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Tin Titanate – the hunt for a new ferroelectric perovskite

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Abstract

We review all the published literature and show that there is no experimental evidence for homogeneous tin titanate SnTiO_3 in bulk or thin-film form. Instead a combination of unrelated artefacts are easily misinterpreted. The X-ray Bragg data are contaminated by double scattering from the Si substrate, giving a strong line at the 2-theta angle exactly where perovskite SnTiO_3 should appear. The strong dielectric divergence near 560K is irreversible and arises from oxygen site detrapping, accompanied by Warburg/Randles interfacial anomalies. The small ($4 \mu\text{C}/\text{cm}^2$) apparent ferroelectric hysteresis remains in samples shown to be pure $(\text{Sn,Ti})\text{O}_2$ rutile/cassiterite, in which ferroelectricity is forbidden. Only very recent work reveals real bulk SnTiO_3 , but it possesses an ilmenite-like structure with an elaborate array of stacking faults, not suitable for ferroelectric devices. Unpublished TEM data reveal an inhomogeneous SnO layered structured thin films, related to shell-core structures. The harsh conclusion is that there is a combination of unrelated artefacts masquerading as ferroelectricity in powders and ALD films; and only a trace of a second phase in PLD film data suggests any perovskite content at all. The fact that X-ray, dielectric, and hysteresis data all lead to the wrong conclusion is instructive and reminds us of earlier work on copper calcium titanate (a well-known boundary-layer capacitor).

Key words: Ferroelectric, lead-free, room-temperature, tin titanate.

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Ferroelectrics are technologically and commercially important materials used in a wide range of applications including as capacitors, memories and for applications utilising their piezoelectric and pyroelectric properties. A large proportion of commercial devices use the ubiquitous ferroelectric material lead zirconate titanate (PZT, $\text{PbTi}_{1-x}\text{Zr}_x\text{O}_3$), due to high T_C , large polarisation, etc. Lead titanate and PZT with c.a. > 50 % Ti^{4+} adopts a highly tetragonal ABO_3 perovskite structure below T_C due to the Pb^{2+} lone pair, however, the deleterious effects of lead on the environment and human health have led to the search for lead-free ferroelectrics.

Tin is within the same group of the periodic table as lead, and like Pb^{2+} , Sn^{2+} possesses an electron lone pair. However, while PbTiO_3 and PZT are well known materials, this is not the case with perovskite SnTiO_3 . Conversely, perovskites with tin in a 4+ oxidation state occupying the B site, *e.g.* BaSnO_3 , have been reported since the mid-20th century. [1]

Interest in perovskite SnTiO_3 was renewed due to recent theoretical/computational studies [2-13], many of which predicted that this material would be a stable, lead-free, room-temperature ferroelectric with high switched polarisation (ca. $100 \mu\text{C}/\text{cm}^2$), [5,8,12] capable of replacing PZT for many device applications. There are of course other lead-free room temperature ferroelectrics that might replace PZT for many commercial applications. However, SnTiO_3 is unusually attractive because it is comprised of cheap and relatively safe ingredients in what was expected to be a robust structure, and in particular had a very large theoretical polarisation. In that sense it was, and remains, of great commercial interest, which has therefore led to renewed efforts to synthesize perovskite structured SnTiO_3 in both bulk and film forms [14-20].

Substitution of small amounts of tin into existing perovskite structures is possible although the resulting site occupation appears to differ – *e.g.* in $(\text{Ba,Ca})\text{TiO}_3$, Sn^{2+} primarily occupies the A-site [21], yet in SrTiO_3 compounds occupation of both A- and B-sites is reported [22-25]. This difference may simply be related to the control of the tin oxidation state with the larger Sn^{2+} preferentially occupying the A-site and smaller Sn^{4+} the B-site. Moreover, it is not impossible to form other homogeneous stable Sn^{2+} oxides including tungstates and titanates, as shown by the work on Sn_2TiO_4 [26], SnNb_2O_6 [27], SnTa_2O_6 [28] and SnWO_4 . [29]

Due to the predicated attributes of perovskite structured SnTiO_3 and its potential as a lead free device material, numerous synthetic methodologies have been employed over a number of years with limited success. Traditional solid state synthesis methods, employing high

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3 temperature reactions, have been unsuccessful due to the disproportionation of SnO and
4 oxidation of Sn²⁺ at elevated temperatures. [30] Reports of such solid state reactions are largely
5 absent from the published literature due to this lack of success. The notable exception is a
6 Bachelor's thesis which reports a number of synthetic routes, including solid state and sol-gel
7 reactions, performed under various atmospheres and over a wide range of temperatures.[18]
8 No perovskite structured material was produced, although a rutile structured SnTiO₄
9 [(Sn,Ti)O₂] was formed using aqueous methods and low temperature reactions.

