

Temperature and frequency dependent dielectric capacitance and polarization performances of low dimensional perovskite based manganese stannate

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ABSTRACT

Manganese stannate perovskite nanoparticles were synthesized by applying a complexation mediated approach. Rietveld refinement of the XRD data exhibited orthorhombic structure with space group of Pnma. The structure included eightfold coordinated Mn²⁺ cation, surrounded by eight O²⁻ anions and formed MnO_8 polyhedra unit. Each polyhedra unit interconnected through the cornersharing SnO_6 octahedra with the formation of a cage-like network. The temperature and frequency dependent dielectric performances of manganese stannate were measured in the form of a device, which exhibited maximum dielectric constant value ~ 3445. The high dielectric constant value was originated due to the contribution of space charge polarization and orientation polarization of dipoles within the measured frequency ranges. Temperature and frequency dependent AC-conduction mechanism of the manganese stannate-based device involved both overlapping large polarons and non-overlapping small polarons. Electric field-dependent of polarization hysteresis loop of the device exhibited the maximum polarization value 1.5 μ C/cm² under the electric field of 3 kV/mm. Under the applied field of 2 kV/mm, the device exhibited a fatigue-free polarization with a maximum value of 0.92 μ C/cm², sustained for 10³ cycles under ambient temperature condition.

1 Introduction

Stannate-based materials exhibited a wide range of physical properties, rendering them highly suitable for utilization in various electronic devices [1–3]. Such kind of ternary oxides are chemically stable and have attracted significant attention due to their versatile performances. Lanthanum-doped BaSnO₃ showed technological potential for non-volatile electronic devices [4]. The investigation of ZnSnO₃ nanostructures was

undertaken by researchers in order to explore their potential implementation in piezoelectric devices owing to their notable polarization characteristic. A scientific study unveiled that the composite of polydimethyl siloxane and ZnSnO₃ nanostructure synergistically functioned as a nanogenerator, exhibiting the capacity to energetically sustain light-emitting diodes and other electronic devices [5]. Asymmetric supercapacitor based on nickel stannate and ferrous stannate demonstrated significant potential for enabling

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self-powered wearable device [6]. Li-ion transport property of Li-doped SrSnO₃ exhibited lower diffusion activation energy and higher diffusivity, implying the potential of the material for Li-ion battery application [7]. The remarkable electrical conductivity and excellent transparency exhibited by the Cd₂SnO₄ film make it highly desirable for applications in solar energy harvesting processes [8]. It is reported that perovskite BaSnO₃ and SrSnO₃ display strong luminescence and photocatalytic performance, respectively [9, 10]. Neodymium-doped SrSnO₃ has been reported for the development of high-power electronic devices [11]. Perovskite structure of $ASnO_3$ (A = Ba, Sr) have superior electron conductivity that rendering them as promising candidates for transparent conducting oxides [12]. Among the various perovskite stannatebased materials [13], PbSnO₃ demonstrated spontaneous polarization and moderate dielectric constant value under an external applied field, however, responded differently for titanate containing Sn⁴⁺ ions, Pb(Ti·Sn)O₃, that influenced the dielectric anomalies and ferroelectric polarization within the system [14]. Perovskite strucutre of ZnSnO₃ has attracted much attention for its unique properties of optical transparency [15], ferroelectric [16] and field-effect transistor applications [17]. It was reported that organic molecule stabilized ZnSnO₃ hybrid structure exhibited better electro-mechanical stress, flexibility, polarization and piezoelectric properties than conventional zinc stannate system [18]. Experimental and theoritical studies revealed that the polarizability of oragnic molecule alters the strucutral and electrical performances of the ZnSnO₃ material [18].

Non-perovskite silver stannate (Ag₂SnO₃) nanocrystal with linear arrangement of Ag-atoms along the c-axis demonstrated the high value of electrical conductivity with low dielectric breakdown strength and polarizability under an applied electric field [19]. However, the dielectric and polarization strength of Ag₂SnO₃ nanocrystal was improved significantly due to the incorporation of carbon nitride in the system that prevents the formation of silver filament [19]. Amorphous CoSnO₃@C system exhibited an excellent cycle life and improved rate capability for lithiumion batteries when applied as an anode material [20]. Graphene oxide decorated CoSnO₃@ZnSnO₃ system showed high energy storage and capacity retention performance for asymmetric supercapacitor application [21]. Composite system of NiSnO₃-graphene displayed as high-performance electrode towards asymmetric supercapacitor application [22]. Acid mediated formation of CuSnO₃ nanoparticles showed photocatalytic and antibacterial applications [23].

