

Physical and electrical properties of SrTiO₃ and SrZrO₃

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Abstract. Perovskite type oxide strontium titanate (SrTiO₃) and strontium zirconate (SrZrO₃) ceramic powder has been synthesized using conventional solid state reaction method. The powders were mixed and ground undergone calcinations at 1400°C for 12 h and sintered at 1550°C for 5h. X-ray Diffraction exposes physical properties SrTiO₃ which exhibit cubic phase (space group: pm-3m) at room temperature meanwhile SrZrO₃ has Orthorhombic phase (space group: pnma). The electrical properties such as dielectric constant (ϵ_r), dielectric loss ($\tan \delta$), and conductivity (σ) were studied in variation temperature and frequency. High dielectric constant of SrTiO₃ and SrZrO₃ were observed at 10 kHz for both samples about 240 and 21 respectively at room temperature. The dielectric loss of SrTiO₃ and SrZrO₃ is very low loss value approximately 0.00076 and 0.67512 indicates very good dielectric.

1 Introduction

Ceramic with perovskite crystal structure have long been investigated due to their excellent ferroelectric, paraelectric properties and chemically stable-structure. Its applicable in displays, Multilayer Ceramic Capacitor (MLCC), electronic/piezoelectric devices, sensors, actuators, transducers, wireless communications [1-5]. The ideal Perovskite structure, which have the general formula ABX₃ are consisting of two different cations (A and B) in equal ratio and an anion (X), which is usually oxygen.

SrTiO₃ and SrZrO₃ are such materials that have been current interest to study due high dielectric constant and its a lead free material. At room temperature, SrTiO₃ has a simple cubic perovskite structure with space group (pm-3m) meanwhile SrZrO₃ has orthorhombic structure with space group (pnma) but both composition undergoes a series of phase transitions by varying the temperature. SrTiO₃ undergoes phase transitions from high to low symmetry [6], while low to high symmetry for SrZrO₃ [7].

SrTiO₃ and SrZrO₃ is a perovskite dielectric material applied to many application fields such as integrated microelectronic and microwave device [8]. These features are attributed by their unique properties such as high dielectric constant, low dielectric loss, tunability, high breakdown strength and low leakage current density [9-11]. Besides, the melting point of SrTiO₃ and SrZrO₃ is 2080°C and 2600°C respectively, making it applicable at high temperatures. In 2001, Shende et al. [11] claim that SrTiO₃ and SrZrO₃ can be used in high-voltage applications because of its high breakdown strengths which these materials are not expected to experience electromechanical failure mechanisms that may result in dielectric breakdown. Parida et al. [12] in 2012 report that SrTiO₃ and SrZrO₃ has high permittivity and low loss make it suitable for microwave antenna application. Based on Wang et al [13] study, high dielectric constant and favourable bias

stability inside SrTiO₃ are widely required for the application of high energy storage density dielectrics.

Numerous attempts have been explored to further improve the properties of SrTiO₃ based ceramics. Among them, doping was considered as an effective approach for altering their properties. ZrO₂ was selected as cation substitute the B-type site of SrTiO₃, because Zr⁴⁺ ions in SrTiO₃ can stabilize the charge of Ti⁴⁺ and suppress the oxygen dissociation when sintered at high temperature [13]. SrTiO₃-SrZrO₃ solid solution is one of them, which shows a super lattice structure due to its cell enlargement as a result of tilting of BO₆ (B = Ti, Zr) octahedral [14]. This type of disorder perovskite solid solution offers exciting new possibilities both in the investigation of fundamental physical behaviour and in the exploitation of novel properties for various applications.

In this study, the electrical properties of SrTiO₃ and SrZrO₃ prepared via solid state reaction method were investigated as respect to its physical structure properties. So, the system is expected to provide access to the desired phase or properties at convenient temperatures.

2 Experimental procedure

The Perovskite-type oxide were prepared by mixing high purity SrCO₃ (99.9% Aldrich), TiO₂ (99.0% Sigma Aldrich), and ZrO₂ (99% Aldrich) in the appropriate stoichiometric ratios. Sample was mixed and ground using pestle and mortar with acetone as mixing medium. The obtained powders were pressed into pellets of diameter 13mm and heated at high temperature 1400°C for 12h with heating rate 5°C/m in the furnace. The samples were sintered for 1550°C for 5h in air followed by characterization.