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16 Most recent work has focused primarily on using soft chemistry routes, such as sol-gel or co-
17 precipitation, and thin-film techniques. In this review we examine the current literature
18 reporting experimental studies of SnTiO₃.
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26 **Co-precipitation from chlorides**

27 Conventional solid state methods employing high sintering temperatures typically lead to
28 oxidation/disproportionation of Sn⁴⁺ precursor reagents. Attempts to prevent the oxidation of
29 the Sn²⁺ have included “soft” chemistry preparation routes which typically permit lower
30 sintering temperatures and superior admixing compared with traditional solid state methods.
31 Two papers report attempts to produce samples of SnTiO₃ via a co-precipitation method using
32 SnCl₂ and TiCl₄ as starting materials [14, 15].
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38 The first, [14] refers to “perovskite type tin titanate (SnTiO₃)” in the introduction while
39 discussing its proposed properties, however, while the author discusses “tin titanate” and refers
40 to “SnTiO₃ powders” the structural data reported are sparse. The paper states that “the
41 formation of tin titanate is evidenced by the characteristic peak of tin titanate in the XRD
42 spectrum” and lists the positions of three peaks from a powder X-ray diffraction (PXRD)
43 pattern measured from powders calcined at 850 °C. However, no PXRD database pattern or
44 crystallographic model is referenced and all other structural/crystallographic information is
45 absent – symmetry (space group and point group), lattice parameters, atom positions, etc. are
46 not reported.
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54 The positions of the three peaks (31.8°, 33.5° and 39.8° 2θ) are similar to those of a simulated
55 perovskite tin titanate pattern published in Ref. [19], based on calculations from previous
56 theoretical studies [5, 12]. This would suggest a large tetragonal strain (cell of $a \approx b \approx 3.80$ Å
57 and $c \approx 4.09$ Å from [19]). However, other tin-titanium containing oxides possess PXRD peaks
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3 close to these 2θ positions listed (e.g., simulated PXRD patterns from crystallographic models
4 from the Inorganic Crystal Structure Database (ICSD) - collection codes 161282, 410690,
5 30664 [31-33]). As bulk perovskite structured SnTiO_3 would be a novel and commercially
6 important material, it is difficult to conclude that ref [14] successfully synthesized the material,
7 due to the lack of structural data presented. Additionally, no dielectric or ferroelectric
8 properties were studied.
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14 A subsequent paper by a different group used a similar co-precipitation method [15] and
15 unambiguously describe the resulting compound as perovskite. Greater details of structural
16 studies are provided, however, the paper is somewhat contradictory; they describe the
17 formation of a new phase and list PXRD peak positions ($21.62, 29.01, 33.4, 34.8, 37.8, 49.09,$
18 50.96 and $59.8^\circ = 2\theta$) cited from an abstract of a master's thesis from which the peak positions
19 were obtained. [34] The thesis abstract, (which appears to be available only via a dissertation
20 publishing site) states that the PXRD peaks of their material, obtained from a different synthetic
21 route, was difficult to match to a Powder Diffraction File card (a reference pattern from
22 database). The authors of Ref [15] then cite Ref [14] when describing their PXRD data as
23 having "characteristic perovskite (*sic*) structural values", however, other than the peak at 33.4°
24 the other two values from Ref. [14] do not match those listed above. Furthermore, there are
25 several issues with the accompanying PXRD pattern: there is a greater number of peaks than
26 those listed in the text, there appears to be two different sets of peaks with dissimilar peak
27 broadness overlying each other (it is not stated if one set is a reference pattern and information
28 on the symbols over certain peaks is likewise omitted), and the figure image is blurred to an
29 extent that the axis scales are illegible. Therefore, based upon this early work by itself, one
30 cannot definitively conclude that perovskite SnTiO_3 was synthesized.
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47 **SnTiO_3 PLD films**

48 The deposition of materials in the form of thin films has various technological advantages and
49 has additionally enabled materials to be formed which are unstable in the bulk form. As such,
50 much recent work on tin titanate has concentrated on the fabrication of thin films using a
51 number of deposition techniques.
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56 Such films have been deposited using pulsed laser deposition (PLD) on a number of different
57 perovskite structured substrates, with a unit cell close to that of the desired SnTiO_3 phase [16].

