

Phase, microstructure and dielectric properties of BaSrZnSi₂O₇ – Ba_{0.5}Sr_{0.5}TiO₃ microwave tunable composite ceramics

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BaSrZnSi₂O₇-Ba_{0.5}Sr_{0.5}TiO₃ composite ceramics were systematically characterized in terms of phase composition, microstructure and dielectric properties. It was found that dielectric permittivity peaks of the samples shifted to low temperatures initially and then kept invariable with increasing BaSrZnSi₂O₇ content. Tunability showed a similar trend to Curie temperature. The variation in Q value was mainly related to whether the 'doping' effect or 'composite' effect was dominated. The sample with 60 wt% BaSrZnSi₂O₇ possessed a high tunability of 16% (~10 kHz), a low dielectric permittivity of 152 and a high Q value of 417 (~2.720 GHz), making it a promising candidate for applications as electrically tunable microwave devices.

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Ferroelectrics are among the candidates to be used in future tunable radio-frequency and microwave devices because of their essential dielectric nonlinearity and moderate loss. Barium strontium titanate (Ba_{1-x}Sr_xTiO₃ or BST) is one of those ferroelectrics with high tunability (T) and low loss (tanδ) [1-3]. BST based compounds have attracted sustained interests due to their wide range of applications in tunable microwave devices, such as oscillators, tunable mixers, delay lines, steerable antennas, parametric amplifiers, varactors, voltage-controlled oscillators, tunable filters and phase shifters [4-8]. All these applications require materials with low dielectric loss, high tunability and moderate dielectric permittivity (<500) [9]. However, pure BST ferroelectric ceramics with high permittivity have difficulty in satisfying the requirements of impedance matching and high power.

Recent studies indicated that adding low-dielectric permittivity non-ferroelectric phase (such as MgO, Al₂O₃, Mg₂SiO₄, Mg₂TiO₄, etc.) [10-18] into ferroelectric material is an effective method to reduce its dielectric permittivity. Low dielectric permittivity is readily achievable, whereas microwave loss is usually increased while tunability is decreased. Addition of MgO was found to suppress dielectric permittivity and losses of BST, but the tunability of the composite ceramics decreased rapidly simultaneously [16]. BST-Mg₂SiO₄ composite ceramics displayed relatively high tunability and adjustable dielectric permittivity. However, these materials were still not satisfactory for their relatively high dielectric loss at

microwave frequencies [17]. Ba_{1-x}Sr_xTiO₃-Mg₂TiO₄ composite ceramics also have similar problems for microwave applications. Al₂O₃-doped Ba_{0.6}Sr_{0.4}TiO₃ ceramics have been investigated by Wu *et al.* [18]. Even though this material processed very low loss and relatively high tunability, the high dielectric permittivity still make it unsuitable for the real applications. BST-Mg₂SiO₄-MgO ternary composites formed by adding MgO into BST-Mg₂SiO₄ binary composites presented readily adjustable dielectric permittivity and high tunability, but their dielectric loss at microwave frequencies was still too high [11]. The reduced dielectric permittivity of BST as a result of addition of low-dielectric permittivity non-ferroelectric phases was at the expense of increase in dielectric losses at microwave frequencies and decrease in dielectric tunability.

BaSrZnSi₂O₇ with an akermanite-type structure shows excellent microwave dielectric properties of high Q value (Q*f = 105000 @ 10 GHz) and low dielectric permittivity (ε = 8.4) [19]. In our present work, we report on the preparation and characterization of xBaSrZnSi₂O₇ (BSZS)-(1-x)Ba_{0.5}Sr_{0.5}TiO₃ (BST50) (x = 0, 5, 10, 25, 40, 50 and 60 wt%) composite ceramics. A systematic investigation on the effect of BSZS on phase structure, microstructure and dielectric properties of BST50 will be presented to evaluate their suitability for microwave applications.