High pressure synthesis route was reported for the preparation of manganese stannate (MnSnO₃) perovskite system that showed magnetodielectic coupling and multiferroic proeprties under the magnetic field [24]. The above system exchibited dielectric constant value of ~ 22 at 300 K under 100 kHz and zero magnetic field conditon. Studies revealed that the ferroelectric phase transition and polarization under external pressure caused the structural distortion of MnSnO₃ system [25, 26]. The distortion in the Mn–O bond length was responsible for the elongation of SnO₆ octahedra unit that improved the field induced polarization behaviour of the material [26]. Amorphous MnSnO₃ also functioned as high-performance electrode materials with superior rate capability and long-term cyclic life for lithium storage systems [27]. Ferroelectric MnSnO₃ was identified as a possible candidate for photovoltaic application due to its small band gap and excellent carrier mobility [28].

In the present study, complexation strategy was applied to sythesis the single phase orthorhombic manganese stannate (MnSnO₃) nanoparticles under ambient temperature and pressure conditions. The Rietveld refinement analysis was performed based on the experimental diffracted data of MnSnO₃ system. A device, based on MnSnO₃, was fabricated on a flexiable substrate and measued the dielectric capacitance, AC-conductivity and electric field dependent polarization under wide range of temperture and frequency conditions. Electrical mobility and polarization performance of the device was correlated with polaron and vacancy mediated mechanisms, respectively.

2 Experimental sections

2.1 Materials

MnCl₂. 4H₂O, K₂SnO₃, 3H₂O and hexamethylenediamine were used in this study without any further purification.

2.2 Synthesis of manganese stannate (MSO) nanoparticles

In a typical synthesis process, 0.12 g of hexamethylenediamine (HMDA) was dissolved in 10 mL of methanol in a conical flask. An aqueous solution of manganese chloride (10 mL) with the concentration of 0.1 mol/dm³ was slowly added to the solution of HMDA, leading to the subsequent formation of a complex of Mn(II)-HMDA with a deep brown colour. The addition of 5 mL of K_2SnO_3 $3H_2O$ (0.1 mol/dm³) dropwise to the complex resulted in the formation of a solid black precipitate at the bottom of the conical flask. The synthesized material was filtered and dried at 80 °C under vacuum. The structural property of the synthesized material was characterized using X-ray diffraction (Philips PANalytical), Raman (Jobin–Yvon T64000) and X-ray photoelectron spectroscopy (VG Multilab 2000) techniques that confirmed the formation of manganese stannate (MnSnO₃).

2.3 Device fabrication and characterization

The flexible manganese stannate (MSO)-based device was fabricated on an indium tin oxide (ITO) coated PET (polyethylene terephthalate) substrate. Initially, a slurry was made by mixing manganese stannate with chloroform and deposited, using a drop-anddry method, on the ITO substrate, acted as a working (bottom) electrode. The deposited material was dried and coated with gold on the top side of the material (top electrode) using the physical vapour deposition technique (EMSCOPE SC 500). The fabricated MSObased device has a dimension with the thickness of ~100 µm and the electrode area of ~21 mm². The electrical studies of the fabricated device were performed under different temperature and frequency conditions.

The temperature and frequency dependent dielectric and polarization performances of the MSO-based device were measured using HP 4284A LCR meter and Sawyer–Tower circuit interfaced with computer controlled temperature chamber. A triangular waveform of frequency 10 Hz was applied to the device for polarization–electric field (P-E) study under varying temperature condition.