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59 One of the disadvantages of film deposition is the usually limited amount of information
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3 obtained using standard laboratory diffraction (i.e. x-ray diffraction, XRD) techniques due to
4 the presence of only a small amount of material which is often orientated such that only a small
5 number of crystallographic planes satisfy diffraction conditions. Typically only a small number
6 of sometimes weak peaks may be observed. As such, only one Bragg peak is observed in their
7 diffraction data, Fig. 1, which in isolation is somewhat inconclusive. However, their electron
8 diffraction data, Figure 2, shows a triclinic cell consistent with an ilmenite SnTiO_3 structure
9 with $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, and lattice dimensions of $a = 5.04 \text{ \AA}$, $b = 5.19 \text{ \AA}$, $c = 14.56 \text{ \AA}$.
10 In discussing why the ilmenite structure is formed the authors of Ref [16] note that, while a
11 number of theoretical studies predict a perovskite SnTiO_3 structure, Ref [35] calculates that the
12 ilmenite structure is more stable in a reducing atmosphere.
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21 The PLD films produced in Ref. [16] do not exhibit any indication of ferroelectricity under
22 measured conditions, however, in reciprocal XRD space maps additional weak lines were
23 detected which do not originate from the substrate or ilmenite phase. The authors of [16]
24 propose that this minor may originate from very small quantities of perovskite, with inferred
25 unit cell of $a = b = 3.76 \text{ \AA}$ and $c = 4.18 \text{ \AA}$, similar to those predicted theoretically for perovskite
26 SnTiO_3 . [12, 16] We note that Ref. [9] conclude that SnTiO_3 is stable in $P4mm$ structure only
27 for $a, b < 3.87 \text{ \AA}$ and distorts to monoclinic $Cm (C1m1)$ for larger lattice constants.
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34 Using a tetragonal perovskite structural model, we have simulated an XRD pattern, Figure 3,
35 of this phase to determine the 2θ positions of the Bragg peaks as they would appear with Cu
36 $K\alpha_1$ radiation. The perovskite structural model used was modified from a PbTiO_3 structure
37 from the Inorganic Crystal Structure Database (collection code 61168, [36]) with space group
38 $P4mm$ as this symmetry has previously been used in computational/theoretical studies of
39 perovskite SnTiO_3 . [2, 37] Pb^{2+} was replaced by Sn^{2+} at the A-site and the lattice parameters
40 were altered to those reported from the PLD film [16] – no other changes were made e.g. to
41 atom positions. The three peak positions reported in the chloride synthesis work [14] discussed
42 above, are close to those in the simulated pattern. Oxides of tin and titanium and metallic tin
43 also have peaks close to those three 2θ values and the powder in [14] had been heated to 850
44 $^\circ\text{C}$ at which Sn^{2+} compounds usually decompose/disproportionate [30] Therefore, while this is
45 not enough to conclude that perovskite SnTiO_3 was actually made in Ref [14], it does
46 demonstrate that the values are consistent with the minor perovskite phase present in the PLD
47 films.
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YMnO₃/SnTiO_{3+x} heterostructure PLD films

Later work by another group attempted to stabilise tin titanate by growing PLD films with alternating layers of YMnO₃, to produce YMnO₃/SnTiO_{3+x} composites with varying numbers of layers [19]. These films were deposited on (100), (111) and (110) Nb:SrTiO₃ (Nb:STO) substrates with 2, 4 or 8 layers. XRD peaks from these films, Figure 4, were attributed in the paper to: ilmenite [two layer film deposited on (100) Nb:STO], a mix of perovskite and ilmenite [4 layer films on (100) and (110)], perovskite and an unidentified phase [4 layers on (111)] and perovskite [8 layers on (100)]. As seen in Figure 4, with the exception of a peak at approximately 33° two theta, the presence and appearance of the other peaks assigned to a perovskite structure changes with layer number and substrate orientation and while this may be due to the orientation of the film (or strain etc.), the authors do not discuss this or any possible origin. They do note the need for further structural characterisation using TEM and state their intention to carry this out, however, no further papers appear to have been published to date.