xBaSrZnSi₂O₇ (BSZS)-(1-x)Ba_{0.5}Sr_{0.5}TiO₃ (BST50) (x = 0, 5, 10, 25, 40, 50 and 60 wt%) composite ceramics

were prepared by the conventional solid-state reaction route. High purity BaCO_3 (99.8%), SrCO_3 (99.0%), TiO_2 (99.9%), ZnO (99.9%) and SiO_2 (99.9%) were used as starting materials. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ and $\text{BaSrZnSi}_2\text{O}_7$ powders were both synthesized at 1200°C . The two components were mixed according to the stoichiometric ratio of x BSZS-(1- x) BST and ball-milled with zirconia media in ethanol for 24 h. The dried powders, mixed with 8 wt% polyvinyl alcohol (PVA), were pressed into disk-shaped pellets. Samples for low frequency dielectric measurement are 10 mm in diameter and 1 mm in thickness, while those for microwave frequency measurements have dimensions of 10/5 mm, 12/6 mm, 15/7 mm and 17/8 mm in diameter/thickness, respectively. The green pellets were burned-out at 550°C for 6 h in air to remove the solvent as well as the binder and then sintered at 1250°C - 1390°C in air.

Phase identification on the sintered ceramics was conducted by using an X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with $\text{Cu K}\alpha$ radiation. Scanning electron microscope (SEM, JSM EMP-800) was used to characterize microstructures of the sintered samples. Temperature dependent dielectric permittivity (ϵ') and loss tangent ($\tan\delta$) of the ceramic samples were measured over 158 K - 338 K at 10 kHz by using an HP4284A precision LCR meter (Agilent, Palo Alto, CA). Room temperature dielectric permittivity versus DC bias voltage was measured at 10 kHz and 293 K by using a Keithley model 2410 (Cleveland, OH) high voltage source coupled with a TH2816A LCR meter (Changzhou, China). Dielectric permittivity and loss at microwave frequencies were measured by using the resonance method [20] with a vector network analyzer (Agilent E5071C).

XRD patterns of the composite ceramics are shown in Fig. 1. Both perovskite BST and akermanite BSZS are observed in all samples. Some weak intensity peaks corresponding to TiO_x are observed, which indicates BST and BSZS reacted during sintering. A close inspection indicates that the diffraction peaks of perovskite shift to lower angles initially and then move gradually to higher angles. Noting their electronegativity and ionic radii of Zn^{2+} , Si^{4+} and Ti^{4+} , Ba^{2+} , Sr^{2+} ions, it is expected that Zn^{2+} and Si^{4+} ions substituted Ti^{4+} and occupied B sites of the perovskite structure. Ion diffusion is supposed to occur between BST and BSZS because secondary phase is detected by XRD. With a coordination number $N=6$, the radii of Ti^{4+} , Zn^{2+} , and Si^{4+} are 0.605 Å, 0.74 Å and 0.40 Å, respectively [21]. First, Zn^{2+} ions occupy B sites of perovskite structure, which led to the diffraction peaks of perovskite to shift to lower angles. Gradually, Si^{4+} ion occupy B sites with continually increasing content of BSZS. As a result, the diffraction peaks of perovskite shift to higher angles. However, the diffraction peaks do not shift when the BSZS concentration exceeded 25wt% in the matrix. It means that there should be a solubility limit of Zn and Si in BST. The lattice parameter, calculated by Jade 5.0 program, is 3.955 Å, 3.959 Å,

3.968 Å, 3.947 Å, 3.945 Å, 3.946 Å, 3.946 Å for BST component of the composite ceramics with 0 wt%, 5wt%, 10wt%, 25wt%, 40wt%, 50wt% and 60wt% BSZS, respectively. These calculated results are in a good coincident with our hypothesis of the ions substitution.