3 Results and discussion

The X-ray diffraction pattern of manganese stannate, Fig. 1A, recorded within the range (2 θ) from 20° to 80°. The diffracted pattern of the synthesized material is similar with an isostructural perovskite SrSnO₃ structure [29–31]. Sharp and well defined diffracted peaks revealed the formation of single phase manganese



Fig. 1 A Rietveld refinement pattern for manganese stannate. The symbol (black circle) is the experimental curve; red solid line is the calculated, blue solid line is the difference between experimental and calculated pattern, green vertical bars are the Bragg-positions of orthorhombic phase. **B** and **C** Unit cell representation of manganese stannate projected along c-axis and **D** represents the tilting in SnO₆ octahedra unit. **E** and **F** Represents the unit cell projection along b-axis and the equivalent electron density mapping of the material (Color figure online)

stannate. The Rietveld refinement analysis was performed on the experimental diffracted (black circle) data of $MnSnO_3$ system. The overall diffracted pattern was refined according to the orthorhombic crystal structure with the space group of Pnma (No. 62). The vertical bar (green colour) represents the Bragg-position of the lattice symmetry. The calculated diffraction pattern (red line) and the corresponding difference (blue line) are attained within the acceptable range of convergent factor (χ^2 = 1.5, R_{wp} = 6.2% and R_p = 4.4%). The refined lattice parameters, a = 5.55 (6) Å, b = 5.54 (4) Å, c = 7.85 (4) Å and $\alpha = \beta = \gamma = 90^{\circ}$ are obtained from the refinement analysis. The detail structural parameters such as atomic positions, lattice occupancy, B_{iso} X-ray density and bond length of the MnSnO₃ system are listed in Table S1 (Supporting information). The observed diffraction pattern revealed the formation of single-phase of MnSnO₃. The unit cell representation of MnSnO₃ system was constructed using the refined lattice parameters, Fig. 1B. The structure consists of eightfold coordinated Mn²⁺ cation, surrounded by eight O²⁻ anions and formed MnO₈ polyhedra unit. Each polyhedra unit interconnected with the cornersharing SnO₆ octahedra with a cage-like network [32, 33] (Fig. S1A, supporting information). Within the unit cell, the oxygen ion is linearly coordinated with two Sn⁴⁺ cations in Sn–O–Sn arrangement and enclosed with four Mn²⁺ cations in a plane, perpendicular to Sn–O–Sn bond, Fig. 1C. The MnSnO₃ structure involved an in-plane tilting of SnO₆ octahedral unit along the c-axis, as highlighted (red arrows) in Fig. 1D and that created a distortion on the local charge distribution. The local charge density mapping of MnSnO₃ unit cell projected along the b-axis, Fig. 1E, was constructed by using G-Fourier 2D contour plot (FullProf software), Fig. 1F. Yellow colour on the charge density scale corresponds to the maximum charge accumulation at Sn-atom site in comparison with oxygen, O_1 and O_2 , (cyan colour) site. The structural stability of orthorhombic manganese stannate was verified from the tolerance factor ($t \sim 0.80$) using Goldschmidt formula (equation S1, supporting information). The deviation of *t*-factor, from ideal value of cubic perovskite ($t \sim 1$), justified the structural distortion of SnO₆ or MnO₈ units, which yielded the lower symmetrical arrangement of MnSnO₃. Similar value of tolerance factor has been reported in other orthorhombic perovskite systems with smaller cationic radii [33–35].

The transmission electron microscope (TEM, JEOL JEM-2100) image, Fig. 2A, shows cube-like morphology of manganese stannate within the size range between 50 and 70 nm. Higher magnification TEM image, Fig. 2B, displays the prominent edges of cubic shaped stannate particle. The selected area electron diffraction (SAED) pattern, Fig. 2C, confirms the crystalline nature of the nanocubes, manifested by regular order of the diffraction spots.