P-E data, Fig. 2 in Ref [19], on the 2 layer film (ilmenite XRD) shows a very small measured polarisation of < 0.05 $\mu\text{C}/\text{cm}^2$ which would be consistent with the non-polar FeTiO₃ ilmenite structure they assign and with the linear P-E response (*i.e.* not ferroelectric) obtained from the principally ilmenite PLD film discussed earlier [16]. For films with four or more layers they measure a larger polarisation but somewhat lossy P-E loops and state that “contributions to the hysteresis loop from movable charges was significant” in certain films. Charge injection is one of a number of artefacts found in bulk and thin films which may obscure the true properties of a material. [38-41] PFM data also indicates possible switching, however, as seen later in recent PFM work on ALD films, possible charging effects may be misleading. Without PUND or TEM measurements and additional PFM experiments, some ambiguity remains. Additionally, the contribution from the intrinsic magnetic and ferroelectric properties of the YMnO₃ layers or from interfacial effects is unclear making it difficult to establish the properties of the SnTiO_{3+x} components of the film structure.

ALD films

Atomic layer deposition (ALD) was used by the authors of ref [42] to obtain films with the aim of producing perovskite structured SnTiO₃. Using titanium and tin precursors, TDEAT and Sn(acac)₂, films of tin titanate (SnTiO_x) were deposited on Si(100) substrates. This synthesis method typically uses lower reaction temperatures and allows better control of oxidation states

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3 and composition through the variation of the annealing conditions of the deposited film [43-
4 46]. Deposited films were annealed under different atmospheres (O_2 , N_2 and H_2) at 350 and
5 650 °C for 5 mins. Using grazing incident angle X-ray diffraction (GIXRD) they found anatase
6 appeared to be the major phase present on both as-deposited and annealed films. This was based
7 on assigning two broad peaks at c.a. 55 degrees 2θ to the 105 and 211 reflections from the
8 anatase structure. However, piezoelectric switching hysteresis loops were demonstrated on
9 films annealed at 350 °C under O_2 , [42,43] which led to additional studies on the film [17],
10 including polarisation-electric field (P-E) and dielectric measurements as well as further PXR
11 data.

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Polarisation-electric field (P-E) measurements yielded hysteresis loops with a remanent
polarisation of $3\mu C/cm^2$ at room temperature and further PUND data was used to determine
the existence of switched polarisation in the film [17]. The latter measurement uses a different
pulse sequence from typical dynamic P-E measurements, consisting of two successive
electrical pulses of the same polarity. Assuming the ferroelectric material is switched during
the initial pulse, the second pulse should have no contribution originating from the switching
of ferroelectric domains and therefore reveal contributions from extrinsic sources such as
leakage current. [47] This is, however, not always the case due to e.g. relaxation. Dielectric
data on this film showed a frequency dependent peak with $T_m \approx 450 - 600$ K, as shown in
Fig3(a) of Ref [17].

Additional peaks were observed in XRD, although the data are somewhat complicated by the
presence of a nominally forbidden Si(200) peak overlying a peak at $33^\circ 2\theta$ which was attributed
to the film. This substrate peak is basis-forbidden but may be present in diffraction patterns
due to multiple (double) diffraction (a process also known as Umweganregung) [48, 49]. Bragg
peaks in XRD patterns originate from the diffraction of incident X-rays from lattice planes of
a crystalline material. In the case where nominally forbidden Bragg peaks are observed due to
multiple diffraction, the incident X-rays have previously diffracted from a lattice plane rather
than originating directly from the X-ray source. The forbidden peak may have variable intensity
and exhibit shoulders and sub-peaks at approximately $33 \pm 2.5^\circ = 2\theta$, as shown in Figure 1 of
Ref [48]. PXR patterns of the substrate lack any such shoulder, Figure 5.

It has previously been demonstrated that when measured on PXR diffractometers operating
in Bragg-Brentano geometry, the intensity of this forbidden peak varies with Φ , the angle
normal to the plane surface of the sample [49]. On such diffractometers it is common to spin

