient photocatalyts [9,10]. The properties of $SrO(SrTiO_3)_n$ have yet been fully explored. They are expected to have applications like $SrTiO_3$.

Strained $SrTiO_3$ can exhibit ferroelectricity even at room temperature [11]. The relatively high tunability of the strained $SrTiO_3$ unfortunately signifies a remarkable increase in both relative permittivity and loss, rendering it less useful for high-frequency applications. The prospect of "engineering" the properties of $SrO(SrTiO_3)_n$ by varying n has stimulated experimental research as well as theoretical studies [12,13]. Its relative permittivity decreases as n decreases [14]. $SrO(SrTiO_3)_n$ may provide new tunable materials which have decreased loss [15]. Wise et al. [14] found that $(Sr_xCa_{1-x})_{n+1}Ti_nO_{3n+1}$ exhibited higher quality factors ($Q = 1/\tan\delta$) than $Sr_{n+1}Ti_nO_{3n+1}$. This paper was aimed to study dielectric properties of $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0$ and 0.5, $n = 1$–4) ceramics.

2. Experimental procedure

$SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0$ and 0.5, $n = 1$–4) ceramics were prepared through the conventional solid-state reaction method. High-purity $BaCO_3$ (99.0%, Sinopharm Chemical Reagent Co., Ltd., China), $SrCO_3$ (99.0%, Sinopharm Chemical Reagent Co., Ltd, China) and TiO_2 (98.0%, Sinopharm Chemical Reagent Co., Ltd., China) powders were used as starting materials. Mixtures based on the compositions of $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0$ and 0.5, $n = 1$–4) were ball-milled with zirconia media in ethanol for 24 h and then dried at 110 °C for 12 h. After drying, the powders were calcined at 1200 °C for 4 h and then re-milled for 24 h. The calcined powders, mixed with 8 wt% polyvinyl alcohol (PVA), were pressed into pellets at 100 MPa. The green pellets were kept at 550 °C for 6 h to remove the solvent and the binder. $SrO(SrTiO_3)_n$ and $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ ceramics were sintered for 5 h in air at 1500 °C and 1450 °C, respectively.

Phase compositions of the ceramics were investigated by means of X-ray diffraction (XRD, Bruker D8 Advanced,

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Germany) with CuK_α radiation. Microstructural information was obtained by using a scanning electron microscopy (SEM, JSM EMP-800). Permittivity as a function of temperature was measured at 10 kHz in the temperature range of −165 to 50 °C, under 0 kV/cm and 30 kV/cm, respectively, using a Keithley model 2410 (Cleveland, OH) high-voltage source, coupled with TH2816A LCR meter (Changzhou, China). Permittivity and loss tangent at microwave frequencies was measured by the Hakki-Coleman dielectric resonator method, using a network analyzer (AV 3629A) in combination with a resonating cavity [16].

3. Results and discussion

XRD patterns of the $SrO(SrTiO_3)_n$ (n = 1–4) ceramics are shown in Fig. 1(a). For the sample with n = 1, Sr_2TiO_4 can be isolated as single phase according to JCPDF Nos. 72-2040 and 72-2041. $Sr_4Ti_3O_{10}$ appears in the samples with $n \geq 2$ as either a major phase (n = 3 and 4) or a second phase (n = 2). Wise et al. [14] reported that $Sr_3Ti_2O_7$ appeared in all samples as either a major phase ($n \geq 2$) or a second phase (n = 1). It can be seen that $SrTiO_3$ diffraction peaks appear in the sample with n = 3 and become stronger as n increases, which is in agreement with the results reported by Wise et al. [14].