Raman spectrum of manganese stannate was measured within the frequency range from 50 to 850 cm^{-1} ,



Fig. 2 A and B Transmission electron microscope images of manganese stannate nanoparticles under different magnification. C The selected area electron diffraction pattern of the nanoparticle



Fig. 3 Raman spectra of manganese stannate, measured within the frequency range from 50 to 850 cm⁻¹. The spectrum was deconvoluted (black colour) in eight Raman active modes ($\nu_1 - \nu_8$) (Color figure online)

Fig. 3. The spectrum was deconvoluted (black colour) into eight Raman active modes (v_1 to v_8). At the low frequency region (50–150 cm⁻¹), the Raman peak positioned at $v_1 \sim 94.3$ cm⁻¹ and $v_2 \sim 126.3$ cm⁻¹ are correspond to soft lattice mode, designated as A_g and B_{2g} respectively, originated from the Mn-SnO₃ vibrations [29, 36]. The v_1 mode is associated with the bending of O–Sn–O bond, along with the vibration of Mn²⁺

cation. At intermediate frequency range, other diffuse modes (B_{2e}) positioned at $v_3 \sim 260 \text{ cm}^{-1}$, $v_4 \sim 359.0 \text{ cm}^{-1}$ and $v_5 \sim 4\tilde{2}3$ cm⁻¹ correspond to the Sn–O–Sn scissoring vibration, bending of Sn-O and torsional mode of SnO₃ unit, respectively [29]. The torsional mode (SnO_3) is further observed as a shoulder like feature in the spectrum, positioned at $v_6 \sim 486.8 \text{ cm}^{-1}$ and $v_7 \sim 570 \text{ cm}^{-1}$. Both v_6 and v_7 vibration modes are associated with the stretching and bending motion of Sn-O and O-Sn-O bonds, respectively [37]. The intense mode at $v_8 \sim 653.2 \text{ cm}^{-1}$ is the signature of SnO₆ octahedra, which is the originated from the stretching vibration of the unit. The off-centre displacement of Sn⁴⁺ cation is responsible for net polarization behaviour of the stannate based perovskite system and is evident from the v_8 mode [28, 38].

X-ray photoelectron spectroscopy (XPS) technique was applied to determine the elemental composition and oxidation states of manganese stannate system. Figure 4A exhibits the survey spectrum that confirm the presence of C, N, Mn, Sn and O elements. The presence of C and N originated from hexamethylenediamine, acted as stabilizer. Figure 4A, inset, shows the high-resolution C1s and N1s spectra. The C1s spectrum, after deconvolution, displays the main peak at 285.3 eV, assigned for C-C bond (pink area) and the green area with a peak positioned at 286.2 eV corresponds to C-N bond. For N 1 s spectra, the peak at 399.5 eV is associated with the nitrogen from -NH₂ group of hexamethylenediamine. Figure 4B, displays high resolution XPS-spectrum of deconvoluted Mn 2p with the spin-orbit splitting components $2p_{1/2}$ and 2p_{3/2}, positioned at 653.7 eV and 642.2 eV, respectively, with a shake-up peak at 645.30 eV, associated with the Mn^{2+} oxidation state [39–41]. The oxidation state of Mn cation is more accurately identified by the Mn 3 s spectrum, Fig. 4C. It was reported that the exchange interaction between the core-level 3 s electron and the unpaired electrons in the 3d valence band causes a separation in the binding energy (ΔE) of Mn 3 s spectra [41]. The present spectra of Mn-3 s exhibit two well defined peaks positioned at 89.8 eV and 84.0 eV with a separation of binding energy $\Delta E \sim 5.8$ eV, confirmed the presence of Mn²⁺ oxidation state for the title material. High-resolution Sn 3d spectra, Fig. 4D, shows two characteristic peaks at 495.1 and 486.6 eV corroborate with Sn $3d_{3/2}$ and Sn $3d_{5/2}$, respectively, indicates the presence of Sn⁴⁺ oxidation state. The deconvoluted O 1 s spectra, Fig. 4E, fitted into two Gaussian peaks and the main peak positioned at ~ 529.5 eV (pink colour)



Fig. 4 A The XPS survey spectrum of the MnSnO₃ system. Inset figures show C 1 s and N 1 s spectrum. High resolution deconvoluted spectrum of **B** Mn 2p, **C** Mn 3 s, **D** Sn 3d and **E** O 1 s

contributed from the lattice oxygen, whereas the other diffuse peak ~ 531.3 eV (green colour) is due to the presence of oxygen vacancy in the manganese stannate system [42].