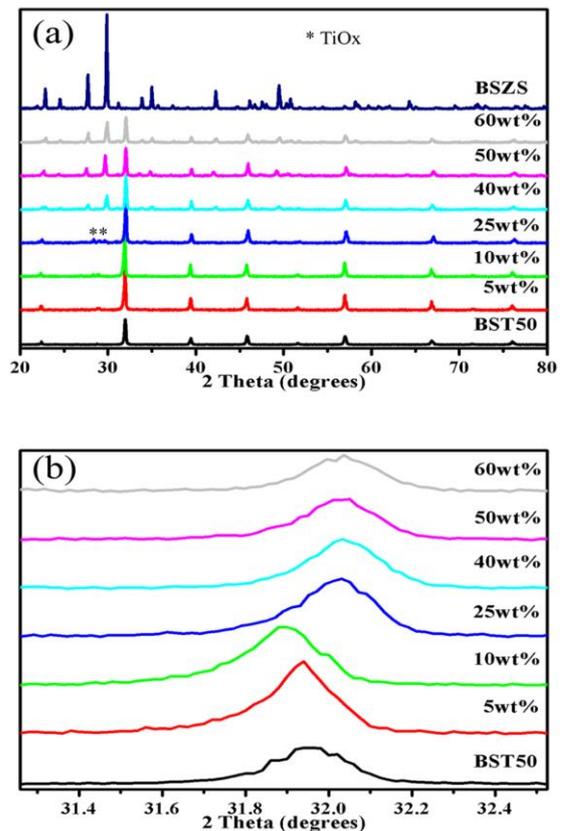


Fig. 1. XRD patterns of the $x\text{BaSrZnSi}_2\text{O}_7-(1-x)\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ($x = 0, 5, 10, 25, 40, 50, 60$ and 100 wt%) composite ceramics.

SEM micrographs of the composite ceramics are presented in Fig. 2. The grain sizes of BST in the composite samples are smaller than that of pure BST (not shown here), which indicates that BSZS is a grain growth inhibitor to BST. It should be noticed that conglutination appears as the BSZS content reaches 40 wt%, which can be attributed to the presence of liquid phases of BSZS at about 1300°C [19]. Sintering temperature is decreased from 1390°C for the 5wt% BSZS composite to 1290°C for the 60wt% BSZS composite. Energy dispersive spectroscopies (EDS) of the composite ceramics are presented in Fig. 3. The EDS results reveal inter-diffusion between BST and BSZS. The area marked as "1" contains a bit of Zn but no Si. Si is detected in the area marked as "2". With further increasing content of BSZS, more Si ion diffuses into BST grain. This implies that solid solutions are formed in the composite ceramics. For example, Ti in BSZS grain from the area marked as "4".

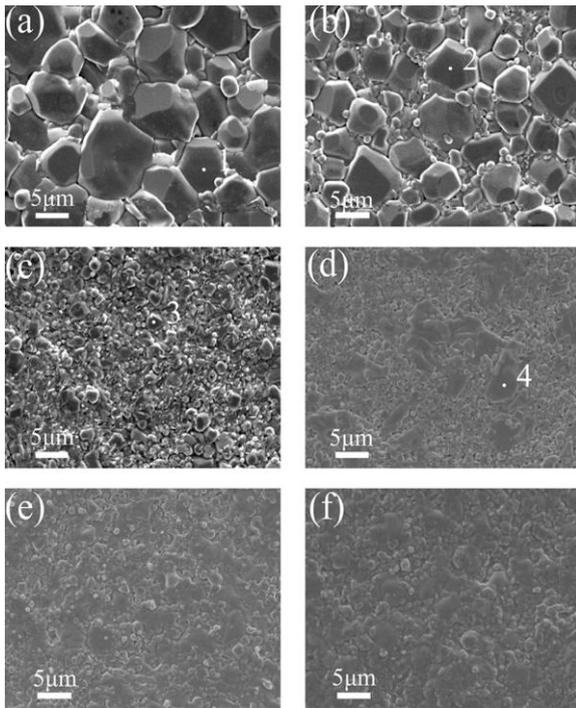


Fig. 2. SEM micrographs of the $x\text{BaSrZnSi}_2\text{O}_7-(1-x)\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ($x = 5, 10, 25, 40, 50$ and 60 wt%) composite ceramics.

Temperature dependences of dielectric permittivity (ϵ) and loss tangent ($\tan\delta$) of all samples measured at 10 kHz are displayed in Fig. 4. Microwave dielectric properties of all samples measured at room temperature are listed in Table 1. Dielectric peaks of all composite ceramics are broadened and suppressed compared with pure BST. The decrease in grain size contributes to the flattened dielectric peaks. The increase in grain boundary and the domain clamping are responsible for the reduction in permittivity [22]. Meanwhile, it is noted that T_C decreases initially and remain almost unchanged for $x \geq 25$ wt%. At low BSZS content, the decrease in T_C , is attributed to the increase in internal stress originating from the reduction in grain size [11]. The ‘doping’ effect, which make the deterioration of both spontaneous polarization of BST and the ferroelectric long-range order due to the replacement of Ti by Zn and Si [23]. This result is coincident with the XRD and EDS analysis. It conclude that when Zn^{2+} and Si^{4+} occupy B site of perovskite ABO_3 structure, they act more acutely on the bond energy of Ti-O [24]. Hence, this type of occupation influences Curie temperature more obviously. With further increase in BSZS content ($x > 25$ wt %), the dielectric permittivity decreases, but T_c dose not shift. This phenomenon can be described by the pure ‘composite’ effects [25]. The decrease in dielectric permittivity is presumably attributed to the dilution effect of BSZS. Temperature dependences of loss tangent ($\tan\delta$) of all samples measured at 293K & 10 kHz are displayed in Fig. 4(b). Weakening of the displacement of Ti^{4+} bound to suppress the domain-wall motion and thus results in the reduction in loss peak, because the loss