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3 the sample within this axis to improve the quality of the data collected, which leads to an
4 averaging of the diffraction from all Φ angles. New data, Figure 5, on one of the ALD films
5 were collected during which the sample was not spun, and as can be seen both the sharp
6 forbidden Si peak and that assigned to the perovskite film, are absent. A peak at high angle
7 (c.a. $117^\circ = 2\theta$) also coincides with a possible Si peak, leaving only the peak around $55^\circ = 2\theta$
8 which consistently occurs in conventional XRD and GIXRD; therefore the structure of the film
9 as determined by X-ray diffraction is somewhat ambiguous. Hence, despite significant
10 improvements over the earlier data from bulk powder samples, the XRD results are by
11 themselves inconclusive.
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22 AFM/PFM has thus far failed to reveal any ferroelectric domains in these samples or in the
23 ALD films studied previously. There are several possible reasons: (a) Any domains are
24 expected to be very small (<30 nm), since the grains are very small, where previously
25 measured; (b) the samples almost certainly are heterogeneous, and the outermost surface layer
26 is ca. 15 nm thick, according to TEM; (c) the surfaces do not appear to be extremely clean, and
27 attempts to clean them may destroy the films. Strong surface charging of half-surfaces occurs,
28 Figure 6; however, as no domains are visible, this may just be surface charging of the whole
29 sample.
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36 To ascertain if charge writing is being observed electrical force microscopy was performed.
37 Two surface areas of the ALD films (indicated by boxes in Figure 6) with opposite polarities
38 were written and then electrical force microscopy performed to probe surface charging. EFM
39 signal is usually indicative of charge being injected into surfaces for a myriad of reasons. As
40 seen in Fig. 6, the signature of charge writing in the written boxes is evident. This signature
41 stays for a few scans meaning it could explain the signal decay seen in piezoresponse images,
42 Fig. 7. This does not rule out ferroelectricity completely but does explain the lack of retention
43 of the written states.
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53 Sol-gel

54 In an attempt to reconcile some of the results discussed above, a sol-gel method was used to
55 produce tin titanate (SnTiO_x) nanoparticles. The two precursors were initially dissolved in
56 solvent; tin acetate in methanol and titanium (IV) isopropoxide in a 1:1 ratio of glacial acetic
57 acid and 2-methoxy ethanol. These were combined and stirred for half an hour and the resulting
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3 solution heated at 250 °C on a hot-plate for 24 hrs. The obtained nanoparticles were calcined
4 at 550 °C for 4 hrs. Circular pellets, with diameter and thickness of 10 mm and 0.650 mm
5 respectively, were pressed and sintered at 550 °C for 4 hrs. In order to carry out the electrical
6 measurements electrodes of an In-Ga alloy were applied to the circular faces of the pellet.
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10 PXRD data are shown in Figure 8. Bragg peaks exhibit extensive broadening, likely size-
11 broadening due to the small size of the crystallites (determined to be c.a. 8-10 nm from TEM).
12 Peak positions are consistent with a rutile structure and Rietveld refinement using a rutile
13 structural model (Inorganic Crystal Structure Database, ICSD, collection code – 161282)
14 accounts for all peaks and gives a reasonably good fit (goodness of fit parameters $\chi^2 = 1.4$, R_{wp}
15 = 0.129, $R(F2) = 0.12$). The crystallographic model used originated from ref [50] and is a
16 tetragonal rutile structure, space group $P4_2/mnm$, with composition $Sn_{0.39}Ti_{0.61}O_2$. Unit cell
17 dimensions of $a = b = 4.67 \text{ \AA}$ $c = 3.08 \text{ \AA}$ were obtained from refinement of the PXRD data.
18 These values are somewhat intermediate of those of rutile structured TiO_2 and SnO_2
19 (cassiterite), [51] which is unsurprising as Sn^{4+} is larger than Ti^{4+} [52].
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28 It should be noted that PXRD is a bulk technique which obtains the spatially averaged structure
29 and that Ti-Sn segregation can occur [53]. SEM and TEM data, Figures 9 and 10 show nano-
30 crystallites with homogenous morphology. SEM/EDAX gives a 1.1:1 Sn:Ti ratio. This ratio is
31 consistent with both rutile and perovskite structures. HRTEM data also gives 110 planes with
32 d-spacing of 0.33 nm.
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37 Raman spectroscopy was performed on the surface of pellets. The odd-parity zone-centre
38 vibrations in the cubic phase have been calculated as []: TO(1), soft (imaginary frequency);
39 LO(1), 80 cm^{-1} ; TO(2), 126 cm^{-1} ; LO(2), 375 cm^{-1} ; TO(3), 505, cm^{-1} ; and LO(3), 689 cm^{-1} .
40 A few experimental values have been reported [7] for wave numbers above 400 cm^{-1} , but they
41 are not in close agreement with predictions, with phonons at 455 cm^{-1} , 619 cm^{-1} , and slightly
42 less than 800 cm^{-1} . As expected, these are close to those in rutile TiO_2 or rutile-structure
43 cassiterite SnO_2 (the latter at 474, 632, and 774 cm^{-1}). [,]
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50 Raman data were obtained for the ambient temperature phase in the present work (Table 1 and
51 Fig. 11) but symmetries are uncertain. Even if there were comparable amounts of rutile-
52 structure and perovskite, the Raman spectra of the latter would be much weaker because in the
53 cubic perovskite phase first-order Raman scattering is forbidden (all ions at inversion centres);
54 so the spectra might be dominated by cassiterite/rutile.
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Table 1. Phonon frequencies in tin titanate

