

Effect of MnO₂ Doping on Dielectric Properties of Ba_{0.7}Sr_{0.3}TiO₃ Ceramics

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Abstract

MnO₂-doped BST ceramics were prepared by the solid-state reaction method. The effect of MnO₂ doping on the microstructure and dielectric properties of BST ceramic materials was studied. The results indicate that at an MnO₂ doping concentration of x=0.4%, the ceramic exhibits the highest density, the dielectric constant is 4939, the dielectric loss is as low as 0.016, and the dielectric tunability reaches the maximum value (49.57%) under an electric field of 15kV/cm. The figure of merit (FOM) of this sample is as high as 31.8. These findings provide a significant experimental foundation for the design of low-loss and highly adjustable BST ceramics.

Keywords

BST Ceramics; MnO₂-Doping; Figure of Merit; Dielectric Tunability.

1. Introduction

Barium strontium titanate (Ba_xSr_{1-x}TiO₃) ceramics are widely used in tunable microwave devices, electrically tunable filters, and phased array antennas due to their excellent dielectric tunability and low dielectric loss [1-3]. However, BST ceramics still face problems such as high dielectric loss and difficulty in optimizing tuning performance in practical applications. Therefore, improving the comprehensive performance of BST ceramics through doping modification is one of the current research focuses [4-6]. Among them, Liao et al. [7] prepared potassium-doped Ba_{0.6}Sr_{0.4}TiO₃ thin films by sol-gel method. The Ba_{0.6}Sr_{0.4}TiO₃ thin film doped with 5% potassium exhibits a well-ordered structure and enhanced dielectric properties. At 275 kV/cm, its dielectric constant is 603, dielectric loss is 0.0083, and tunability is 49.0%. Qin et al. [8] reported the preparation of Y-doped Ba_{0.6}Sr_{0.4}TiO₃ thin films on LaAlO₃ substrates by PLD. The crystallization and dielectric properties of Y-BST films were improved. The results showed that when the Y doping amount was 1.5mol%, the dielectric properties of BST films were improved compared with those of undoped BST films. At 300 kV/cm, the tunability increased from 48.5% (pristine BST) to 82.7% (1.5mol% Y-doped BST). As a common dopant, MnO₂ can affect the dielectric properties in ferroelectric ceramics by regulating defect concentration, charge compensation and polarization mechanism [9, 10]. However, the effect of Mn doping on the dielectric loss, tunability and figure of merit (FOM) of BST ceramics is still unclear. Therefore, this study systematically studies the effect of MnO₂ with different contents on dielectric loss, dielectric constant and tunability by introducing different contents into BST ceramics to optimize the overall performance of BST ceramics.

2. Experiment Procedure

2.1 Sample Preparation

$\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3\text{-xMnO}_2$ ($x=0.2\%$, 0.4% , 0.6% , 0.8%) ceramic samples with different mass fractions were prepared by solid phase reaction method, where x is the molar fraction of the substance doped with Mn^{4+} . Analytical-grade pure BaCO_3 (99.9%), SrCO_3 (99.9%), TiO_2 (99.9%) and MnO_2 (99%) were accurately mixed according to the molar ratio of each element. Deionized water was used as the solvent for ball milling and mixing. The powder was dried and sieved, and then calcined at 1100°C . The synthesized powder was sieved and ball milled for the second time. After drying, 3 wt% polyvinyl alcohol (PVA) was added as a binder for granulation. After weighing the granulated ceramic powder in an appropriate amount, pour it into a mold with a diameter of 15 mm and press it into a ceramic body of a certain shape using a flat vulcanizer. The pressure is 1 MPa and the pressure holding time is 10 s. Finally, sinter it at 1350°C for 4 h to obtain a ceramic sample. Coat the front and back of the ceramic sheet with low-temperature silver paste, dry it in a blast drying oven, and cool it to room temperature. The ceramic sample coated with electrodes can be tested for various dielectric properties.