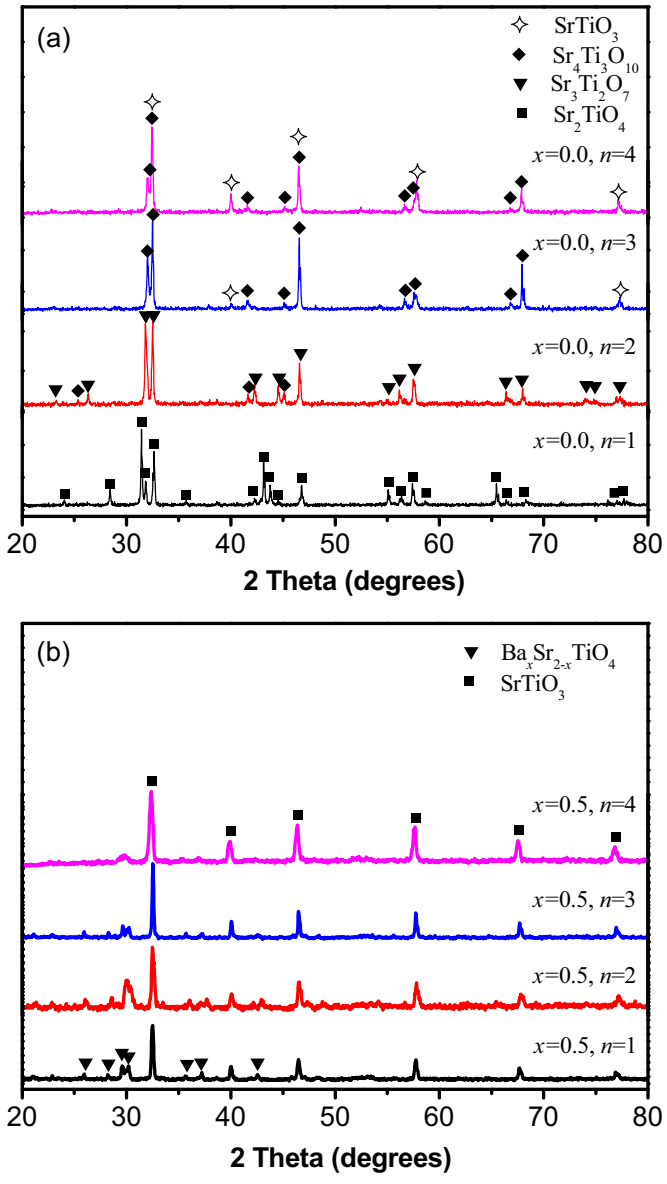

Fig. 1. XRD patterns of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ (x = 0.0 and 0.5, n = 1–4) ceramics: (a) x = 0.0 and (b) x = 0.5.

Fig. 1(b) shows XRD patterns of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ (n = 1–4) samples. All members have additional diffraction lines besides $SrTiO_3$ peaks, which can be assigned to $Ba_xSr_{2-x}TiO_4$ [17]. It means that $Ba_xSr_{2-x}TiO_4$ is more stable than $Ba_xSr_{1-x}TiO_3$. Meanwhile, it is notable that the $Ba_xSr_{2-x}TiO_4$ diffraction peaks become weaker as n increases. According to Wise et al. [14], $(Sr_xCa_{1-x})_3Ti_2O_7$ could be single phase. Single phase $(Sr_xRE_{1-x})_3Ti_2O_7$ ceramics were also reported by Wang et al. [18,19]. Here, $(Sr_xBa_{1-x})_3Ti_2O_7$ was not formed, which may be attributed to the destroyed symmetry of TiO_6 by the substitution for Sr^{2+} with larger Ba^{2+}. Wang et al. found that higher symmetry of TiO_6 was achieved by the substitution for Sr^{2+} with smaller RE^{2+} [20].

As shown in Fig. 2, the n = 1 and n = 2 samples have homogeneous microstructure with grains of 2–10 μm, while the n = 3 and 4 samples have a bimodal microstructure, consisting of pellet-shaped grains with a size of ~50 μm and fine grains of 2–10 μm. Block-like grains and porous microstructures are observed in n = 3 and n = 4 samples because the migration of grain boundaries was hindered during sintering [21].

Fig. 3 shows SEM image of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ (n = 1–4) ceramics. The $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ ceramics except that with n = 1 have quite dense microstructure. The n = 1 sample has a bimodal microstructure, consisting of vermiculate-shaped grains of 2–5 μm, and platelet grains with a size of ~8 μm, whereas the $n \geq 2$ samples have a homogeneous microstructure. Compared to $SrO(SrTiO_3)_n$ ($n \geq 3$), the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ ($n \geq 3$) ceramics has no platelet grains, possibly due to the formation of an orthorhombic Ba_2TiO_4-type structure [17].

