

Effect of Pb(Ti, Sn)O₃ on the dielectric properties of high dielectric constant X8R BaTiO₃-based ceramics

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Abstract The high dielectric constant X8R dielectric materials could be sintered at 1,240 °C by doping 2.5 mol% Pb(Ti,Sn)O₃ additives into the BaTiO₃ ceramics, with a dielectric constant greater than 3,400 at 25 °C, dielectric loss lower than 2.0% and temperature coefficient of capacitance (TCC) less than ±15% from −55 to 150 °C, which satisfied X8R specification. The effects of Pb(Ti,Sn)O₃ on the microstructure and dielectric properties of BaTiO₃-based ceramics were investigated. Doped with Pb(Ti,Sn)O₃ additives, the partial solid solution was formed between Pb(Ti,Sn)O₃ and BaTiO₃. Due to the high Curie point of Pb(Ti,Sn)O₃, the Curie point of the ceramics was markedly shifted to higher temperature about 150 °C, and the temperature coefficient of capacitance curves was flattened. The increase of the tetragonality (*c/a* ratio) and the fine microstructure were resulted in the increase of dielectric constant. With Pb(Ti, Sn)O₃ content up to 3 mol%, the depression of Ti⁴⁺'s polarization and the decrease of the tetragonality (*c/a* ratio) were resulted in the decrease of dielectric constant.

1 Introduction

The future developments in high performance multilayer ceramic capacitors, driven by the market requirements, are miniaturization and high volumetric efficiency. Keys to

achieve the goal are to increase the capacitance of multilayer ceramic capacitors, which requires the increase in the dielectric constant (ϵ) of active dielectric layers between internal electrodes [1, 2]. Meanwhile, multilayer ceramic capacitors (MLCCs) have come into use for harsh conditions, such as the engine electronic control unit (ECU) and programmed fuel injection (PGMFI) [1–3]. These modules are subjected to high temperature above 130 °C. MLCCs that only meet the X7R (−55 to +125 °C, temperature coefficient of capacitance TCC $\leq \pm 15\%$ or less) characteristics are not good enough to be used. MLCCs have to satisfy the X8R specification (−55 to +150 °C, TCC $\leq \pm 15\%$ or less) for automotive applications. Therefore, it is most important and critical to research and develop high- ϵ X8R dielectric materials.

Barium titanate (BaTiO₃) was a well-known material for X7R capacitors [4]. The BaTiO₃–Nb₂O₅–Co₂O₃–Sm₂O₃ system, capable of sintering in air atmosphere, was known as high-permittivity, temperature-stable materials conforming to X7R specification. The doping mechanism of Nb₂O₅, Co₂O₃ in BaTiO₃-based system was clear. When Nb₂O₅ and Co-oxide were used as a pair of dopants, the donor and the acceptor could replace the Ti site by forming the composite cation of $[\text{Nb}_{2/3}^{5+}\text{Co}_{1/3}^{2+}]^{4+}$, which could produce the core–shell structure [5, 6]. It was very helpful to flatten the ϵ -T curve. Manganese addition has proved to be effective in reducing dielectric loss ($\tan\delta$) in barium titanate compound, and $\tan\delta$ at room temperature was about 1.0% [7]. Unfortunately, since their Curie point (*T_c*) was about 130 °C, it was very difficult for BaTiO₃–Nb₂O₅–Co₂O₃–Sm₂O₃–MnCO₃ system materials to satisfy the X8R characteristics at temperature above 130 °C according to the Curie–Weiss law $\epsilon = C/(T - T_c)$. Therefore, increasing and broadening the *T_c* was helpful to improve the temperature stability of ϵ to meet the X8R requirement.

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Pb(Ti,Sn)O₃(PTS) was an attractive piezoelectric material because of its strong ferroelectricity at room temperature and a high Curie temperature of 296 °C [8, 9]. In addition, PTS can form solid solution with BaTiO₃ because of the same perovskite structure. In our research, it has been found that the T_c of BaTiO₃ was greatly increased as high as 150 °C. The high- ϵ X8R dielectric materials were developed by the addition of PTS to BaTiO₃-Nb₂O₅-Co₂O₃-Sm₂O₃-MnCO₃ ceramics. The effects of PTS content on the dielectric properties and microstructure were investigated. The aim of this research was to discuss the role of PTS addition and its potential in development of high- ϵ X8R system for MLCCs applications.