2.2 Characterization

The X-ray diffractometer D8 Advance from Bruker, Germany, was used to measure the range from 10° to 80° . The TM3030 scanning electron microscope (SEM) from Hitachi, Japan, was used to observe the microstructure of the ceramic samples. The experimental density (ρ) of each component ceramic was measured by the traditional Archimedean drainage method at 25°C and 1.01×10^5 Pa. The dielectric temperature spectrum of the sample at $-50 \sim 125^\circ\text{C}$ was tested using an LCR meter (Agilent, E4980AL) paired with the DMS-2000 dielectric temperature spectrum test system, and the dielectric properties of the sample were tested at a frequency of (10^2 to 10^6 Hz). The dielectric tunability of the sample with a thickness of 1 mm was measured using the CV (applied voltage of 1500V, test frequency of 1 kHz) test module of the TF Analyzer 2000E ferroelectric analyzer (external amplifier, which can extend the voltage to 10 000V) from aixACCT, Germany. The dielectric constant of each sample was measured under a DC bias electric field ranging from 0 to 15 kV/cm.

3. Results and Discussion

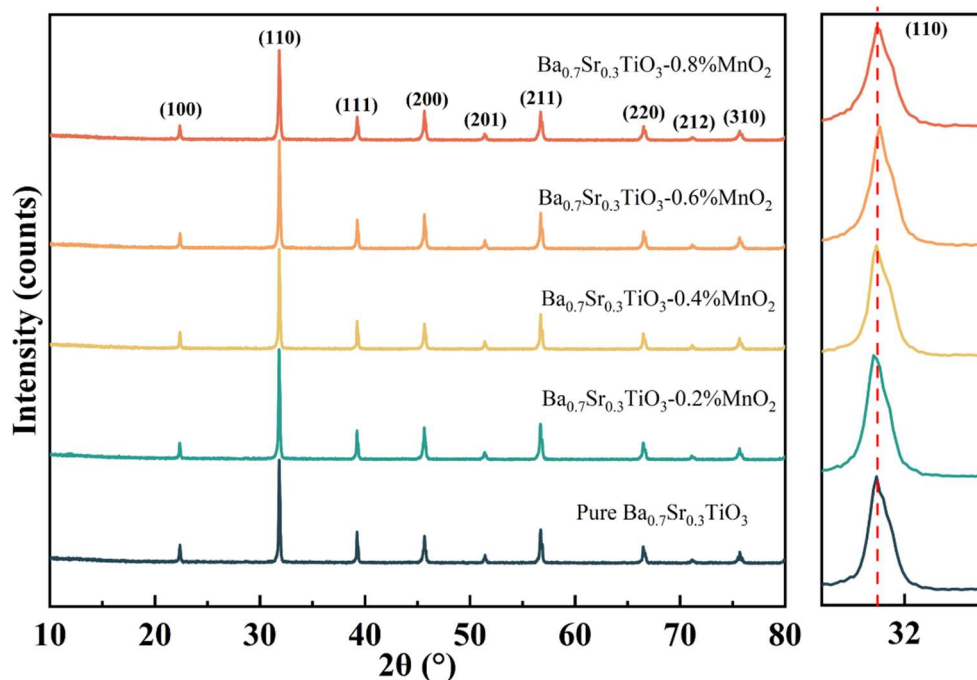


Figure 1. XRD patterns of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramics doped with different MnO_2 contents

Figure 1 shows the XRD patterns of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) ceramics doped with different contents of MnO_2 . After comparing with the standard PDF card using Jade software, it is found that the diffraction peaks of all samples are consistent with the diffraction peaks contained in PDF#890274, and there is no obvious impurity peak, which indicates that all samples are single perovskite structures, and no second phase is found at the resolution of the X-ray diffractometer. It shows that Mn^{4+} successfully enters the BST lattice. It can be seen from Figure 1 that due to the small amount of MnO_2 doping, the XRD change is not obvious.

Figure 2 shows the SEM images of BST ceramic samples with different Mn^{4+} doping amounts. As can be seen from the figure, all samples have a dense microstructure, and no obvious pores are observed on the grain surface. Under low doping ($x=0.2\%$, $x=0.4\%$, $x=0.6\%$), the grain size gradually increases with the increase of the doping ratio, and the grain boundary is relatively clear. This is because the appropriate amount of Mn^{4+} doping replaces Ti^{4+} to produce lattice defects, reduce the nucleation barrier, thereby promoting grain growth, reducing the sintering temperature, and improving the density. As shown in Figure 2(d), under high doping, the grain size is significantly reduced and the particles are refined. This is because as the Mn^{4+} doping amount increases, the defect content increases, the number of crystal nuclei increases, and the grain size decreases.