Similar to that of quantum paraelectric $SrTiO_3$, Curie temperature of the $SrO(SrTiO_3)_n$ sample is also very low (< −165 °C). Temperature-permittivity curves of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ (x = 0.0 and 0.5, n = 1, 2) ceramics measured at 30 kV/cm are almost identical to those at 0 kV/cm, indicating that their tunabilities are almost zero in the temperature range of −165 to 50 °C. Temperature dependencies of permittivity of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ (x = 0.0 and 0.5, n = 3, 4) ceramics, measured at 0 kV/cm and 30 kV/cm, are displayed in Fig. 4. Calculated tunabilities at −150 °C and −100 °C are listed in Table 1. The increase in tunability of the $SrO(SrTiO_3)_n$ ceramics with increasing n is due to the increase in TiO_6 content. The tunability at −150 °C of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ samples markedly increases as compared to that of the $SrO(SrTiO_3)_n$ ceramics, whereas their tunabilities at −100 °C are almost the same, suggesting the formation of $Ba_xSr_{2-x}TiO_4$ instead of $Ba_xSr_{1-x}TiO_3$ [22]. The tunability of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ (x = 0.0 and 0.5, n = 3, 4) ceramics decreases with increasing temperature, which is attributed to

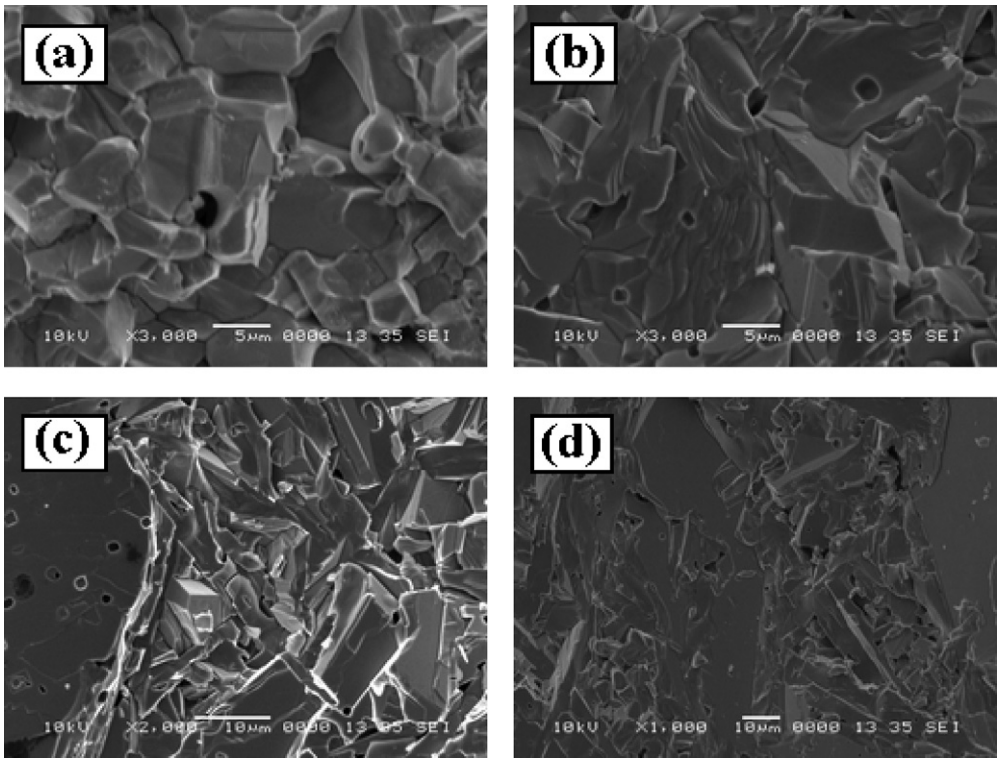

Fig. 2. Cross-section SEM images of the $SrO(SrTiO_3)_n$ ceramics: (a) $n = 1$, (b) $n = 2$, (c) $n = 3$ and (d) $n = 4$.

the fact that residual polar/distorted clusters are absent when the temperature is far beyond Curie temperature.