The Temperature (30–100 °C) and frequency (from 100 Hz to 1 MHz) dependent dielectric performances of manganese stannate (MSO) was measured in the form of a device. The real part of the dielectric constant (ϵ') under different temperature condition is shown in the Fig. 5A. At 30 °C the device shows dielectric constant (ϵ') ~ 330 and achieved a maximum value of (ϵ') ~ 3445 at 100 °C, under the frequency condition of 100 Hz. It is evident from the figure that the ϵ' value decreases with increasing frequency. The origin of high dielectric constant was due to the contribution

Fig. 5 A Real part of dielectric constant (ε') versus frequency curves, recorded under different temperature conditions, from 30 to 100 °C. B The variation of tan (δ) curves as a function of temperatures. C Arrhenius fitting of activation energy, extracted from the peak position of tan (δ) curves. **D** Linear variation of ε'' curves on log-log scale and E fitted slope 'm' value and the corresponding W_{max} with respect to temperature



of space charge polarization and orientation polarization of dipoles within the measured frequency ranges. The organic-inorganic hybrid system was found to generate the structural defects or oxygen vacancies, leading to the creation of trap charges at the interface of the material [19, 43, 44]. For the current device, the trap charges are accumulated near the interface and produced space charge polarization towards low frequency region, resulted high value of dielectric constant (below 1 kHz). As the frequency increases, the space charges exhibit limited ability to align with the frequency direction, leading to a decrease in the polarization contribution and consequently resulting in a low value of the dielectric constant. Frequency above 1 kHz, the dielectric property is predominantly depending on orientation polarization of dipoles. Dipolar type of interaction in manganese stannate originated from the SnO₆ and MnO₈ units [45]. Each unit considered as a separate dipole consisting of Mn–O and Sn–O network, Fig. S1B (supporting information). These dipoles are aligned along the external field direction and contributed for the orientation polarization. A relaxation process occurs in these dipoles at a characteristic frequency (f_{max}), which is associated with a peak in the dielectric loss (tan δ) curve, Fig. 5B. With rising temperature, tan δ peaks

are shifted towards higher frequency side (direction of arrow) and the behaviour was associated with a thermally activated process. The peak frequency (f_{max}) as function of temperature (1/T) is plotted and fitted with the Arrhenius equation: $f_{max}^{Me} = f_0 \exp(-E_a/K_bT)$, Fig. 5C. The activation energy value, $E_a \sim 0.13$ eV, suggested the formation of polaronic charges either via long-range or short-range columbic interaction between lattice ions. Similar behaviour has also been reported in other hybrid perovskite systems [46, 47]. The frequency dependent imaginary part of dielectric constant (ε'') under different temperature conditions are plotted in log-log scale, Fig. 5D. The linear behaviour of the curves indicates the polarization process was followed by hopping conduction mechanism [48]. The hopping contribution in the dielectric constant was estimated from the temperature dependent ε'' curves using Giuntini relaxation model [49], $\epsilon m = A\omega^m$, (m < 0), where $m = -4K_BT/W_{max}$. The parameter A is a constant and temperature dependent factor. The exponential factor 'm' denotes the interaction between electrical dipoles, and W_{max} is the maximum barrier height. Figure 5E displays the graphical representation of fitted ε'' curves (for all temperatures) with calculated slope 'm' and W_{max} . The value of '*m*' enhances with rising temperature and maximum barrier height (W_{max}), between the trap states, decreases with increasing temperature.

AC-conductivity (σ_{ac}) of the MSO-based device was measured within the frequency range from 100 Hz to 1 MHz under different temperature conditions (30-100 °C), Fig. 6A, (semi-log scale). The conductivity curves display a change in slope at an intermediate frequency (above 10 kHz), marked by solid line, and separated into two regions, (I) and (II). Towards low frequency region (I), below 10 kHz, a weak plateau like feature followed by a weak frequency dependent behaviour was observed. In region (II), a considerable increase in the conductivity of the device was noticed and reached to a maximum value of $\sigma_{ac} \sim 0.21$ S/m at 100 °C. The overall AC-conductivity behaviour is modelled according to the Jonscher's power law, $\sigma_{ac} = \sigma_0 + A(T)\omega^S$, where σ_0 is the frequency independent conductivity, A is the temperature dependent factor and the parameter 'S' determine the conduction