2 Experimental procedures

2.1 Pb(Ti, Sn)O₃ preparation

Reagent-grade PbO, TiO₂ and SnO₂ were used as the starting materials. The solid solution was prepared according to Pb(Ti_{1-x},Sn_x)O₃, $x = 0.45$. The powders were ball milled in deionized water for 7 h, and dried. The PTS was synthesized at 1,050 °C for 2 h.

2.2 X8R samples preparation

Reagent-grade BaTiO₃, Nb₂O₅, Co₂O₃, Sm₂O₃, MnCO₃ and synthesized PTS were used as the starting materials. The samples were prepared according to BaTiO₃ (calcined at 1,100 °C×2 h) + (2–2.5 mol%) Nb₂O₅+ (1–2%) Co₂O₃+ (1–3 mol%) Sm₂O₃+ (0.5–1.2mol%) MnCO₃+ (1.5–3 mol%) PTS. Samples were produced with four different PTS contents, which were 1.5, 2, 2.5 and 3 mol% respectively. The powders were ball milled in deionized water for 8 h, and dried, sieved, then pressed into disks with 15 mm diameter. The disks were sintered at 1,240 °C for 4 h.

2.3 X8R samples measurement

The ϵ and $\tan\delta$ were measured by Agilent 4278 Capacitance Meter at 1 KHz, with temperature range of –55 to 160 °C. TCC equaled to $(C-C_{25\text{ }^\circ\text{C}})/C_{25\text{ }^\circ\text{C}}$, where C and C_{25 °C} represented the capacitance value at measuring temperature and at 25 °C respectively. The surface microstructure of sintered samples was observed with Scanning Electron Microscopy (SEM, Philips XL 30).The core-shell structure was observed with Scanning Electron Microscopy (NanoSEM430, FEI). The phases existed in ceramics were examined using an X-ray diffractometer (XRD, Rigaku 2038X) with Cu K α radiation ($\lambda = 0.15406$ nm) at a step

width of 0.02° and a scan rate of 2°/min. The lattice parameters were derived from XRD data by least square fit.

3 Results and discussion

3.1 XRD and SEM analysis

Figure 1 shows X-ray analysis of samples doped with different content of PTS. As shown in Fig. 1, main phase was BaTiO₃, and non-ferroelectric phases Ti_{0.1}Sn_{0.9}O₂, Ti₉O₁₇, TiO were formed in all samples. Within the XRD resolution limit, the Nb, Co, Sm and Mn elements were not detected in the profile. The phases of specimen with different content of PTS were similar to each other. X-ray analysis indicated that the partial solid solution was formed between BaTiO₃ and PTS. However, the PTS phase was not detected in the XRD profile, which meant the solid solubility of PTS in the BaTiO₃-based ceramics >3 mol. The diffraction peaks round 45° were separated from each other for four samples, corresponding to the crystal plane of (002) and (200) respectively, which indicated that the crystal structure of four samples was typically tetragonal [2]. The intensity of non-ferroelectric phases was decreased as increasing PTS content.

Figure 2 shows SEM images of samples doped with different content of PTS. Two types of grains were observed in the ceramics. All samples were composed of matrix fine grains and secondary phase grains. According to XRD analysis, the matrix fine grains were BaTiO₃, and secondary phase grains were Ti_{0.1}Sn_{0.9}O₂, Ti₉O₁₇ and TiO non-ferroelectric phases which were formed the liquid

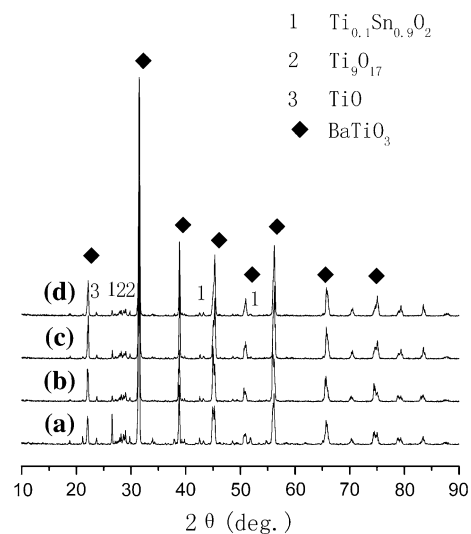


Fig. 1 X-ray analysis of samples doped with different content of PTS (a) Doped with 1.5 mol% PTS (b) Doped with 2 mol% PTS (c) Doped with 2.5 mol% PTS (d) Doped with 3 mol% PTS