Microwave dielectric parameters of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0.0$ and 0.5, $n = 1$–4) ceramics are also listed in Table 1. For the $SrO(SrTiO_3)_n$ series, permittivity increases with increasing n, whereas Q value slightly decreases. Structurally, both permittivity and Q value of a material depend on its composition and crystal structure. For microwave dielectrics,

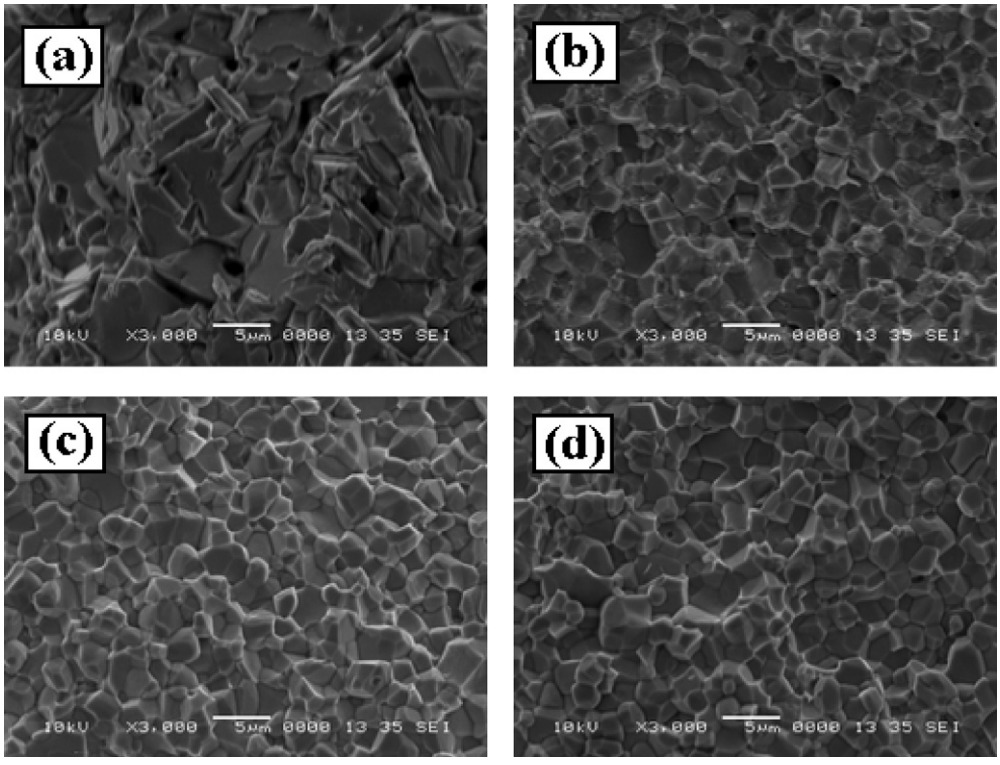

Fig. 3. Cross-section SEM images of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ ceramics: (a) $n = 1$, (b) $n = 2$, (c) $n = 3$ and (d) $n = 4$.

Table 1
Dielectric properties of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0$ and 0.5, $n = 1$–4) ceramics.

Samples	Tunability (30 kV/cm) (%)		Resonant frequency (GHz)	ε	Q value
	at −150 °C	at −100 °C			
$x = 0.0$, $n = 1$	–	–	6.531	32.6	1963
$x = 0.0$, $n = 2$	–	–	3.448	59.2	1359
$x = 0.0$, $n = 3$	–	–	3.214	79.1	1290
$x = 0.0$, $n = 4$	11.35	6.49	2.519	102.3	1126
$x = 0.5$, $n = 1$	–	–	6.733	39.9	383
$x = 0.5$, $n = 2$	–	–	4.518	86.5	495
$x = 0.5$, $n = 3$	6.05	3.75	4.034	145.5	853
$x = 0.5$, $n = 4$	23.61	5.27	3.157	210.4	553