Calculated (present work)	Symmetry phase	Experiment	LO Cubic SnO ₂	Rutile TiO ₂	Cassiterite cm ⁻¹
90	E(TO)	100			
134	E(LO)	140	80	143 B _{1g}	123 B _{1g}
218	E(TO)	---			
230	E(LO)	---			
232	A ₁ (TO)	---			
243	A ₁ (LO)	248			
319	E(TO)	---			
399	A ₁ (TO)	---			
448	E(LO)	442	375	443 E _g	474 E _g
462	A ₁ (LO)	---			
530	E(TO)	---			
633	E(LO)	628		610 A _{1g}	632 A _{1g}
704	A ₁ (TO)	---			
820	A ₁ (LO)	798	689	844 B _{2g}	774 B _{2g}

Dielectric measurements as a function of temperature are presented in Fig. 12. Frequency-dependent features in both the relative permittivity and normalised loss, $\tan \delta$, occur at similar temperatures to that of the dielectric peak observed in the ALD film [17]. However, these features are only observed on heating – they are largely absent on cooling, Fig. 12(c) and (d) and during further heating and cooling cycles. The samples were sintered at 550 °C for 4 hours and so the observed behaviour is unlikely to originate from a transformation to a new phase.

Unfortunately, it is well established that non-ferroelectric materials deposited onto semiconducting or metal blocking electrodes can sometimes produce large dielectric peaks in the 200-500 C temperature regime which typically exhibit a frequency dependence [54]. Replacement of the Schottky electrodes Ag or Au with more ohmic contacts such as In-Ga also provides discrimination between intrinsic dielectric peaks and electrode contributions.

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3 Non-ferroelectric (Sn,Ti)O₂ compounds, which have been studied for use as a potential device
4 material for gas sensors and varistors, also display complex conductivity and dielectric
5 properties.[55] These issues include: the existence of non-ohmic grain boundaries in transition
6 metal doped SnO₂,[56] immiscibility of tin/titanium, [55], reported different conduction
7 processes - band conduction in SnO₂ and hopping in TiO₂ [57] and differences in conduction
8 with thermal cycling. [58]
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12 Impedance data is also similarly complex - the impedance complex plane (Cole-Cole) plot
13 measured at 475 K shown in Figure 13 gives what appears to be a semi-circle and a low
14 frequency tail, indicative of a Warburg element [59, 60]. This resembles the response obtained
15 from a Randles circuit, an equivalent circuit which is often used to model processes at interfaces
16 [59, 60]. Not only is it extremely linear over a long range, but it makes the required angle of
17 45 degrees (gradient of slope is 1.00, Figure 14). Equivalent circuit models should not be
18 derived from single data sets as it is often the case that other electroactive regions within the
19 sample simply do not contribute to the data at that specific temperature (*i.e.* their time constant
20 is outside the spectroscopic measuring window). With increasing temperature the low
21 frequency tail becomes non-linear before forming an additional semi-circle. The higher
22 frequency section of this new feature is still somewhat linear initially (Figure 14) – it is
23 therefore difficult to determine if the ‘tail’ represents true diffusion, as Warburg elements are
24 normally interpreted, or merely the high frequency response of the other feature moving into
25 the measured frequency range. If it is the former, such linearity has previously been attributed
26 to a change from semi-infinite to finite length diffusion,[59] with the linear region being
27 described as the “transition region”. [60]
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43 There is also a large and as yet unexplained change in sample resistance of x100. We attribute
44 all these phenomena in dielectric response near T=500K, including the “Warburg” element as
45 due to abrupt emptying of oxygen traps. Artefacts from e.g. the electrode-interface effects and
46 oxygen vacancy de-trapping etc. are common [54], and the observed features in dielectric and
47 impedance data are likely to be extrinsic in origin. The inference of oxygen site depinning is
48 not just an unsupported hypothesis. The reversible surface charging (Fig.6 and 7) reported in
49 the new AFM study of the ALD films (bright metallic with +10 V applied; dark with -10V
50 applied) is compatible with that, as is the lack of domain walls in the AFM images.
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3 Polarisation-electric field (P-E) measurements on the pellets are shown in Figure 15 (a). A
4 linear (albeit slightly leaky) dielectric response is obtained at 100 Hz; with decreasing
5 frequency the loop opens up, however, this is unlikely to be due to ferroelectric switching.
6 These hysteresis loops are reproducible but cannot be intrinsic, since they do not evidence a
7 Curie temperature above which they disappear and are present in specimens that are shown to
8 be pure rutile/cassiterite. They may arise from charge trapped at the electrode-dielectric
9 interface and as discussed previously we suspect they are oxygen traps.