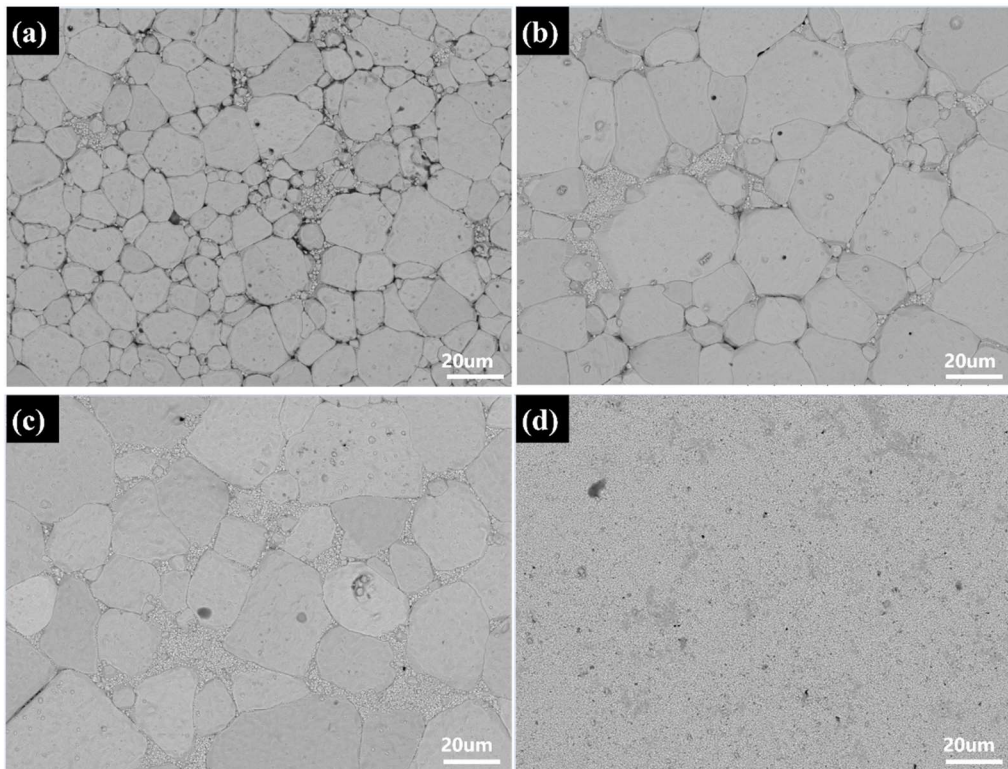


Figure 2. SEM images of BST ceramics with different Mn^{4+} doping amounts (x)
(a. $x=0.2\%$, b. $x=0.4\%$, c. $x=0.6\%$, d. $x=0.8\%$)

Figure 3 shows the experimental density changes of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramics doped with different contents of MnO_2 . As shown in Figure 3, MnO_2 doping can increase the density of BST ceramics, and the density reaches the highest when $x=0.4\%$. This is mainly because Mn^{4+} doping can enter the BST lattice, partially replace Ti^{4+} ions, form defects, thereby reducing the nucleation barrier and playing a role in assisting sintering. However, the experimental results show that excessive Mn^{4+} content will lead to a downward trend in density.

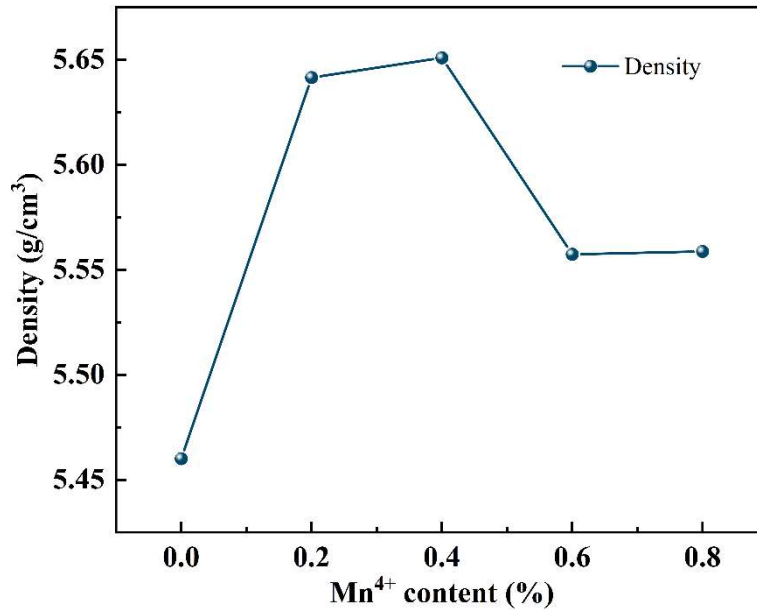


Figure 3. Experimental density diagram of Ba_{0.7}Sr_{0.3}TiO₃ ceramics doped with different contents of MnO₂