peak in ferroelectric region near T_C is thought to be originated from domain-wall motion [26]. On the other hand, the presence of high concentration oxygen vacancies results in the increase in losses at higher temperatures [27], as shown in Fig. 4(b).

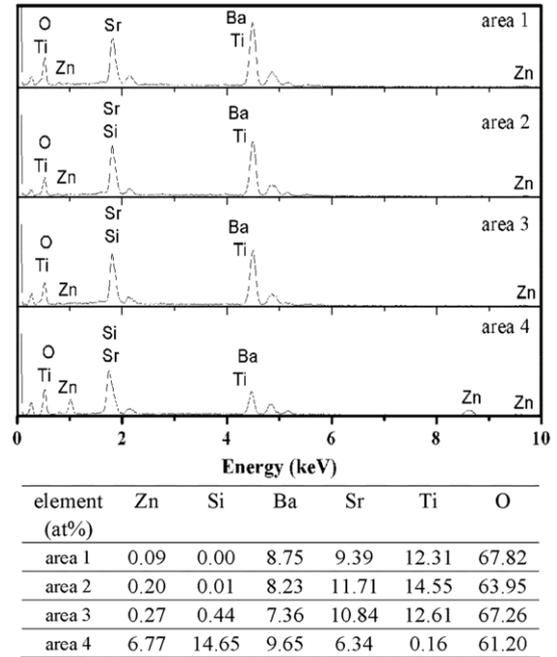


Fig. 3. Representation EDS spectra of the $x\text{BaSrZnSi}_2\text{O}_7-(1-x)\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ composite ceramics.

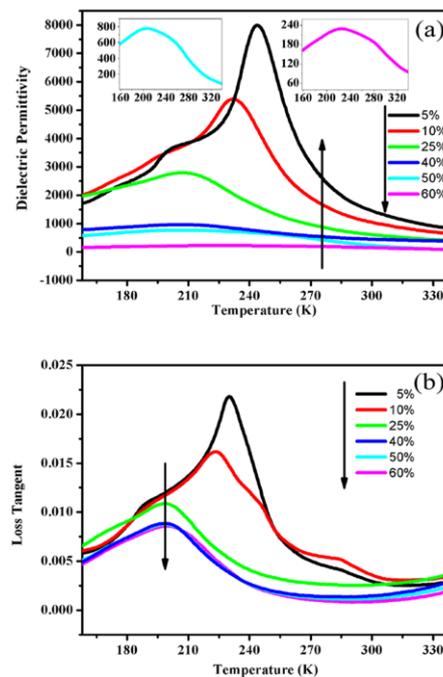


Fig. 4. Temperature dependences of dielectric permittivity and loss tangent of the $x\text{BaSrZnSi}_2\text{O}_7-(1-x)\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ ($x = 0, 5, 10, 25, 40, 50$ and 60 wt%) composite ceramics at 10 kHz.