Fig. 6 A AC-conductivity pattern of MSO-based device at different temperatures from 30 to 60 °C (bottom) and 70–100 °C (top). The curves are fitted according to the Jonscher's power law (red line) for two different region I and II. **B** Variation of S_1 and S_2 parameters with temperature. **C** Activation energy (E_a) plots at 1 kHz and 1 MHz, fitted (red line) according to the Arrhenius relation. **D** Hopping conduction path for large polaron (LP) and vacancy mediated small polaron (SP) inside the Sn–O lattice unit (Color figure online)

mechanism and the value varies in between 0 < s < 1. The parameter S_1 and S_2 were extracted for regions (I) and (II), respectively, using the linear fitting of the Jonscher's law and plotted the values as function of temperature in the Fig. 6B.

Different mechanisms have been proposed to explain the temperature and frequency dependent AC-conductivity of the charge carriers in the materials [50]. For the region (I), the S_1 values were decreased with increasing temperature (between 30 and 70 °C) and then increased with increasing temperature (above 70 °C), such kind of behaviour is associated



Fig. 7 A Electrical impedance (Z) versus frequency curve (loglog scale) at selected temperature (30, 60, 80 and 100 °C). **B** Variation of real (Z') and imaginary part (Z'') of electrical impedance at selected temperature (30 and 100 °C) on a log–log scale. **C** Variation of real (Z') part of the electrical impedance of the device extracted at 30 °C and 100 °C. The solid line (green colour) shows the linearity of curves (Color figure online)





Fig. 8 Main panel shows the Nyquist plots (Z' vs. Z'') at selected temperature (30, 60, 80 °C) and inset (I) for 100 °C. The experimental curves are fitted according to the equivalent circuit model, inset (II)

with the overlapping large polaron tunnelling conduction process [44, 46, 51]. For the region (II), the S_2 values were increased between 30 and 70 °C and then decreased with increasing temperature, above 70 °C, suggested the hopping contribution of small

polaron. The variation of AC conductivity (σ_{ac}) as a function of temperature (1/T) is represented by the Arrhenius relation; $\sigma_{ac}(T) = \sigma_0 \exp(-E_a/K_BT)$, where σ_0 is a pre-exponential factor and E_a is the activation energy of the polaron for the regions (I) and (II). A linear fit of the above equation, $\log \sigma_{ac}$ vs. 1/T, delivers the value of $E_a \sim 0.15 \text{ eV}$ and $E_a \sim 0.12 \text{ eV}$ for two different regions (I) and (II) under the frequency condition of 1 kHz and 1 MHz, respectively, as illustrated in the Fig. 6C. Higher value of E_a for the region (I) is related to the formation of large polaron that migrate over long range distance. With increasing frequency, for region II, the motion is restricted within the localized state. The large polaron (LP) forms predominantly from the distorted SnO₆ octahedra units and the oxygen vacancy-related formation of small polaron (SP) near the Sn–O bond, as illustrated in the Fig. 6D [46].

The electrical impedance (*Z*) of the device under different temperature conditions (30, 60, 80 and 100 °C), are illustrated in the Fig. 7A (log–log scale). The Z value decreases with rising frequency and temperature. The real (*Z'*) and imaginary (*Z''*) part of the electrical impedance for selected temperatures (30 and 100 °C) are plotted in the Fig. 7B. At 30 °C, the linear variation of log (*Z'*) versus log (*f*) with a slope value of ~ – 0.81, over the entire frequency range, was

Fig. 9 A Polarization-electric field (P-E) hysteresis pattern of MSO-based device, measured at 10 Hz. Arrow indicates the increment of P-E loop with applied electric field. Variation of **B** P_{max} and $\mathbf{C} \mathbf{P}_{r}$ and \mathbf{E}_{c} values with respect to the applied field. D Temperature dependent (30-100 °C) P-E loop and **E** the variation of P_{max} , P_{r} and E_c values at 2 kV/mm applied field. F Room temperature polarization stability (P_{max}) of the device under 10³ switching cycles under applied field of 2 kV/mm





Fig. 10 A P-E hysteresis loop performance of the device under repeated cycles (1, 500 and 1000) under ± 2 kV/mm field condition. **B** Electrical breakdown strength (kV/mm) of the device with respect to the time scale (s)

noticed, whereas a plateau like feature was more prominent towards low frequencies at 100 °C, Fig. 7C. Such behaviour in the Z' curve was originated from the contribution of space charges in the device.

