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# Low-loss (1-x)Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>-xCaTiO<sub>3</sub> microwave dielectric ceramics with medium permittivity

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#### ABSTRACT

In the present work, a series of  $(1-x)Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}-xCaTiO_3$  (x = 0.02, 0.03, 0.05, 0.1 and 0.2, BSLT-CT) functional ceramics were synthesized via co-firing the mixtures of  $Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}$  and CaTiO\_3 powders. Crystal structure and microwave dielectric properties were investigated together thermally stimulated depolarization currents (TSDC). Scanning electron microscopy (SEM) would be explored. X-ray diffraction confirms that these compounds display a single hexagonal phase with perovskite structure and the diffraction peaks shift to high angles with increasing CaTiO\_3 content. Raman spectra uncover O<sub>h</sub> symmetry deviation and distortions of oxygen octahedra. The variation of the CaTiO\_3 addition has a direct impact on the dielectric properties of the (1-x)BSLT-xCT ceramics at microwave frequency. TSDC was conducted to acquire the defects associated with extinsic microwave loss mechanism. The main type of defect in BSLT-CT is oxygen vacancy ( $V_0^{\bullet*}$ ), namely involving in-grain and across-grain relaxation. The increase of CaTiO\_3 prompts the increase of oxygen vacancy concentration, which may induce microwave loss. At x = 0.2, the microwave dielectric properties of specimens are  $e_r = 47.1$ ,  $Q \times f = 41,200$  GHz and  $\tau_f = -5.3$  ppm/°C, respectively.

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#### 1. Introduction

The high-speed progress in wireless communication and wireless broadband network technology has guided an ever-increasing demand for microwave dielectrics. Many kinds of microwave dielectrics have been commercially employed in a wide range of applications from cell phones to Internet of things, usually as waveguides, substrates, antenna, filters, resonators, microwave capacitance and other pivotal components in microwave devices [1–15]. To meet the practical application of dielectric elements, three critical parameters of microwave dielectrics are demanded:

https://doi.org/10.1016/j.jallcom.2019.153011 0925-8388/© 2019 Elsevier B.V. All rights reserved. high permittivity ( $\varepsilon_r$ ) for device miniaturization, high quality factor  $(Q \times f)$  or low dielectric loss  $(\tan \delta = 1/Q)$  for frequency selectivity and low temperature coefficient of resonant frequency  $(\tau_f)$  for temperature stability [3–9]. Among them, microwave dielectrics with medium permittivity ( $\varepsilon_r > 30$ ) are applicable to mobile and satellite telecommunications. To date, many reports have been focused on the design, combination, structure and properties of medium-permittivity materials family [6-10]. Microwave dielectric ceramics with perovskite structure or related structures have been intensively investigated, such as cubic, tetragonal, hexagonal and orthorhombic polymorphs [1-15]. Meanwhile, hexagonal perovskite are fascinating due to their novel structure characteristics and good dielectric properties at microwave bands [1,2,6–15]. Hexagonal perovskite illustrate three types of crystal structures, namely, the shifted, the twinned and the fully-filled one, which are less universal than their cubic close-packed counterparts [6-8,10-15]. In particular, the B-site deficient hexagonal compounds may be depicted by the general formula  $A_n B_{n-1} O_{3n}$  and these compounds represent the structure characteristics of (n-1)corner-sharing octahedral layers separated by a vacant octahedral

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layer. At the same time, the majority of the  $A_nB_{n-1}O_{3n}$  members are classified into the shifted type [7,12,13].