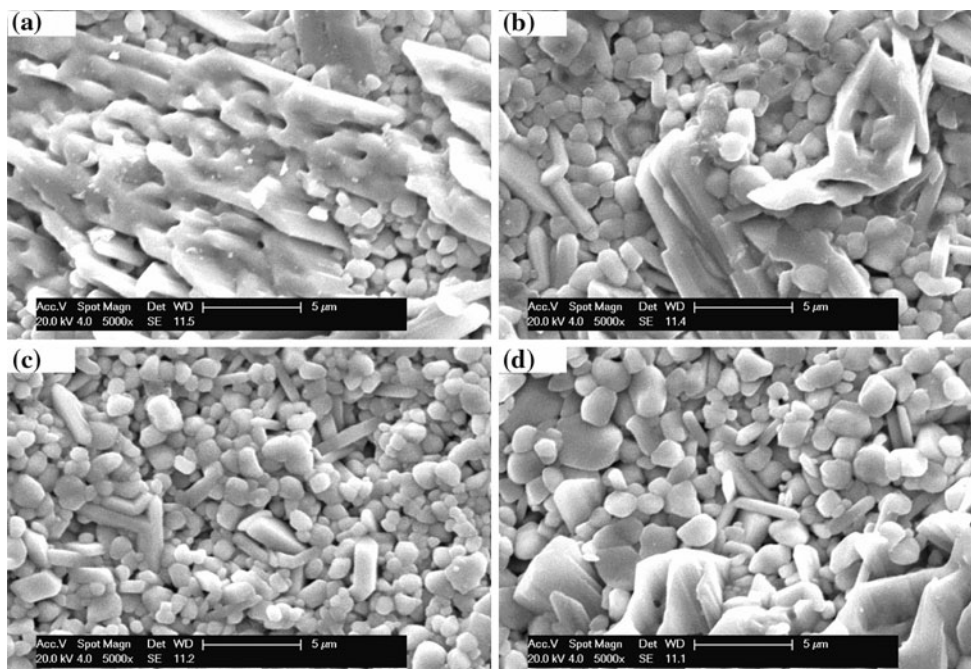


Fig. 2 SEM images of samples doped with different content of PTS **a** Doped with 1.5 mol% PTS **b** Doped with 2 mol% PTS **c** Doped with 2.5 mol% PTS **d** Doped with 3 mol% PTS

phase during the sintering. As shown in Fig. 2c, the sample doped with 2.5 mol% PTS was predominantly composed of fine grains with smooth surface and clear boundaries, although a small amount of strip grains were observed.

For the sample doped with 2.5 mol% PTS, a fine structure in the core and a coarse structure in the shell were observed in Fig. 3, so this sample was the core–shell type.

3.2 The effect of Pb(Ti, Sn)O₃ additives on dielectric properties of high dielectric constant X8R BaTiO₃-based ceramics

Figure 4a shows temperature dependence of ϵ for BaTiO₃ ceramics doped with different content of PTS sintered at 1,240 °C for 4 h. The T_c of BaTiO₃ ceramics was greatly increased to 150 °C by the additive of PTS, while pure BaTiO₃ has a T_c of 130 °C. The shift of T_c from 130 to 150 °C was attributed to the replacement of Ba²⁺ (0.136 nm) with Pb²⁺ (0.118 nm). The melting point of PbO was as low as 886 °C, which meant the Pb–O bonds were weakened in the perovskite ABO₃ structure, which induced that the Ti–O bonds were strengthened after PTS were doped to BaTiO₃. The interaction between Ti⁴⁺ and its near O²⁻ were so strong that Ti⁴⁺ could not resume its seat unless the thermal vibration of Ti⁴⁺ were enhanced and the ferroelectricity were weakened by high temperature. Hence, T_c was increased by the addition of PTS. On the other hand, in the perovskite ABO₃ structure, A-site ion was at the center of oxygen dodecahedron, and there were

eight oxygen octahedrons held down directly by A-site ion. In addition, more oxygen octahedrons were pinned indirectly by A-site ion. So although a few A-site ions were replaced, vast Ti–O bonds could be influenced. That is to say, T_c was greatly improved although a few A-site ions were replaced by Pb²⁺ [10]. Meanwhile, the partial solid solution was formed between BaTiO₃ and PTS. The T_c of solid solution was determined by the mole percentage of ingredients [11]. The T_c of PTS was as high as 296 °C, so the T_c of BaTiO₃ ceramics doped with PTS was shifted to higher temperature.