Figure 8 exhibited the Nyquist plots (symbol), for selected temperatures (30, 60 80 and 100 °C), that extracted the individual contributions of nanoparticle (grain) and particle interfaces (grain boundary) for the electrical impedance. The device shows wide semi-circular arc at temperatures 30 °C and 60 °C, suggested an overlapping contribution of individual components. The Nyquist plot transformed into two semi-circular arc for the temperature 80 °C, Fig. 9 and for 100 °C, Fig. 9, inset (I). The smaller arc followed by larger arc were originated from nanoparticles and nanoparticles boundary effect, respectively. The experimental Nyquist plot were fitted (solid line) with an equivalent electrical circuit model, Fig. 9, inset (II). The circuit consists of two separate components, $R_g Q_g$ and $R_{gb} Q_{gb}$, connected in parallel

combination. The first component $R_g Q_g$ is related to the nanoparticle whereas, the second R_{gb}Q_{gb} component associated with particle boundary. The parameters R and Q correspond to resistive and capacitive components, respectively, of the MSO-based device. The component Q is considered as constant phase element (CPE) of the electrical circuit and related to the impedance (Z^*) by the relation, $Z^*_{CPE} = 1/(i\omega)^n Q$, where, ω is angular frequency and n is the exponential factor. For an ideal capacitor the value of n = 1, when n < 1 that deviates to non-ideal capacitive element Q [52]. The extracted impedance parameters as listed in Table S2 (supporting information). At higher temperature, both capacitive components (Qg, Qgb) values are increased and the resistive components $(R_g \text{ and } R_{gb})$ values are decreased. The localized conduction of polaronic charges, inside the particle, are more capacitive in nature, which significantly enhanced the Q_g values. The decrease of resistive values in the device with increasing temperature supported the thermally activated conduction process inside particles and the interfaces.

Polarization–electric field (PE) hysteresis loops of the device under various field conditions (1.0, 1.5, 2.0, 2.5 and 3.0 kV/mm) are illustrated in Fig. 9A, at 30 °C. The polarization of the device exhibited a direct relationship with the magnitude of the applied electric field. At the electric field of 3 kV/mm, the maximum polarization (P_{max}) value ~ 1.5 μ C/cm² was achieved, Fig. 9B. The polarization hysteresis behaviour of the device was originated from the dipolar interaction of SnO₆ and MnO₈ polyhedra units. Each polyhedra consist of $Mn^{\delta+}-O^{\delta-}$ and $Sn^{\delta+}-O^{\delta-}$ dipoles, and the response of these dipoles along the field direction contribute to the hysteresis effect for the device. At initial field conditions ($\leq 1.5 \text{ kV/mm}$), the device exhibited unsaturated slim hysteresis loop due to inefficient applied field for dipole orientation. These dipoles retain their initial orientation and exert a restorative force opposing the external field, resulting in a narrow polarization hysteresis curve [53]. A step-like increment in the values of remanent polarization (P_r) and coercive field (E_c) were observed above an applied field of 1.5 kV/mm, Fig. 9C. Such kind of increment was originated due to the gradual increase of interaction of the non-aligned dipoles with strengthening of applied field. Figure 9D illustrates the temperature-dependent (30-100 °C) hysteresis pattern. The formation of oxygen vacancies and the defective dipoles were created in the device