There have been several researches on the structure-property relationships of the B-site deficient hexagonal perovskites with medium permittivity ( $\varepsilon_r > 30$ ) and modest Q × f and  $\tau_f$  values, which displays a good potential being applied in microwave components and devices [6-8,10-15]. I.N. Jawahar et al. reported the structure and microwave dielectric properties of  $A_5B_4O_{15}$  (A = Ba. Sr, Mg, Ca, Zn; B=Nb, Ta) ceramics [11]. Among these materials, 5CaO-2Nb<sub>2</sub>O<sub>5</sub>, 5CaO-2Ta<sub>2</sub>O<sub>5</sub>, 5ZnO-2Nb<sub>2</sub>O<sub>5</sub> do not indicate a single hexagonal phase compounds analogous to A<sub>5</sub>B<sub>4</sub>O<sub>15</sub>. Y. Tohdo et al. reported that the sites of  $Ba^{2+}$  and  $La^{3+}$  in  $BaLa_4Ti_4O_{15}$  were successfully distinguished via X-ray single crystal analysis, regardless of the similarity for atomic scattering factors [14]. Trolliard et al. reported that the different intergrowth compounds exist in  $Ba_{11}Nb_8TiO_{33}$ ,  $Ba_{16}Nb_{12}TiO_{48}$  and  $Ba_{21}Nb_{16}TiO_{63}$  [13]. L. Fang et al. also reported Ba<sub>3</sub>La<sub>2</sub>Ti<sub>2</sub>Nb<sub>2</sub>O<sub>15</sub> and Ba<sub>2</sub>La<sub>3</sub>Ti<sub>3</sub>NbO<sub>15</sub> ceramics have high dielectric constant above 43 accompanied with high  $Q \times f$ up to 21,726 GHz and low  $\tau_f$  value [15]. In our previous reports, we investigated the structure and microwave dielectric properties of Ba<sub>1-x</sub>Sr<sub>x</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and Ba<sub>1-x</sub>Ca<sub>x</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> ceramics [6]. Among these compounds, Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (BSLT) sintered at 1500 °C shows microwave dielectric properties of  $\varepsilon_r$  = 44.7, Q × f = 45,000 GHz and  $\tau_f = -7.5 \text{ ppm}/^{\circ}\text{C}$ . To meet the requirement of applications, the  $\tau_f$ value of BSLT should be modulated close to 0 ppm/°C. To obtain a stable  $\tau_f$  coefficient, it is a common approach to combine a positive  $\tau_f$  material with a negative  $\tau_f$  one [3]. In this work, we choose CaTiO<sub>3</sub> as  $\tau_f$  compensator into the BSLT matrix. It is well known that CaTiO<sub>3</sub> is an orthorhombic perovskite with microwave dielectric properties of  $\varepsilon_r = 170$ ,  $Q \times f = 8000$  GHz, and  $\tau_f = +800$  ppm/°C. Lately, thermally stimulated depolarization current (TSDC) technique has been utilized to illustrate the electrical behavior of inorganic dielectric materials [16-22]. Depending on the TSDC spectra, defects can be qualitatively analyzed which exist in the material's body, such as dipoles, trap charges, space charges, etc [16–22]. Most importantly, it can provide new insight to comprehend defects and extrinsic dielectric loss mechanisms.

In the present work, a series of  $(1-x)Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}-xCaTiO_3$ (x = 0.02, 0.03, 0.05, 0.1 and 0.2, BSLT-CT) functional ceramics were synthesized by co-firing the mixtures of  $Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}$  and CaTiO<sub>3</sub> powders. The effects of CaTiO<sub>3</sub> on the crystal structure, microwave dielectric performance and TSDC behavior of  $Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}$  were investigated systematically.

#### 2. Experimental procedure

The  $(1-x)Ba_{0.6}Sr_{0.4}La_4Ti_4O_{15}-xCaTiO_3$  (x = 0.02, 0.03, 0.05, 0.1 and 0.2) polycrystalline ceramics were synthesized through the solid-state reaction process. Analytical reagents BaCO<sub>3</sub>, SrCO<sub>3</sub> and CaCO<sub>3</sub> (99.9%, Sinopharm Chemical Reagent Co. Ltd.) and La<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> (99.99%, Aladdin Chemistry Co. Ltd.) were used as starting materials. In accordance with the stoichiometric ratio of Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and CaTiO<sub>3</sub>, these raw powders were weighed and mixed with zirconia balls for 4 h in ethanol medium. Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and CaTiO<sub>3</sub> powders were synthesized firstly and calcined at 1300 °C and 1000 °C for 4 h, respectively. Then, the calcined Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and CaTiO<sub>3</sub> powders were weighed and mixed with different mole ratios. The powder mixtures were remilled for 4 h in ethanol. Accompanied by an organic binder polyvinyl alcohol (PVA, 5 wt%), the fine powders were pressed into cylinders (approximately 5 mm in height) and disks (approximately 0.8 mm in height) with a diameter of 10 mm under uniaxial pressure of about 200 MPa and 100 MPa, respectively. Afterward, these specimens were sintered at 1480–1540  $^\circ\text{C}$  for 4 h in air with a heating rate of 3 °C/min.

Crystalline structures of specimens were characterized using Xray diffraction (XRD) with CuKa radiation (Bruker D8 Advance, Germany) with a step size of 0.01°. The surface morphologies were conducted on a scanning electron microscopy (SEM; MERLIN VP Compact, Carl Zeiss, Jena, Germany). Bulk densities of these sintered ceramics were achieved through the Archimedes method. Micro-Raman data were collected utilizing a Raman spectra meter (HR800, Horiba Jobin Yvon, Villeneuve D'ascq, France). Microwave dielectric properties were conducted on a network analyzer (HP8720ES, Hewlett-Packard, Santa Rosa, USA) together with a temperature chamber (Espec, MC-811T, Osaka, Japan). The relative permittivities at microwave range and the unloaded guality factors  $(Q \times f)$  were assessed by the Hakki-Coleman post-resonator method through exciting the TE<sub>011</sub> resonant mode and in the cavity method through exciting the TE<sub>01 $\delta$ </sub> mode, separately [23,24]. The test cavity was put in the Espec temperature chamber and the shift of resonant frequency under TE<sub>011</sub> mode was collected in the temperature of 25–80 °C, so the  $\tau_f$  value can be acquired by utilizing the following formula.