Figure 4 (a) shows the curve of the dielectric constant of the sample at a test frequency of 1 kHz. As shown in the figure, with the increase of Mn⁴⁺ content, the Curie temperature of the sample gradually decreases. When the doping amount x=0.8%, the Curie temperature is as low as 18°C. This is because Mn ions are multivalent ions. In the process of excessive doping of Mn ions to replace Ti⁴⁺, Mn³⁺ and Mn²⁺ will appear, thereby generating oxygen vacancies and changing the phase transition behavior of BST. Figure 4 (b) shows the change of the dielectric constant of BST doped with different contents of MnO₂ with frequency. With the increase of the test frequency, the dielectric constant of the sample gradually decreases. This is because the dipole polarization in the ferroelectric material cannot maintain the electric field change at higher frequencies, which shows the typical properties of dielectric materials [11]. With increasing MnO₂ doping, the dielectric constant of BST ceramics exhibits a decreasing trend, primarily due to inhibited grain growth caused by excessive MnO₂ addition.

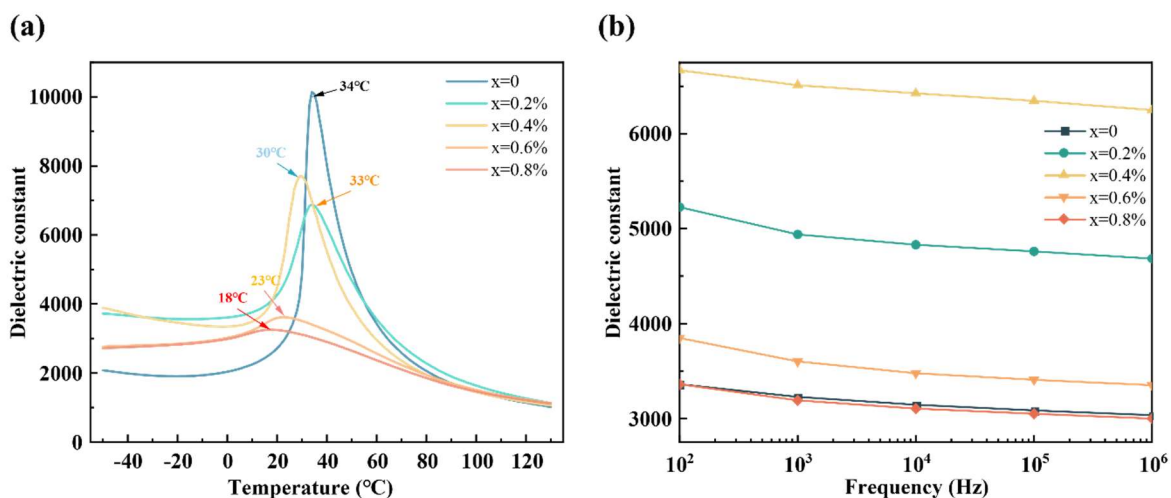


Figure 4. Dielectric constant-temperature curve of BST ceramics doped with different contents of MnO₂ (a) and (b) the change of dielectric constant with frequency

Figure 5 (a, b, c, d) shows the change of dielectric constant of Ba_{0.7}Sr_{0.3}TiO₃ ceramics doped with different contents of MnO₂ under different electric field strengths. It can be seen from the figure that the change of dielectric constant with electric field strength shows a typical nonlinear relationship, which is usually manifested as a peak within a certain electric field range. In order to further analyze the dielectric behavior of BST doping, we fitted the experimental data, and the curves in Figure 5 (a, b, c, d) are the fitting results. The fitting model accurately describes the dielectric properties of the composite material. As can be seen from Figure 6, when x=0.4%, the dielectric constant is the highest and the tuning rate is the best.