X-ray Diffraction (XRD) were conducted at room temperature to determine the crystalline structure of all samples by using X-Ray Diffractometer (Model: D2 PHASER from Bruker AXS) in a 2 θ range from 10°

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to 80°, using Cu K α 1 radiation. The electrical properties such as dielectric constant (ϵ_r), dielectric loss ($\tan \delta$), by making use of impedance-capacitance-resistance (LCR) meter (Model: HIOKI 3522-50 LCR HiTESTER) at temperature 30-600°C. For this purpose, sintered pallets were coated with silver paste as electrode. Samples are measured over the frequency range of 10 Hz – 100 kHz with different temperature.

3 Results and Discussion

The structures of the oxide SrTiO₃ and SrZrO₃ were first studied using powder X-ray diffraction data within 10° to 80° value of 2 θ in range as shown in **Figure 1(a) and**

conductivity(σ) as well as impedance (Z) were studied

1(b). All the peaks are sharp and there is no unwanted peak is found in XRD pattern, representing the crystal is single phase without any impurities and identical to the pdf reported [SrTiO₃=PDF00-035-0734] and [SrZrO₃=PDF01-076-9442]. From the diffraction pattern, the lattice parameter along with the average crystallite size for both the samples has been calculated as shown in **Table 1**. SrTiO₃ was indexed Cubic phase (space group: P m -3 m) with unit cell with lattice constant formulated by a = 3.9000Å which are in contrast to the orthorhombic structure of the SrZrO₃ with unit cell with lattice constant formulated by a = 5.7915Å, b=5.8129Å, c=8.2000Å.

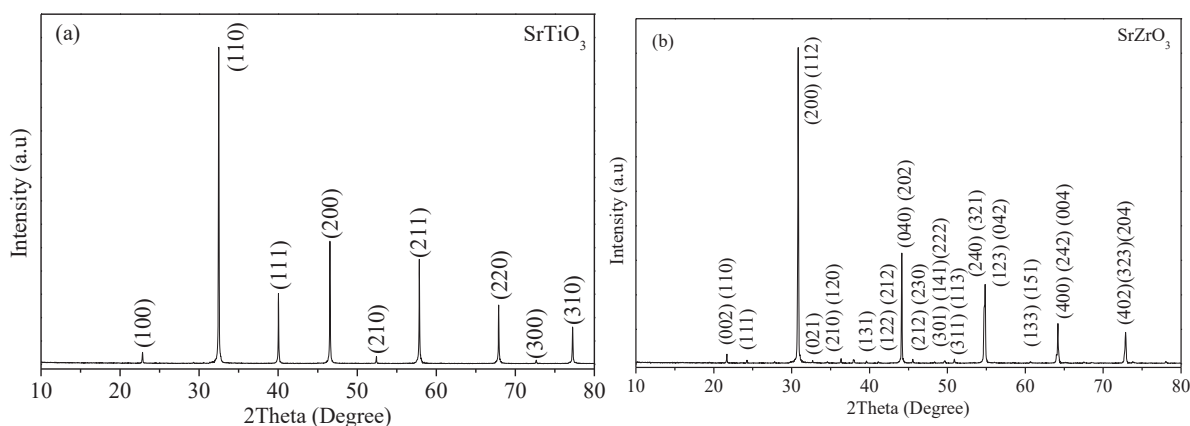


Fig. 1. Index XRD pattern of (a) SrTiO₃ (b) SrZrO₃

Table 1 Lattice parameter,crystallite size and space group of SrTiO₃ and SrZrO₃

	SrTiO ₃	SrZrO ₃
a (Å)	3.9000 (1)	5.7915 (1)
b (Å)	-	5.8129 (1)
c (Å)	-	8.2000 (1)
V (Å³)	59.5 (1)	276.1 (1)
Crystallite Size	973.14	796.86
Space Group	P m -3 m	P n m a

The Dielectric Constant (ϵ_r) was calculated from the measured capacitance (C_p) obtain by LCR meter between 30 - 600°C temperatures. The variations of dielectric constant with temperature at some selected frequencies for SrTiO₃ and SrZrO₃ ceramics are shown in **Figure 2(a) and 2(b)**. For SrTiO₃ ceramics, the dielectric constant decreases gradually up to a certain temperature and increases rapidly with increasing temperature. Similar phenomenon of the dielectric constant was observed in SrZrO₃ ceramics. There is no curie peak detected for both sample in the whole measurement temperature range. The dielectric constant of SrTiO₃ much higher compared to SrZrO₃ dielectric constant is decrease in from $\epsilon_r = 240$ (SrTiO₃) to $\epsilon_r = 21$ (SrZrO₃) is due to the decrease in ionic polarization [15].