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

The disk specimens were polished and pasted silver electrodes for TSDC characterizations and other electrical measurements. We used the electrometer/high resistance meter (6517B; Keithley Instruments, Inc., Cleveland, OH) to collect current data. Temperature environment was provided by the quatro temperature controller of Novocontrol Technologies (Novocontrol, Montabaur, Germany). In the TSDC process, the disk was heated to a polarization temperature (T<sub>p</sub>) in the range of 175 °C-340 °C and then was loaded with a dc electric field (E<sub>p</sub>) of 2 kV/cm for 10 min (t<sub>p</sub> = 10 min). At this moment, the disk was rapidly cooled down to a starting temperature (about 0 °C) and depolarized for 10 min. After that, the disk was heated at a rate of 6 °C/min and the released current was gathered to identify TSDC.

#### 3. Results and discussion

Fig. 1 demonstrates the typical X-ray diffraction patterns of the BSLT-CT ceramics sintered at 1480 °C and 1540 °C. XRD data of CaTiO<sub>3</sub> ceramic sample sintered at 1400 °C is indicated for phase composition analysis. In Fig. 1(a), all the BSLT-CT compositions sintered at 1480 °C demonstrate a single hexagonal perovskite crystalline phase. The orthorhombic phase of CaTiO<sub>3</sub> or other second phase can not be detected in the matrix. As the sintering temperature increases to 1540 °C (shown in Fig. 1(b)), all specimens demonstrate the hexagonal structure similar to previous studies and the secondary phases are not indexed either. It can be further confirmed that the composite phases are not formed, but new solid solutions are attained for BSLT-CT compositions under x < 0.2. Fig. 1(c) and (d) exhibits the enlarged diffraction peaks at around  $52-58^{\circ}$  (20) of the BSLT-CT ceramics sintered at 1480 °C and 1540 °C, respectively. It can be further demonstrated that there is no effect of sintering temperature on structural transformation. Compared with BSLT (x = 0), there is no obvious shift of diffraction peaks under  $x \le 0.05$ . As x further increases to 0.1 and 0.2, the gradual shift can be clearly observed towards high angle. Based on the situation, the addition of CaTiO<sub>3</sub> has little effect on the lattice for  $x \le 0.05$ , however, with increasing x value to 0.1 and 0.2, the lattice is gradually shrunk. Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> (A<sub>5</sub>B<sub>4</sub>O<sub>15</sub>) shows the hexagonal perovskite phase with B-site cation deficiency, exactly as  $AB_{n-1/n}O_3$ . CaTiO<sub>3</sub> belong to the classical orthorhombic perovskite ABO<sub>3</sub> [19]. From the view of ionic radii,  $Ca^{2+}$  and  $Ti^{4+}$  can be easily incorporated into hexagonal lattice to form solid solutions.

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Fig. 1. X-ray diffraction patterns of (1-x)Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>-xCaTiO<sub>3</sub> (x = 0.02, 0.03, 0.05, 0.1 and 0.2) ceramics sintered at (a) 1480 °C and (b) 1540 °C. The enlarged diffraction peaks at around 52–58° (2θ) sintered at (c) 1480 °C and (d) 1540 °C.

However, the difference of  $AB_{n-1/n}O_3$  and  $ABO_3$  may arouse the alterations in crystal structure, namely, the extent of cation deficiency, the shrinkage or expansion of lattice cell, the thickness and filling of oxygen octahedra. These alterations will affect the phase composition and microwave dielectric properties of the BSLT-CT material system [1,2,6].

Raman spectroscopy is an effective method for determining crystal structure [2,8,25]. Fig. 2 demonstrates Raman spectra of the BSLT-CT ceramics sintered at 1500 °C. According to the literatures,



Fig. 2. Raman spectra of BSLT-CT ceramics sintered at 1500 °C.

the TiO<sub>6</sub> oxygen octahedron with O<sub>h</sub> symmetry has six fundamental vibration modes in hexagonal perovskite, including symmetric stretching mode  $v_1(A_{1g})$ , asymmetric stretching mode  $v_2(E_g)$  and  $v_3$  $(F_{1u})$ , asymmetric bending mode  $v_4$   $(F_{1u})$ , symmetric bending mode  $v_5(F_{2g})$  and the inactive mode  $v_6(F_{2u})$  [2,25]. The group theoretical considerations manifest the 15 internal modes of oxygen octahedra as  $A_{1g} + E_g + 2 F_{1u} + F_{2g} + F_{2u}$ . Among them,  $A_{1g}$ ,  $E_g$ ,  $2F_{1u}$ , and  $F_{2g}$  modes are Raman active and  $F_{2u}$  mode is inactive [2,25]. Furthermore, the O<sub>h</sub> symmetry deviation may result in the line broadening or even splitting. As seen in Fig. 2, the Raman spectrum of each BSLT-CT specimen displays eight bands with the same vibration bands. Specific spectral data and band assignments of the BSLT-CT ceramics are exhibited in Table 1. It is reported that the symmetric stretching vibrations of the face-sharing oxygen octahedra appear in the 850-1000 cm<sup>-1</sup> region in the hexagonal perovskite, however, those of the corner-connected octahedra generally appear in the 700-850 cm<sup>-1</sup> region [2]. Hence, band 1 centered at about