The dielectric tunability (T) of the material is determined by the following formula, and there is a nonlinear relationship between its dielectric constant and the applied electric field.

$$T = \frac{\varepsilon_{(0)} - \varepsilon(E)}{\varepsilon_{(0)}} \times 100\% \quad (1)$$

Where $\varepsilon_{(0)}$ and $\varepsilon(E)$ are the dielectric constants under zero electric field and a certain DC electric field, respectively. Figure 6 shows the relationship between the dielectric tunability of BST ceramics doped with different MnO₂ contents and the MnO₂ content. When the MnO₂ doping amount is 0, the dielectric tunability of BST ceramics is the highest. As the MnO₂ doping amount increases, the dielectric tunability shows a downward trend, and the tunability of the BST-doped sample is the highest when x=0.4%. Therefore, x=0.4% is the optimal doping ratio, which can improve the tuning rate while maintaining a higher dielectric constant, and can be used as the best doping scheme for BST tunable devices.

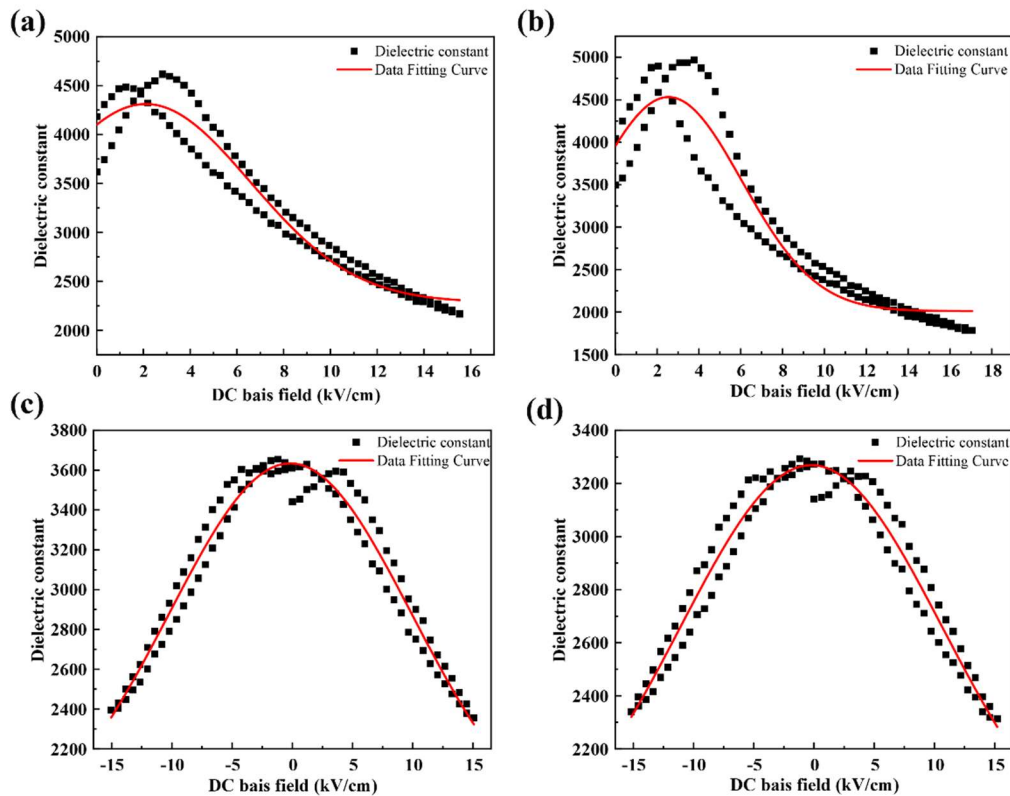


Figure 5. Relationship between dielectric constant and electric field of BST ceramics doped with different contents of MnO₂: (a) x=0.2%; (b) x=0.4%; (c) x=0.6%; (d) x=0.8%;