Figure 3(a) and 3(b) shows the Capacitance against frequency, the spectrum displace toward higher

frequency. SrTiO₃ exhibit capacitance of average 10⁻⁹ ~ 10⁻¹⁰ F, meanwhile SrZrO₃ show to have capacitance value in range of 10⁻¹⁰ ~ 10⁻¹¹ F, Thus the range of capacitance probably belonged to grain boundary [16]. The highest capacitance value is obtain at temperature 600°C which give 2.9x10⁻⁹ F for SrTiO₃ and 1.3x10⁻¹⁰ F for SrZrO₃ at 1 kHz. The capacitance related to the ability of SrTiO₃ and SrZrO₃ sample to collect and store energy in the form of an electrical charge.

Figure 4(a) and 4(b) shows the dielectric loss ($\tan \delta$) of SrTiO₃ and SrZrO₃. The dielectric loss for the SrTiO₃ measured at below temperature 200°C shows very small loss which about 0.00191 but by increasing the temperature from 200°C to 600°C, the dielectric loss

value fluctuate and increased at about 1. However, for SrZrO₃ below 300°C the dielectric loss is less than 1 but increasing after 300°C. The dielectric loss of SrTiO₃

ceramics seems to remain similar trend but it gives much higher of loss as compared to SrTiO₃.

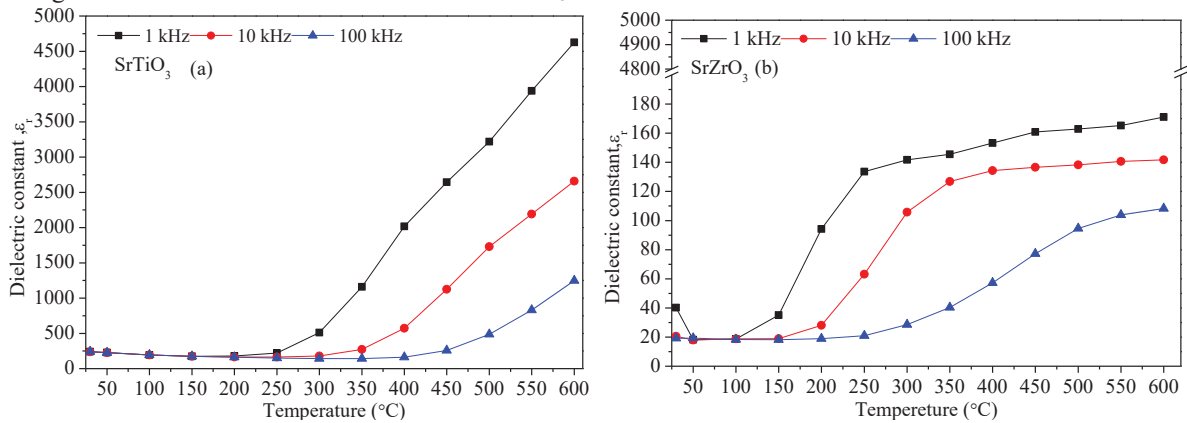


Fig. 2. Temperature dependence of dielectric constant (ϵ_r) for (a) SrTiO₃ (b) SrZrO₃