ladie	1				
Mode	bands	and	corresponding	assignments	of (1-x)Ba <sub>0.6</sub> Sr <sub>0.4</sub> La <sub>4</sub> Ti <sub>4</sub> O <sub>15</sub> -xCaTiO <sub>3</sub>
ceram	ics.				

Serial number	$\mathbf{x} = 0$	x = 0.05	x = 0.1	x = 0.2	Assignments
Band 1			791.3	793.7	$v_{1,} A_{1g} [TiO_6]$
Band 1	730.9	733.1	733.4	737	-
Band 2	453.5	453.5	453.5	455.9	ν <sub>4</sub> , F <sub>1u</sub> [TiO <sub>6</sub> ]
Band 3	344.9	346.1	343.7	341.3	$\nu_{5}, F_{2g}$ [TiO <sub>6</sub> ]
Band 4	291.8	291.8	294.2	293	Lattice modes
Band 5	272.5	277.3	279.7	280.9	Lattice modes
Band 6	217.1	220.6	221.8	219.4	Lattice modes
Band 7	151.9	153.1	154.3	154.3	Lattice modes
Band 8	131.4	132.6	132.6	131.4	Lattice modes

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730 cm<sup>-1</sup> corresponds to the mode  $v_1(A_{1g})$  of the corner-connected octahedra. In principle, the  $A_{1g}$  mode band denotes a statistical chance of ions of different types occupying adjacent octahedra and the higher frequency corresponds to the stronger bonds [8]. According to Table 1, the gradual movement of the  $A_{1g}$  mode can be observed towards the higher wave number (higher frequency). The  $A_{1g}$  mode locates at 730.9 cm<sup>-1</sup> for x = 0, and moves to 737 cm<sup>-1</sup> for x = 0.2. Increasing x up to 0.1 and 0.2, the visible splitting of  $A_{1g}$ appears on its higher frequency side  $(791-794 \text{ cm}^{-1})$ . So the distortion of oxygen octahedral cage and the variation of bond lengths may be reason for the  $A_{1g}$  spectral change and splitting. Band 2 and Band 3 corresponds to the  $v_4$  ( $F_{1u}$ ) mode at about  $453 \text{ cm}^{-1}$  and the  $v_5$  ( $F_{2g}$ ) mode at about  $340 \text{ cm}^{-1}$ , respectively. Band 4, 5, 6, 7 and 8 located below 295 cm<sup>-1</sup> correspond to lattice modes. Due to the complexity of translational and rotational vibration of the oxygen octahedral cages and cation-O stretching vibration, a clearer assignment of these bands can not be done. With the increase of the CaTiO<sub>3</sub> content from x = 0 to 0.2, the slight shift of vibration band from 2 to 8 to higher frequencies are observed in Table 1, which is induced by the different CaTiO<sub>3</sub> content. The shrinkage of lattice cell results in a decrease of vibration scope in the equilibrium position, which means the higher wave number or blue shift. In the present case of a small amount of CaTiO<sub>3</sub> content (x  $\leq$  0.05), these bands do not alter much, which is consistent with the XRD analysis above.

Fig. 3 depicts the typical microstructure characteristics of the BSLT-CT ceramics: (a) x = 0.1 at 1480 °C, (b) x = 0.1 at 1520 °C, (c) x = 0.1 at 1540 °C, (d) x = 0.2 at 1480 °C, (e) x = 0.2 at 1520 °C and (f) x = 0.2 at 1540 °C. As shown in Fig. 3(a) and (d), the sintering condition of 1480 °C gives the specimen a microstructure with small-size grains and a few pores. At higher sintering temperature of 1520 °C and 1540 °C, each specimen displays a pretty dense microstructure accompanied with enhanced grain growth. These grains distribute uniformly with platelet-shaped characteristics.