Material type	Synthesis condition	Crystal structure	Dielectric capacitance	Polarization perfor- mance	References
Polycrystalline Ti doped BaSnO ₃ and PbSnO ₃	SSR(HT)	Cubic-BaSnO ₃ tetrago- nal- PbSnO ₃	ε'~40-83	Spontaneous $P \sim 0.4 \ \mu C/cm^2$	[14]
Polycrystalline ZnSnO ₃	SSR (HT/HP)	Rhombohedral	-	Ferroelectric P ~ 59 μ C/ cm ²	[16]
Nano-composite ZnSnO ₃ -polymer	Soft-chemical route	Rhombohedral	-	Dipolar polarization	[18]
Polycrystalline and thin film BaSnO ₃	SSR, MBE route	Cubic, Cubic	ε' ~ 90–120 and ε' ~ 15–17	_	[44, 54]
Polycrystalline Sb- doped BaSnO ₃	Thin film	Orthorhombic		Polarization P~40 μC/ cm ² at 40 kV/mm	[55]
Polycrystalline Er doped SrSnO3 (Sr _{1-x} Er _x SnO _{3-δ})	Sol-gel route	Orthorhombic	$\varepsilon' \sim 10-50$, phase transi- tion	-	[56]
Hybrid Ag ₂ SnO ₃ , and Ag ₂ SnO ₃ -CN nano- particles	Wet-chemical route	Orthorhombic	$\varepsilon'\!\sim\!445$ and $\varepsilon'\!\sim\!780$	$P \sim 0.05 \ \mu C/cm^2$ and $P \sim 0.31 \ \mu C/cm^2$	[19]
Polycrystalline MnSnO ₃	SSR (HP) and (HT)	Hexagonal, and rhom- bohedral	dielectric anomalies, $\varepsilon' \sim 17$ (estimated)	Simulated P~55 μ C/ cm ²	[21, 22, 24]
hybrid MnSnO ₃ nano- particles	WCR, ambient T/P	Orthorhombic	ε' ~ 330 at 30 °C, ε' ~ 3445 at 100 °C	P~1.5 μC/cm ² at 3 kV/ mm	In this work

 Table 1
 The synthesis method, crystal structure and electrical properties of some reported stannate based materials

SSR solid state reaction, WCR wet-chemical route, MBE molecular beam epitaxy, HT high temperature, HP high pressure, T/P temperature/pressure

with rising temperature and that caused the reduction of $P_{max'}$ $P_{r'}$ and E_c values, Fig. 9E. The device maintained a stable P_{max} value of ~ 0.92 μ C/cm² over the repeated switching cycles under the applied field of 2 kV/mm, Fig. 9F. A fatigue free polarization was observed in the device at 30 °C for 10³ cycles under the applied field of 2 kV/mm, Fig. 10A. However, the device showed electrical breakdown at ~ 3.3 kV/mm and sustained the field for a period of 50 s, Fig. 10B. The presence of oxygen vacancies within the lattice potentially contributes to the formation of a conductive pathway, which offers a plausible explanation for the occurrence of electrical breakdown in the device. The synthesis method, crystal structure and electrical properties of some reported stannate based materials are presented in a tabular format (Table 1).

4 Conclusions

Orthorhombic crystal structure of manganese stannate nanoparticles with space group of Pnma has been synthesized by applying an organic-inorganic complexation mediated route. The structure included eightfold coordinated Mn²⁺ cation, surrounded by eight O²⁻ anions and formed MnO₈ polyhedra unit. Each polyhedra unit interconnected through the corner-sharing SnO₆ octahedra with the formation of a cage-like network. Microscopic analysis of manganese stannate particles displayed a cube-like morphology within the size range between 50 and 70 nm. Temperature and frequency dependent dielectric performances of manganese stannate based device exhibited maximum dielectric constant (ϵ') value of ~ 3445 at 100 °C and 100 Hz frequency condition. The high dielectric constant value was originated due to the contribution of space charge polarization and orientation polarization of dipoles within the measured frequency ranges. Temperature and frequency dependent AC-conduction mechanism of the manganese stannate-based device involved both overlapping large polarons and nonoverlapping small polarons. Electric field-dependent of polarization hysteresis loop of the device exhibited the maximum polarization value ~ $1.5 \ \mu C/cm^2$ under the electric field of 3 kV/mm. Under the applied field of 2 kV/mm, the device exhibited a fatigue-free polarization with a maximum value of ~ $0.92 \ \mu C/cm^2$, sustained for 10^3 cycles under ambient temperature condition. The above results demonstrate that manganese stannate nanoparticle based device has the potential as a capacitor in microelectronic applications.

Author contributions

SG investigated the material, writing the original draft and KM conceptualization, writing-review and editing.

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Data availability

Data will be made available on request.

Declarations

Conflict of interest The authors declare no competing financial interest.

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