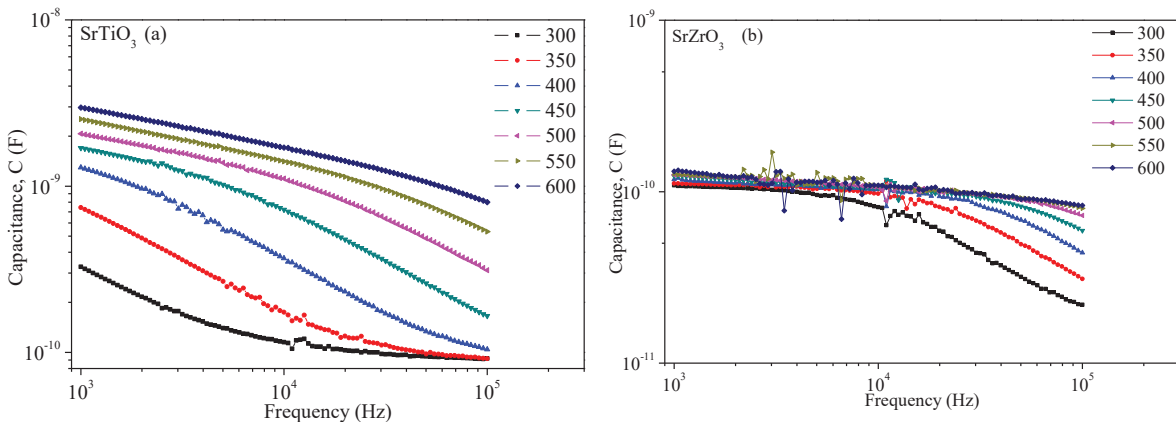


Fig. 3. Frequency dependence of capacitance for (a) SrTiO₃ (b) SrZrO₃

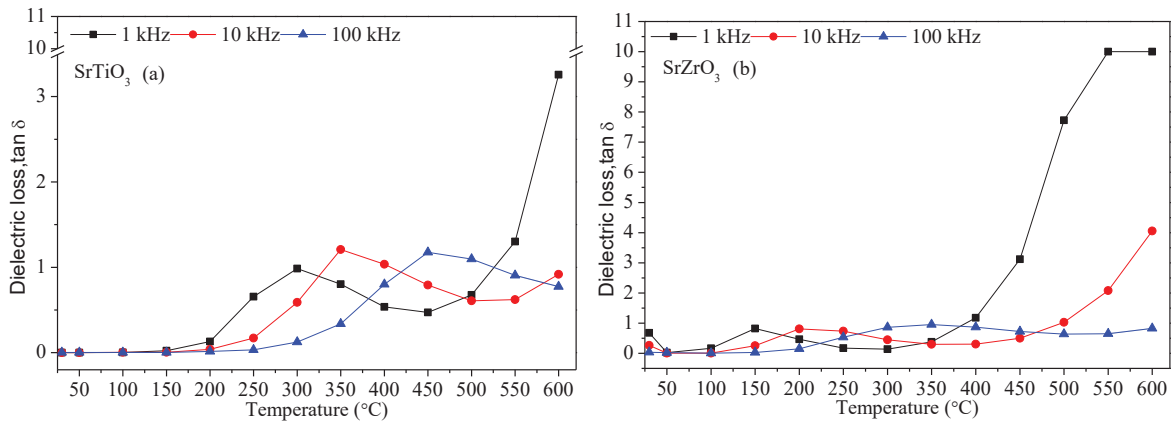


Fig. 4. Temperature dependence of Dielectric loss ($\tan \delta$) for (a) SrTiO₃ (b) SrZrO₃