Fig. 4 presents the bulk densities and microwave dielectric properties of the BSLT-CT series ceramics sintered at different temperature. As shown in Fig. 4(a), the density of each composition increases initially and then tends to be saturated in a broad temperature window. Herein, the suitable sintering temperature can be determined to be 1500 °C for each composition and the sinterability of BSLT-CT compounds has not been affected by the content difference of CaTiO<sub>3</sub>. It is noted that the bulk densities display the minor differences under the same sintering condition for the composition of  $x \le 0.05$ . While further increasing CaTiO<sub>3</sub> content, the value of density decreases gradually, because the molar mass of



**Fig. 4.** Bulk densities and microwave dielectric properties of BSLT-CT ceramics with sintering temperature: (a) bulk densities, (b) dielectric constants and (c)  $Q \times f$  values.

CaTiO<sub>3</sub> is lower than that of Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>. As shown in Fig. 4(b) and (c), the variation of microwave dielectric properties ( $\varepsilon_{\rm r}$  and  $Q \times f$ ) against sintering temperature demonstrate an analogous trend with bulk densities. The permittivity and  $Q \times f$  value increases with increasing sintering temperature and thereafter become almost saturated. The variation trend should be attributed to the densification and grain growth of ceramic specimens. Table 2 displays the relative densities and microwave dielectric properties of well-sintered BSLT-CT ceramics at 1500 °C. Pure BSLT compound was sintered under the same condition for comparison. All well-sintered BSLT-CT ceramics possess a high densification >97%. At this moment, the effects of porosity, grain size, and grain boundary on microwave properties may be neglected for well-sintered BSLT-CT series ceramics. It can be seen from Table 2 that the microwave  $\varepsilon_{\rm r}$  shows a slight increase with increasing the CaTiO<sub>3</sub> content. At



**Fig. 3.** Typical microstructure characteristics of BSLT-CT ceramics: (a) x = 0.1 at 1480 °C, (b) x = 0.1 at 1520 °C, (c) x = 0.1 at 1540 °C, (d) x = 0.2 at 1480 °C, (e) x = 0.2 at 1520 °C and (f) x = 0.2 at 1540 °C.

Table 2

Relative densities and microwave dielectric properties of well-sintered BSLT-CT ceramics at 1500  $^\circ\text{C}.$ 

Samples (x)	Relative density (%)	$\varepsilon_{\rm r}$ (Post)	Qf (Shielded) GHz	τ <sub>f</sub> ppm/°C
0	97.6	44.7	45,000	-7.5
0.02	98.4	46.05	31,400	-11.9
0.03	98.7	46.21	31,600	-14.2
0.05	98.6	46.28	31,700	-11.5
0.1	98.2	47.72	44,200	-7.0
0.2	99.1	47.14	41,200	-5.3

x = 0.02 and 0.2, the microwave  $\varepsilon_r$  values are respectively 46.05 and 47.14. For microwave dielectrics (especially, the solid solutions), dielectric permittivity is intrinsically determined by ionic polarizability. Actually, the end-member CaTiO<sub>3</sub> of the title compound also displays the dielectric permittivity of 170. With different CaTiO<sub>3</sub> content, the well-sintered BSLT-CT ceramics have relatively high  $Q \times f$  values. The  $Q \times f$  value decreases initially from 45,000 (x = 0) to 31.700 GHz (x = 0.05) and then shows a rebound to 44.200 GHz (x = 0.1). As x increases further to 0.2, it slightly decreases to 41.200. Meanwhile, the variation of the temperature coefficient of resonant frequency ( $\tau_f$ ) against the CaTiO<sub>3</sub> content can be seen from Table 2. With the addition of CaTiO<sub>3</sub>, the  $\tau_f$  value is found to move obviously in the negative direction. When x = 0.03,  $\tau_f$  is about  $-14.2 \text{ ppm/}^{\circ}\text{C}$ . With the continual increase of CaTiO<sub>3</sub>, the  $\tau_f$  value moves in the positive direction. When x = 0.1 and 0.2, the  $\tau_f$  values are -7.0and -5.3 ppm/°C, respectively. So far, excellent microwave dielectric properties can be obtained for the BSLT-CT ceramics sintered at 1500 °C with x = 0.2, accompanied by  $\varepsilon_r$  = 47.1, Q × f = 41,200 GHz and  $\tau_f = -5.3 \text{ ppm/}^{\circ}\text{C}$ , respectively.