As shown in Fig. 4a, the similar curve shapes were observed for 1.5–3 mol% PTS doped samples. As the samples show two peaks in their ϵ -T curves, the core–shell

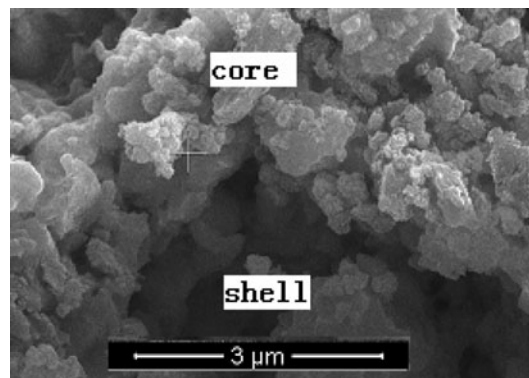


Fig. 3 SEM images of the outer shell (coarse structure) and the inner core (fine structure) of the sample doped with 2.5 mol% PTS

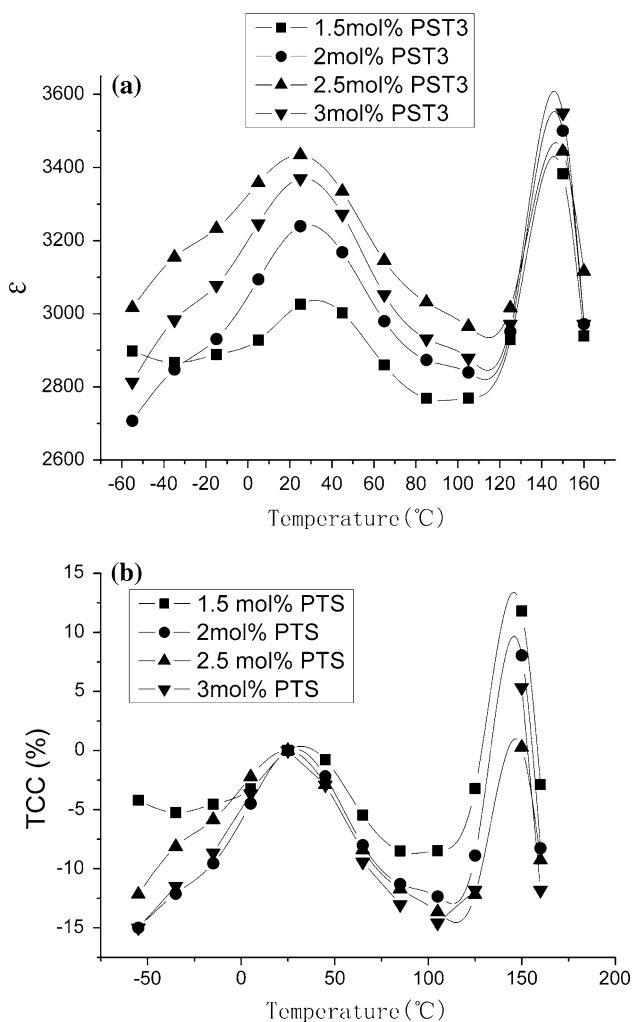


Fig. 4 Temperature dependence of **a** ϵ , **b** TCC of the BaTiO₃ ceramics with various PTS contents (sintered at 1240 °C for 4 h)

structure was existed in the ceramics. The core–shell structure of the samples doped with 2.5 mol% PTS was observed in Fig. 3. Figure 4b shows the temperature dependence of TCC of the BaTiO₃ ceramics with various PTS contents. Doped with 1.5–3 mol% PTS, the TCC of BaTiO₃ ceramics was less than $\pm 15\%$ from -55 to 150 °C, which satisfied the X8R specification. The ceramics doped with 2.5 mol% PTS exhibited the highest ϵ (3400) at 25 °C. XRD analysis indicated that non-ferroelectric phases were decreased as increasing PTS content. According to Lichtenecker formula:

$$\ln \epsilon = x_1 \ln \epsilon_1 + x_2 \ln \epsilon_2 + x_3 \ln \epsilon_3 + \dots + x_n \ln \epsilon_n \quad (1)$$

So, why the ϵ was decreased when the content of non-ferroelectric phases was increased was explained well by equation (1).