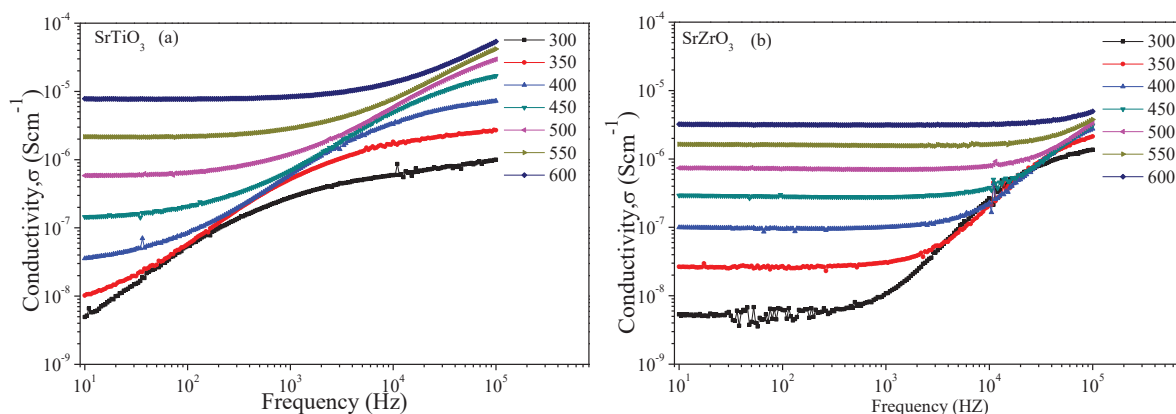


Fig. 5. Frequency dependence of conductivity (σ) for (a) SrTiO₃ (b) SrZrO₃

The frequency dependent conductivity for SrTiO₃ and SrZrO₃ in the temperature range of 300–600°C was shown in **Figure 5(a) and 5(b)**. The conductivity observed for SrZrO₃ slightly lower as compared to pure SrTiO₃. For SrTiO₃ it shows that the conductivity increased by increasing temperature which behave like typical dielectric ceramic. The dc conductivity was about $4.9 \times 10^{-9} \text{ Scm}^{-1}$ to $7.7 \times 10^{-6} \text{ Scm}^{-1}$ and $5.3 \times 10^{-9} \text{ Scm}^{-1}$ to $5.2 \times 10^{-6} \text{ Scm}^{-1}$ for SrZrO₃. SrZrO₃ show the conductivity behaviour at frequency 10 Hz and 10 kHz. This phenomenon are related to the conductivity of grain boundaries as reported by Liu [17]

4 Conclusions

SrTiO₃ and SrZrO₃ was phase pure after heating at 1400°C for 12h. SrTiO₃ exhibit cubic structure with space group pm-3m however SrZrO₃ exhibit orthorhombic structure with space group pnma. This is proven by the change in unit cell and volume of the samples. In term of the dielectric properties, SrTiO₃ have much higher value of dielectric constant which is 240 compare to SrZrO₃ is 21 at 10 kHz. The dielectric loss of SrTiO₃ is 0.00191 and SrZrO₃ is 0.26547. Besides, at 400°C the conductivity of SrTiO₃ is $7.8 \times 10^{-6} \text{ Scm}^{-1}$ and $3.2 \times 10^{-6} \text{ Scm}^{-1}$ for SrTiO₃. Overall the properties of SrTiO₃ is much better than SrZrO₃.

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References

1. M. T. Sebastian, Dielectric Materials for Wireless Communication, Elsevier, Amsterdam, Netherlands, pp. 49–77, (2008).
2. A. A. Vives, Piezoelectric Transducers and Application, 2nd edition, Springer, Berlin, pp. 509, (2008).

3. K. Uchino, Ceram. Int., **21**, 309–315 (1995).
4. S. S. Park, Integrated Ferroelectrics, **74**, 87-94 (2005).
5. N. Zakaria, R. A. M. Osman, M. S. Idris, *AIP Conference Proceedings*, 1756, 090006, (2016).
6. F. W. Lyte, Appl. Phys., **35**, 7, 2212-2215 (1964).
7. R. E. A. McKnight, C. J. Howard, M. A. Carpenter, *J. Phys. Condens. Matter*, **21**, 015901 (2009).
8. T. A. T. Sulong, R. A. M. Osman, and M. S. Idris, *AIP Conference Proceedings*, 1756, 070003 (2016).
9. J. Zhao, X. Wu, L. Li, X. Li, *Solid-State Electron*, **48**, 2287–2291 (2004).
10. J. Xie, H. Hao, H. Liu, Z. Yao, Z. Song, L. Zhang, Q. Xu, J. Dai, M. Cao, *Ceram. Int*, **42**, 12796–12801 (2016).
11. P. K. Petrov, E. F. Carlsson, P. Larsson, M. Friesel, G. I. Zdravko, *J. Appl. Phys.* **84**, 3134–3140 (1998).
12. R. V. Shende, D. S. Krueger, G. A. Rossetti Jr, S. J. Lombardo, *J. Am. Ceram. Soc.*, **84**, 7, 1648–50 (2001).
13. S. Parida, S. K. Rout, V. Subramanian, P. K. Barhai, N. Gupta, V. R. Gupta, *J. Alloy. Compd*, **528**, 126–134 (2012).
14. Z. Wang, M. cao, Z. Yao, Z. song, G. Li, W. Hu, H. Hoa, H. Liu, *Ceram. Int*, **40**, 14127–14132 (2014).
15. T. K. Y. Wong, B. J. Kennedy, C. J. Howard, B. A. Hunter, T. Vogt, *J. Solid State Chem.*, **156**, 255-263 (2001).
16. T. Tsurumi, T. Teranishi, S. Wada, H. Kakemoto, M. Nakada, J. Akedo, *J. Cer. Soc. Japan*, 774-781(2006).
17. J. T. S. Irvine, D. C. Sinclair, and A. R. West, *Adv. Mater.*, **2**, 3, 132-138 (1990).
18. L. N. Liu, C. C. Wang, X. H. Sun, G. J. Wang, C. M. Lei, T. Li, *J. Alloy. Compd.*, **552**, 279–282 (2013).