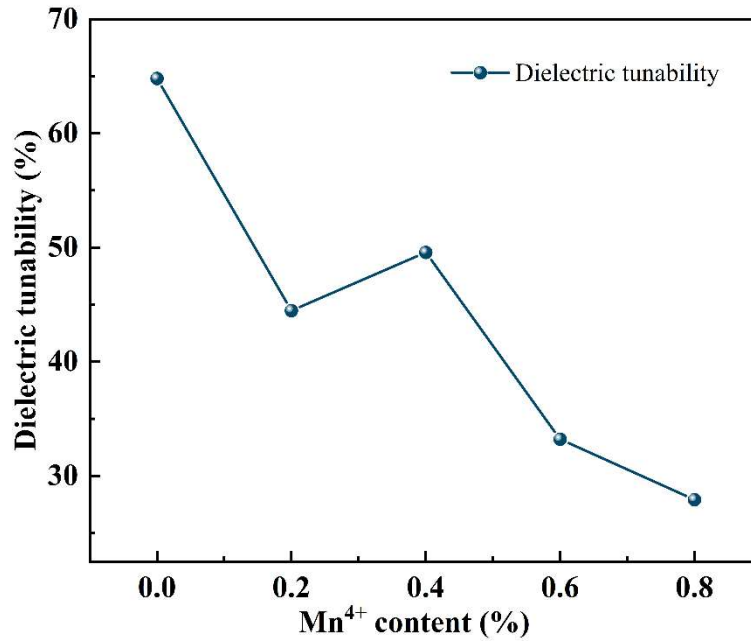


Figure 6. Dielectric tunability of BST ceramics doped with different MnO₂ contents

Figure 7(a) shows the change of dielectric loss of BST ceramics doped with different contents of MnO₂ with frequency. As shown in the figure, as the test frequency increases, the dielectric loss first decreases and then increases. This is because the interface charge relaxation effect at low frequencies weakens, and the dielectric loss decreases accordingly. However, in the high-frequency range, dipole relaxation loss and local conductivity effects dominate, resulting in a significant increase in dielectric loss. When x=0.4%, the sample has the lowest dielectric loss. This is because Mn⁴⁺ replaces Ti⁴⁺, reducing the oxygen vacancy concentration and thus reducing polarization hysteresis loss. The figure of merit (FOM) reflects the comprehensive performance of the material. This parameter is defined as the ratio of dielectric tunability to dielectric loss. The higher the value, the better the tuning performance of the material [12]. As shown in Figure 7(b), when x=0.4%, the sample has the highest figure of merit, indicating that the dielectric performance of the sample is best when the MnO₂ doping amount is 0.4%. Table 1 shows the dielectric properties of BST-xMnO₂ with different compositions.

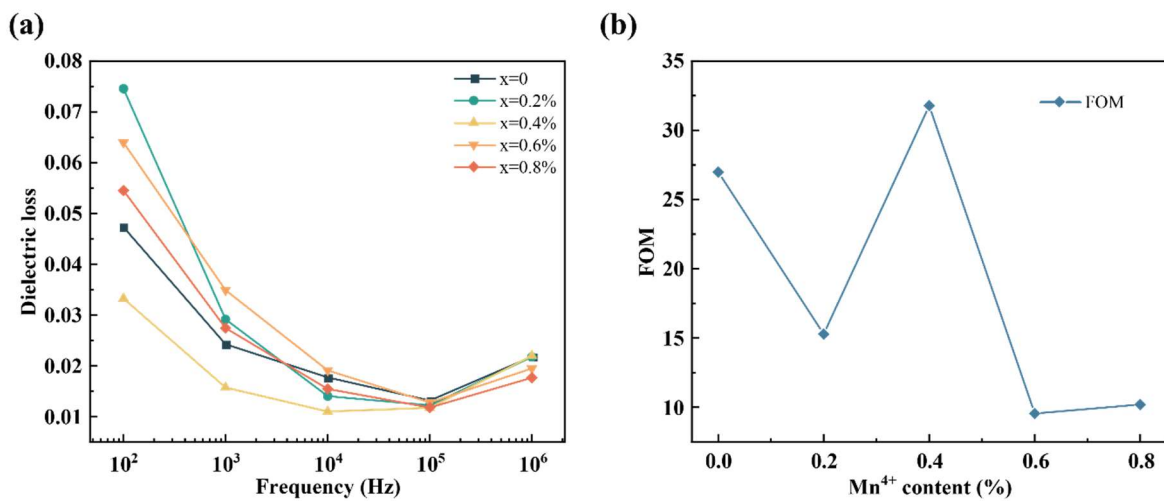


Figure 7. BST ceramics doped with different contents of MnO₂ (a) Dielectric loss versus frequency (b) Merit factor of ceramic material