As shown in Table 1, the lattice parameters and tetragonality (c/a ratio) were derived from XRD data by least square fit. The tetragonality (c/a ratio) was increased as the

Table 1 The lattice parameters and the tetragonality (c/a ratio) of BaTiO₃ ceramics doped with different content of PTS

	a (nm)	c (nm)	c/a
Doped with 1.5 mol% PTS	0.400458	0.40364	1.007946
Doped with 2 mol% PTS	0.399826	0.40309	1.008164
Doped with 2.5 mol% PTS	0.399854	0.403122	1.008173
Doped with 3 mol% PTS	0.400688	0.403685	1.00748

content of PTS increasing from 1.5 to 2.5 mol%. Because the grain core possessed the tetragonal structure of pure BaTiO₃, the tetragonality (the c/a ratio) was associated with the volume fraction of grain core [12]. Doped with 2.5 mol% PTS, the c/a ratio was as high as 1.008173, which suggested that the volume fraction of the tetragonal grain core was increased, whereas the volume fraction of the cubic grain shell was decreased. According to the Lichtenecker formula, the ϵ of the ceramics was increased accordingly. The fine and homogeneous grains were responsible for good dielectric properties. SEM indicated that fine and homogeneous grains were observed at 25 °C with 2.5 mol% PTS additives, which also gave rise to the increase of ϵ .

On the other hand, ϵ was reduced with increasing PTS content up to 3 mol%. Doped with abundant amount of PTS, Pb²⁺ ion (0.12 nm) substituted for A-site (Ba²⁺ 0.135 nm) in ABO₃ structure. It formed cationic vacancies, for the radius of Pb²⁺ was much smaller than Ba²⁺. Those vacancies would result in the shrinkage of crystal lattice in some direction. Meanwhile, Sn⁴⁺ (0.069 nm) substituted for B-site (Ti⁴⁺ 0.061 nm) in ABO₃ structure. Sn⁴⁺ possessed larger radius in B-site, so the volume of tin centered eight oxygen octahedrons was increased. Hence, the volume of titanium centered eight oxygen octahedrons was decreased. So the active space for Ti⁴⁺ was decreased, and Ti⁴⁺ ions were restricted to the center of oxygen octahedrons. Thus Ti⁴⁺'s polarization was depressed, then ϵ was decreased accordingly. As shown in Table 1, the decrease of the tetragonality (c/a ratio) suggested the volume fraction of the tetragonal grain core was decreased, whereas the volume fraction of cubic grain shell was increased. According to the Lichtenecker formula, the ϵ of the ceramics was decreased accordingly. Moreover, $\tan \delta$ of four samples was lower than 2.0% at 25 °C, which satisfied X8R specification.

4 Conclusions

The ceramics doped with 2.5 mol% PTS, exhibited the highest ϵ (about 3,400) at room temperature, which satisfied X8R specification. Doped with PTS additives, the Tc of the ceramics was markedly shifted to higher temperature

about 150 °C. The substitution of Pb^{2+} for the A-sites in BaTiO_3 strengthened Ti–O bonds, resulting in the increase of T_c . Because the T_c of the PTS ingredients was as high as 296 °C, the T_c of the ceramics doped with PTS was shifted to higher temperature. XRD analysis proved that as the content of PTS increasing, the non-ferroelectric phases were decreased, and the tetragonality (c/a ratio) was increased, which resulted in the increase of ϵ . SEM indicated that doped with 2.5 mol% PTS, fine and homogeneous grains were observed, which also gave rise to the increase of ϵ . With PTS content up to 3 mol%, the substitutions of ions for A-site and B-site, resulted in the shrinkage of crystal lattice in some direction and the decrease in the volume of titanium centered eight oxygen octahedrons. Thus Ti^{4+} 's polarization was depressed, then ϵ was decreased accordingly. The decrease in the tetragonality (c/a ratio) was also resulted in the decrease of ϵ .

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