10 PUND data (measurement described previously for ALD films and more generally in Ref [47])
11 of these samples indicate little or no actual switching of polarisation, Fig 15(b). The value of
12 polarisation for successive pairs of pulses (P and U; N and D) are very similar which suggests
13 that the primary switching pulses (P and N) do not contain a contribution from the switching
14 of domains – i.e. that the response is purely extrinsic.

25 26 27 **Bulk SnTiO₃ using soft chemistry**

28 Most recently a bulk form of SnTiO₃ has been successfully produced using a soft chemistry
29 method. [20] To avoid oxidation/disproportionation of Sn²⁺ the authors of Ref [20] used a
30 multi-step metathesis synthesis by first forming a layered K₂Ti₂O₅ compound. This was
31 heated with SnCl₂·2H₂O at 300 °C under vacuum for 24 hours, after which the KCl salt by-
32 product was removed with washing, leaving SnTiO₃. However, this bulk SnTiO₃ powder
33 does not contain perovskite, instead forming an ilmenite-like structure [20] which could not
34 be indexed directly to the conventional ilmenite structure as identified in the previous PLD
35 films.[16] This was due to the highly layered nature of the structure with ilmenite-like slabs
36 separated by van der Waals gaps from the lone pairs of Sn²⁺ and as a result forming multiple
37 stacking orders and twin domains [20]. A combination of a number of polytypes, each
38 modelling different stacking sequences, was required to account for the observed structural
39 data, with electron energy loss spectroscopy and nuclear magnetic resonance data supporting
40 the resulting local structure/symmetry.

41 Despite the structural complexity introduced by the different stacking sequences, the bulk
42 SnTiO₃ obtained by this group shares similarities most with the PLD films produced in Ref
43 [16] – i.e. the major product is ilmenite or an ilmenite-like structure rather than perovskite.
44 The non-layered nature observed in the PLD films may simply be a consequence of the
45 synthesis method. Diehl et al. calculated that the different stacking sequences were
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3 comparable in energy in the bulk form and that, using electron localisation function and
4 density functional theory, the lone pairs of the Sn^{2+} directed the structure. [20] In the PLD
5 films strain, low dimensionality, synthesis temperatures etc. seems to favour the simpler
6 ilmenite structure. Another possible explanation is the role of the layered $\text{K}_2\text{Ti}_2\text{O}_5$ starting
7 material.
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11 12 13 **Conclusions**