Table 1. Dielectric properties of BST-xMnO₂ with different compositions

Composition	T _c /°C	tanδ (1 kHz)	T/% (15kV/cm, 1kHz)	FOM
BST	34	0.024	64.8	27.0
BST-0.2%MnO ₂	33	0.029	44.5	15.3
BST-0.4%MnO ₂	30	0.016	49.6	31.8
BST-0.6%MnO ₂	23	0.035	33.2	9.5
BST-0.8%MnO ₂	18	0.027	27.9	10.2

4. Conclusion

Ba_{0.7}Sr_{0.3}TiO₃-xMnO₂ (x=0.2%, 0.4%, 0.6%, 0.8%) ceramic samples with different mass fractions were prepared by solid phase synthesis. Scanning electron microscopy results show that all samples have a dense microstructure, increased grain size, and clear grain boundaries. The sample has the best dielectric properties when x=0.4%. At a test frequency of 1 kHz, the Curie temperature is 30°C, the dielectric constant is 4939, the loss is 0.016, the FOM is as high as 31.8, and the tunability is 49.57% at 15kV/cm. The results of this study provide theoretical and experimental basis for the optimal design of BST ceramics in microwave tuning devices.

References

- [1] AHMED A, GOLDTHORPE I A, KHANDANI A K. Electrically tunable materials for microwave applications [J]. Applied Physics Reviews, 2015, 2(1).
- [2] AREDES R G, ANTONELLI E, NETO L P S, et al. Tunability behavior of (Ba, Ca)(Zr, Ti) O ceramic capacitors powered by thermally induced phase transitions with applications to nonlinear transmission lines [J]. IEEE Transactions on Plasma Science, 2022, 50(10): 3371-8.
- [3] PAN X, MENG B, YANG Q, et al. Dielectric properties of A and B-site doped BaTiO₃-based high-entropy ceramics prepared by fast hot-pressing sintering [J]. Ceramics International, 2024, 50(3): 5806-17.
- [4] GUO Z, PAN L, BI C, et al. Structural and multiferroic properties of Fe-doped Ba_{0.5}Sr_{0.5}TiO₃ solids [J]. Journal of magnetism magnetic materials, 2013, 325: 24-8.
- [5] LAISHRAM R, SINGH K C, PRAKASH C. Enhanced dielectric loss of Mg doped Ba_{0.7}Sr_{0.3}TiO₃ ceramics [J]. Ceramics International, 2016, 42(13): 14970-5.
- [6] LIU Y, TANG Y, TAO Y, et al. Ultralow thermal conductivity and high thermoelectric performance induced by multiscale lattice defects in Cu-doped BST alloys [J]. CrystEngComm, 2024, 26(1): 100-9.
- [7] LIAO J X, WEI X B, XU Z Q, et al. Effect of potassium-doped concentration on structures and dielectric performance of barium-strontium-titanate films [J]. Vacuum, 2014, 107: 291-6.
- [8] QIN W F, ZHU J, XIONG J, et al. Electrical behavior of Y-doped Ba_{0.6}Sr_{0.4}TiO₃ thin films [J]. Journal of Materials Science: Materials in Electronics, 2007, 18(12): 1217-20.
- [9] WANG X, LV S, ZHANG C, et al. The structural and electrical properties of Mn-doped Ba_{0.6}Sr_{0.4}TiO₃ films prepared by metal organic deposition method [J]. Journal of Alloys and Compounds, 2013, 576: 262-4.
- [10] DIAO C, LIU H, HAO H, et al. Enhanced recoverable energy storage density of Mn-doped Ba_{0.4}Sr_{0.6}TiO₃ thin films prepared by spin-coating technique [J]. Journal of Materials Science: Materials in Electronics, 2018, 29(7): 5814-9.
- [11] WU T, PU Y, GAO P, et al. Influence of Sr/Ba ratio on the energy storage properties and dielectric relaxation behaviors of strontium barium titanate ceramics [J]. Journal of Materials Science: Materials in Electronics, 2013, 24: 4105-12.
- [12] SUN Z, LIU W, LI Q, et al. Relaxor behaviour and nonlinear dielectric properties of lead-free BZT–BZN composite ceramics [J]. Ceramics International, 2021, 47(2): 2086-93.