Among the three critical parameters of microwave dielectrics,  $Q \times f$  and  $\tau_f$  are quite difficult to understand. Microwave dielectric losses typically include intrinsic and extrinsic losses, such as phase composition, porosity, grain size, grain boundary, interfacial polarization, defects, etc. For the well-sintered BSLT-CT ceramic specimens with the single hexagonal phase, the effects of phase composition, porosity, grain size, and grain boundary on microwave dielectric loss can be ignored. According to Table 2, the  $Q \times f$ value initially drops, then rebounds, and then slightly falls back. In order to explain the origin of the  $Q \times f$  variation, two characteristic points are reasonable to be considered on the crystal structure: cation distribution and shift in cationic positions [1,2,14,15]. The above XRD and Raman analysis indicate the alteration of crystal environment with the variation of the CaTiO<sub>3</sub> content. In view of the crystal structure, the addition of CaTiO<sub>3</sub> has little effect on the crystal lattice for  $x \leq 0.05.$  As  $\text{Ca}^{2+}$  and  $\text{Ti}^{4+}$  incorporates into the hexagonal lattice, the radii difference caused by the different cation distribution bring the lack of resemblance and contribute to the local distortion, which may ruin the  $Q \times f$  value. Further increase in CaTiO<sub>3</sub> content, the lattice is gradually shrunk. The shrink of lattice and cation sites may limit the cation movements in the closepacked layers of oxygen, which may enhance the  $Q \times f$  value. As x varies from 0.1 to 0.2, although the crystal lattice is shrinking, the  $Q \times f$  value still has a slight drop, which is probably related to defects. Moreover, on the basis of the relevant literatures, oxygen octahedra of hexagonal perovskite also play an important role in  $\tau_f$ value [7,12,13]. Raman spectra also indicate the distortion of oxygen octahedral cages and the variation of bond lengths. A small amount of CaTiO<sub>3</sub> probably leads to the slight variation of octahedral thickness and in turn causes the movement of  $\tau_f$  in the negative direction. As CaTiO<sub>3</sub> content increases further, the effect of oxygen octahedron or crystal structure may be weakened. Finally, the additional amount of the end member CaTiO<sub>3</sub> impacts the microwave dielectric properties of the resulted compounds.

Besides the inherent intrinsic loss and the above mentioned factors.  $O \times f$  value is also affected by the extrinsic defects, such as defect dipoles, trap charges and space charges, etc [16-22,26]. To further obtain insight into the extrinsic loss mechanisms, the TSDC characterizations were conducted on the BSLT-CT ceramic samples well sintered at 1500 °C. Fig. 5 gives the schematic illustration of depolarization current procedure through thermal stimulation. When the dc  $E_{\rm p}$  is defined as the positive direction for system apparatus, the observed negative current is the true depolarization current (thermally stimulated discharge). Fig. 6 depicts TSDC plots of the (1-x)BSLT-xCT ceramics under various polarization temperatures at a fixed polarization field of 2 kV/cm: (a) x = 0.02, (b) x = 0.1 and (c) x = 0.2. The insert in (b) and (c) shows the detailed peak A of x = 0.1 and 0.2, respectively. The heating rate is 6 °C/min and the polarization and depolarization time are both 10 min. For each composition, the spectra are basically composed of two distinct relaxation peaks, which are labeled as peak A and peak B. Namely, the low-temperature peak A appears in the range of 200–250 °C and the high-temperature peak B appears in the wide temperature window of 260-350 °C. Herein, two different defect relaxation mechanisms are suggested in these title compounds. As illustrated in Fig. 6 and its inserts, the relaxation peak temperature (T<sub>m</sub>, where the maximum peak value occurs) and the peak magnitude (J<sub>max</sub>, TSDC peak density) show clear variations under different T<sub>p</sub>. Both J<sub>max</sub> and T<sub>m</sub> of peak A initially increase with the enhanced T<sub>p</sub>, then saturate gradually, decrease or swamp ultimately. As for peak B, its J<sub>max</sub> and T<sub>m</sub> shift to higher values with increasing T<sub>p</sub>. Comparing with peak A, peak B appears in higher temperature zone and exhibits higher magnitude. Note worthily, the initial appearance of peak B lags behind the peak A. When the



Fig. 5. The schematic illustration of depolarization current procedure through thermal stimulation.

#### 6

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**Fig. 6.** TSDC plots of (1-x)BSLT-xCT ceramics under various polarization temperatures at a fixed polarization field of 2 kV/cm: (a) x = 0.02, (b) x = 0.1 and (c) x = 0.2. The inserts in (b) and (c) show the detailed peak A of x = 0.1 and 0.2, respectively. The heating rate is 6 °*C*/min and the polarization and depolarization time are 10 min.

peak B initially appears, the breaking point  $T_p$  are 275 °C, 250 °C and 200 °C for x = 0.02, 0.1 and 0.2, respectively. It can be seen that the  $T_p$  breaking point shifts to lower value as x increases. In addition, it can be clearly observed from Fig. 6(a) that  $J_{max}$  and  $T_m$  of peak B shows a regular variation depending on  $T_p$ . However, in Fig. 6(b), the  $T_m$  value slightly increases from 341.5 °C to 353.5 °C with increasing  $T_p$ . Similarly, the  $T_m$  of peak B in Fig. 6(c) also indicates a slight increase. In truth, these  $T_m$  values are extremely close to the end of temperature ramp, thus the original shifts of defect relaxation may be masked. Fortunately, the limitation of the test equipment does not disturb our analysis.