polarizability dominates permittivity [23]. As n increases, the SrO content decreases, so that average ionic polarizability increases, thus increasing permittivity [14]. The intrinsic loss strongly depends on permittivity [24]. The Q values of our samples are lower than those reported by Wise et al. [14], which may be related to the purity of raw materials, and second phases and porosity of the ceramics. Compared to that of $SrO(SrTiO_3)_n$, permittivity of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ ceramics is higher, whereas their Q values are markedly lower. Because the polarizability of Ba^{2+} (1.55×10^{-30} m^3) is higher than that of Sr^{2+} (0.864×10^{-30} m^3) [25], Ba^{2+} substitution for Sr^{2+} causes an increase in permittivity. The low Q value of the $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ series is probably attributed to the formation of the $Ba_xSr_{2-x}TiO_4$ phase.

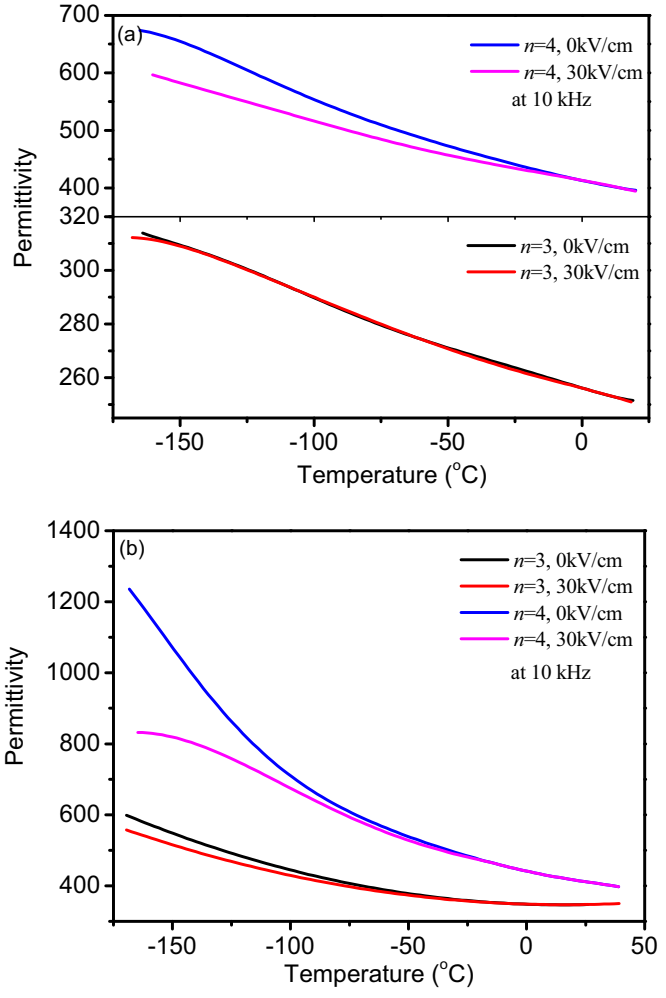

Fig. 4. Temperature dependences of permittivity of the $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($x = 0.0$ and 0.5, $n = 3$, 4) ceramics: (a) $x = 0.0$ and (b) $x = 0.5$.

4. Conclusions

For $SrO(SrTiO_3)_n$ series, Sr_2TiO_4 was single phase, while $Sr_3Ti_2O_7$ and $Sr_4Ti_3O_{10}$ were not single phase. $Sr_4Ti_3O_{10}$ appeared in the samples with $n \geq 2$ as either a major phase ($n = 3$, 4) or a second phase ($n = 2$). $SrTiO_3$ appeared in the sample with $n = 3$ and its amount increased as n increased. Ba^{2+} substitution for Sr^{2+} caused the formation of $SrTiO_3$ and $Ba_xSr_{2-x}TiO_4$. Meanwhile, it promoted the formation of equiaxed grains instead of block-like ones. $SrO(Sr_{1-x}Ba_xTiO_3)_n$ ($n = 1$, 2) had no tunability over −165 to 50 °C. As n increased, the tunability increased. Compared to $SrO(SrTiO_3)_n$ series, $SrO(Sr_{0.5}Ba_{0.5}TiO_3)_n$ series had higher permittivity and higher tunability, but lower Q value.

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