Table 1. Microwave and dielectric properties of the samples with different contents of BaSrZnSi₂O₇.

x	Dielectric properties (at 10 kHz)				Microwave properties		
	T _c (K)	At about 293K		Tunability(%) at 30kV/cm bias	Resonant frequency (GHz)	ε (at resonant frequency)	Q (1/tanδ)
		ε'	tanδ				
0	247	2035	0.0010	24	1.130	1611	424
5	243	1673	0.0034	23	1.309	1433	221
10	232	1172	0.0043	22	1.570	1021	174
25	207	672	0.0025	19	1.936	634	147
40	207	470	0.0013	17	2.417	451	303
50	207	288	0.0012	17	3.076	270	382
60	207	161	0.0008	16	2.720	152	417

DC bias field dependent dielectric permittivity curves of the ceramics at 293K and 10 kHz are not shown here. The dielectric properties and calculated tunability of the samples are summarized in Table 1. The tunability of the composite ceramics is decreased gradually with increasing content of BSZS. In the present study, the reduction in tunability can be attributed to the decreased amount of BST. The sample with 60 wt% BSZS shows a dielectric permittivity of 161 and a tunability of 16% (at 30 kV/cm and 293K). This tunability is much higher than those of the composite ceramics based on BST and other additives [28].

Microwave dielectric properties of the samples measured at room temperature are also listed in Table 1. Dielectric permittivity values of the composite ceramics are slightly decreased at microwave frequencies as compared with those at low frequencies (under 1 MHz). The samples with low BSZS content possess higher loss tangent than that of pure BST at both low frequency and microwave frequency. This deterioration in loss should be attributed to the formation of solid solutions due to the incorporation of foreign ions [29], which is attributed to the damage of harmoniousness and B-site ordering of the ABO₃ perovskite structure [30]. It is recognized that the degree of B-site cation ordering is critical for maintaining a high quality factor Q of ABO₃ ceramics [31-33]. The Q values in microwave region decrease with decreasing ordering degree of B-site ions [33-34]. In BST-BSZS ceramics, the B sites of ABO₃ perovskite structure are considered to be occupied by Zn²⁺, Si⁴⁺ and Ti⁴⁺. Owing to different ionic radius and force constants of Zn²⁺, Si⁴⁺ and Ti⁴⁺, two adjacent corner share oxygen octahedron may become nonequivalent, which causes Zn²⁺, Si⁴⁺ and Ti⁴⁺ to be distributed throughout the B sites. Therefore, there is a distribution of phonon frequencies, resulting in a broadband, characteristic of “disordering” type. These short range ordering effects result in decrease of Q value

of BST-BSZS ceramics. This observation is consistent with that reported by Harley et al. [35]. Therefore, the main reason for the increase in loss tangent in microwave frequency of the two phases composite is disordering caused by the ions diffusion between the two components. On the other hand, as a acceptor, the charge defects caused by the substitution of Zn²⁺ for Ti⁴⁺ are compensated by oxygen vacancies(V_O^{''}).



This assumption was strongly supported by the report of Copel *et al.* [36]. The electrons resulted from the generation of oxygen vacancies hopped between titanium ions, which provided a mechanism for dielectric loss [37]. The increase in oxygen vacancy concentration eventually resulted in an increase in dielectric loss. However, with further increasing in BSZS content, Q values of the samples dramatically increases. As shown in Table 1, the Q value increases from 147 for x=25.0 wt% to 417 for x=60 wt%. The samples with high concentration of BSZS possess high Q value due mainly to the “composite” effect of the dielectric component with good microwave properties. [19] It is worth mentioning that the sample with 60 wt% BSZS has a high Q value of 417 at ~3.307 GHz, a high level of tunability (~16% at 30 kV/cm) and an appropriated value of dielectric permittivity (~152 at zero biasing).

BaSrZnSi₂O₇-Ba_{0.5}Sr_{0.5}TiO₃ composite ceramics have been fabricated and characterized. XRD results showed that dominate phases of the sintered ceramics were Ba_{0.5}Sr_{0.5}TiO₃ and BaSrZnSi₂O₇. The introduction of BSZS resulted in a change in lattice parameter of the perovskite phase in the composite ceramics. T_C peaks of the composite ceramics were suppressed, broadened and

shifted to lower temperature, due to the inter-diffusion between BST and BSZS. The increase in Q value was due to the ‘composite’ effect of the attendance of high Q value dielectric material BSZS. The BSZS-BST composite ceramics simultaneously had a high Q value and tunability as well as a low dielectric permittivity. Specifically, the sample with 60 wt% BSZS is a suitable material for electrically tunable microwave devices because of its excellent properties: a Q value of 417 at ~2.720 GHz, a high level of tunability (~16% at 30 kV/cm biasing) and an appropriated dielectric permittivity (~152 at zero biasing).

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