According to literatures and the relaxation behavior discussed over, it can be deduced that both peak A and peak B are associated with oxygen vacancies ( $V_0^{\circ}$ ) [16–22]. Utilizing the initial rise method, the activation energies ( $E_a$ ) of peak A and peak B can be calculated and the results are presented in Table 3 [16–22]. The fitted  $E_a$  value of peak A lines in a range of 0.27–0.43 eV as x increases from 0.02 to 0.2, while that of peak B 0.37–0.81 eV. These values are also comparable with our previous work [1,2]. In polycrystalline ceramics, relaxations of oxygen vacancies usually consist

Table 3	
Activation energies $E_a$ for the TSDC relaxation A and B	•

T <sub>p</sub> (°C)	Activation Energy (eV) Peak A				Activation Energy (eV) Peak B					
	0.02	0.03	0.05	0.1	0.2	0.02	0.03	0.05	0.1	0.2
200	0.30	0.30	0.28	0.27	0.28	_	_	_	_	_
250	0.36	0.36	0.36	0.40	0.42	_	_	_	_	_
275	0.36	0.38	0.36	0.43	0.43	_	_	_	_	_
290	0.36	0.40	0.35	_	_	0.48	_	_	_	0.37
305	0.36	0.41	0.36	_	_	0.57	_	_	0.37	0.50
320	0.35	0.40	0.36	_	_	0.49	_	_	0.51	0.73
340	0.35	0.42	-	-	-	0.63	0.57	0.71	0.63	0.81

of two parts: in-grain relaxation and across-grain-boundary relaxation. In the process of TSDC ramp, partial oxygen vacancies move initially inside grains, further more  $V_0^{\bullet\bullet}$ , and then they are hindered by the grain boundaries, which separately corresponds to the appearance, rise and saturation of peak A. Under the driven force of polarization and temperature ramp, these hindered  $V_0^{\bullet\bullet}$ may step across of the barrier of grain boundaries, which is responsible for peak B presented at higher temperature. From the activation energies, the relaxation features and literatures, it can be suggested that the physical origins of peak A and peak B are ascribed to the in-grain relaxation and across-grain-boundary relaxation of  $V_0^{\bullet\bullet}$ , respectively [1,2,16–22]. With the further elevation of polarization conditions, the current densities of the in-grain oxygen vacancies may be swamped by the magnitude variations of the across-grain-boundary relaxation. Eventually, the main defect type in the BSLT-CT ceramics is oxygen vacancies.

As a matter of fact, oxygen vacancies are inevitable in the sintering process of oxide ceramics. Especially for the Ti-containing ceramics, the reduction of  $Ti^{4+}$  and the oxygen loss are considered to be the real origin of oxygen vacancies under high temperature sintering conditions [18,21,26]. The reduction of  $Ti^{4+}$  can be described as the following equation:

$$2\mathrm{Ti}_{\mathrm{Ti}} + \mathrm{O}_{\mathrm{o}} \Leftrightarrow 2(\mathrm{Ti}_{\mathrm{Ti}})^{/} + V_{\mathrm{o}}^{\bullet\bullet} + \frac{1}{2}\mathrm{O}_{2} \tag{2}$$

In order to a direct contrast, Fig. 7 displays the variations of TSDC plots: (a) at the same  $T_p$  of 200 °C, (b) at the same  $T_p$  of 305 °C and (c) with the similar magnitude as x varies. As shown in Fig. 7(a), the variation of peak A can be seen at the same low  $T_p$  of 200 °C as x changes from 0.02 to 0.2. The current density values do not show obvious difference at  $x \le 0.05$ . As x increases to 0.1 and 0.2, the values show a gradual increase. While, the variation of peak B can be seen at the same high  $T_p$  of 305 °C in Fig. 7(b). Excluding the

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Fig. 7. The variations of TSDC plots: (a) at the same T<sub>p</sub> of 200 °C, (b) at the same T<sub>p</sub> of 305 °C and (c) with the similar magnitudes as x varies.

difference of current magnitudes, the variations of peak A and peak B are analogous as x varies. In Fig. 7(c), the current density of peak B shows a slight increase at T<sub>p</sub> of 340 °C as x changes from 0.02 to 0.05. In other words, it can be illustrated that the similar magnitude corresponds to the decrease of T<sub>p</sub> with increasing x. Fig. 8 displays the T<sub>p</sub> dependence of J<sub>max</sub> for peak B on x values. Each composition shows a gradual increase in J<sub>max</sub> with the enhanced T<sub>p</sub>. Simultaneously, it can be clearly illustrated that J<sub>max</sub> shows increment as x increases for the same T<sub>p</sub> condition. J<sub>max</sub> increases slightly as x changes from 0.02 to 0.05, while J<sub>max</sub> increases remarkably from 0.05 to 0.2. Taking T<sub>p</sub> = 320 °C for instance, the J<sub>max</sub> of x = 0.02, 0.03 and 0.05 is  $1.28 \times 10^{-7}$ ,  $1.69 \times 10^{-7}$  and  $2.78 \times 10^{-7}$  A/m<sup>2</sup>, respectively. While,  $4.95 \times 10^{-6}$  A/m<sup>2</sup> and  $1.6 \times 10^{-5}$  A/m<sup>2</sup> for x = 0.1 and



Fig. 8. The  $T_p$  dependence of  $J_{max}$  for peak B under the different x values.

0.2, respectively. Especially, the  $J_{max}$  of x = 0.2 is approximately two orders of magnitude greater than that of x = 0.02 under the same polarization condition. According to the Langevin function, higher TSDC current densities correspond to higher defect concentrations [18,21]. Hence, the above mentioned TSDC variations should be prompted by the concentration difference of oxygen vacancies and the concentration value increase gradually as x increases. In our previous reports, the different crystal structure and different connection of oxygen octahedra can result in different types and depths of defects [1,2,18,21]. Between two end members of Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> and CaTiO<sub>3</sub>, the crystal structure and connection of oxygen octahedra are different to some extent. Although Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> is a kind of vacancy-containing perovskite (a vacant octahedral layer), the variation of CaTiO<sub>3</sub> content affects directly the concentration of oxygen vacancies for the title compounds. The difference of  $AB_{n-1/n}O_3$  and  $ABO_3$  may arouse the change of ions occupation in crystal structure. Apart from the oxygen loss, more oxygen vacancies are created due to the reduction of superabundant Ti ions that are introduced by CaTiO<sub>3</sub>. Actually, we also find in our experiments that the J<sub>max</sub> of oxygen vacancies of CaTiO<sub>3</sub> is much higher than that of Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub> under the same polarization condition and these two end members also show different types of defects (not shown here).

Oxygen vacancies are believed to produce anharmonic vibrations and consequently lead to extrinsic loss [26]. Hence, higher microwave loss should be induced with the increase of CaTiO<sub>3</sub> content. As a matter of fact, the variation of the  $Q \times f$  value in BSLT-CT compounds is not consistent with the characteristics of TSDC. Herein, oxygen vacancy defects contribute to the microwave loss, but they don't dominate the variation of the  $Q \times f$  value. Though the concentration of oxygen vacancies at x = 0.2 is higher than other compositions, high  $Q \times f$  values can still be harvested. It can be concluded that crystal structure as an intrinsic factor plays a more important role on microwave loss in this case. Both intrinsic and

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extrinsic factors are eventually responsible for microwave dielectric loss mechanisms. Interestingly, the solubility limit of CaTiO<sub>3</sub> and its effects on crystal structure, phase composition and microwave dielectric properties need to be further investigated.

#### 4. Conclusions

Microwave dielectrics of (1-x)Ba<sub>0.6</sub>Sr<sub>0.4</sub>La<sub>4</sub>Ti<sub>4</sub>O<sub>15</sub>-xCaTiO<sub>3</sub> (x < 0.2) with medium permittivity were successfully synthesized through the solid-state reaction process. All the BSLT-CT compositions demonstrate the single hexagonal perovskite crystalline phase and the well-sintered BSLT-CT ceramics possess a high densification >97%. XRD and Raman analysis both reveal the variation of crystal environment with the introduction of CaTiO<sub>3</sub>. As increase CaTiO<sub>3</sub> content, the microwave  $\varepsilon_r$  shows a slight increase, the  $Q \times f$  value decreases initially and then increases, the  $\tau_f$  value first move towards the negative direction and then towards the positive direction. TSDC result demonstrates that the main defects in BSLT-CT compounds are oxygen vacancies. The concentration of oxygen vacancies increases gradually with increasing CaTiO<sub>3</sub> content. Oxygen vacancy defects induce the microwave loss, but don't dominate the variation of the  $Q \times f$  value in BSLT-CT compounds. In this case, the behavior of microwave loss is mainly influenced by the crystal structure as a more important intrinsic factor. Excellent microwave dielectric properties can be obtained for the BSLT-CT ceramics sintered at 1500 °C with x = 0.2, namely,  $\varepsilon_r = 47.1$ ,  $Q \times f = 41,200 \text{ GHz and } \tau_f = -5.3 \text{ ppm/}^{\circ}\text{C}.$ 

#### Author contribution section

Xiaohua Zhang: Conceptualization, Methodology, Formal analysis, Writing - Original Draft Preparation. Ning Chang: Data Curation. Jie Zhang: Formal analysis. Yuanyuan Zhou: Writing - Review & Editing. Zhenxing Yue: Resources, Supervision, Funding acquisition. Longtu Li: Supervision

#### **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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