14 Perovskite ferroelectric tin titanate has not yet been made in thin films or bulk as single-phase
15 material. It clearly does exist, for example in a minor phase prepared via PLD, and possibly
16 as a single-phase powder via titanium chloride processing. Despite its toxicity, this process
17 should be examined further in laboratories with proper safety facilities.
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21 The electrical data are largely dominated near $T=500\text{K}$ by abrupt emptying of oxygen traps,
22 not a ferroelectric phase transition. AFM shows that these surfaces can be emptied or filled
23 via $+10\text{V}$ and -10V but that domains do not form.
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27 The PUND switching data are in themselves not unambiguous evidence of ferroelectricity.
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29 Several studies suggest highly inhomogeneous products, with nano-phase separation. This
30 may account for differences in published XRD data.
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34 As a Key Issues Review, this report is not intended to be the definitive story, but merely a guide
35 to help new researchers through the literature, which is not all self-consistent.
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41 The synthesis of bulk perovskite SnTiO_3 presents many problems including the thermal
42 stability of the SnO and propensity of Sn^{2+} to oxidation. Additionally, Sn^{4+} in the B-site of
43 perovskites and related structures appears to inhibit ferroelectricity. [61] Preparation routes
44 which preserve (or generate) Sn^{2+} are needed to both produce the perovskite structure and for
45 optimal ferroelectric properties.
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51 Does the extreme difficulty in preparing these tin compounds in the Sn^{2+} valence state make
52 further work unwise? If not, what approaches might be tried next? At present the results
53 show that the products obtained are usually ilmenite or cassiterite/rutile (without mixed
54 phases), depending upon processing parameters. However, some nano-layer results have
55 been found at U. Conn., for which we do not have permission to reproduce. So the
56 production of inhomogeneous layered or core-shell samples might be possible.
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3 We suggest future studies into the soft chemistry synthesis method which produced bulk
4 ilmenite SnTiO_3 in Ref [20], including investigating the possibilities of changing reaction
5 conditions or the potassium intermediate structure to influence the stacking arrangements of
6 ilmenite or favour the formation of perovskite SnTiO_3 . Other synthesis methods may also be
7 worth considering including high pressure and newer cold sintering methods. Work on the
8 densification of tin monoxide, SnO , has recently been reported using cold sintering, [62] and
9 the technique has previously been used to produce PZT and LiFePO_4 . [63] The low
10 temperatures employed may allow the preservation of the Sn^{2+} state, allowing stoichiometric
11 SnTiO_3 to be formed, possibly with the perovskite structure.
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20 Generally speaking, however, this does not look like a thesis project at a typical university
21 now, but instead might require a larger, better-funded industry effort to stabilize Sn^{2+}
22 valences in the presence of oxygen, perhaps involving two-step processes. Thus far, PLD,
23 ALD, and conventional solid state reactions have been emphasized, but more sophisticated
24 deposition techniques might be tried. ALD has the advantage of lower processing
25 temperatures. It is worth keeping in mind that $\text{SrTiO}_3:\text{Si}$ has been successfully prepared in
26 the past via MBE, most recently at modest temperatures [64-67] and earlier work succeeded
27 in producing stable films via an intermediate atomic layer. [68]
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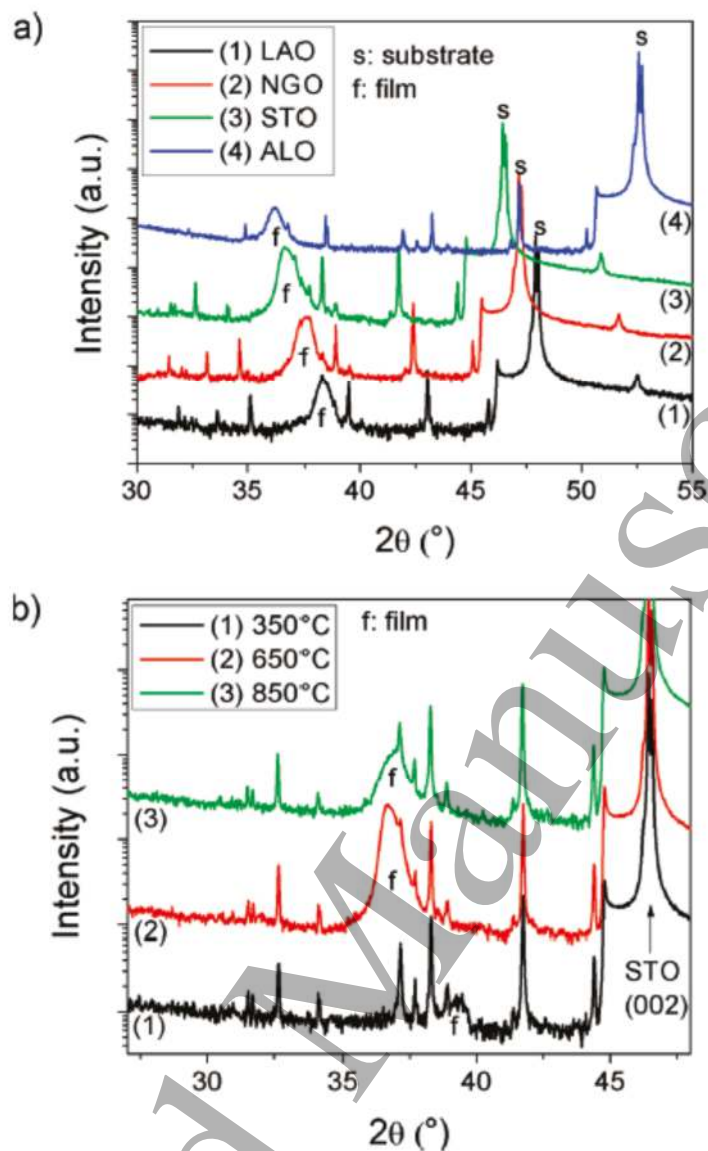


Figure 1: Powder X-ray diffraction patterns of SnTiO_3 films grown by Driscoll et al. showing (a) films deposited on a range of substrates and (b) films deposited on STO (001) at various temperatures. Reprinted with permission from Fix et al. *Cryst. Growth Des.* 2011, 11, 1422. [16] Copyright 2011 American Chemical Society.

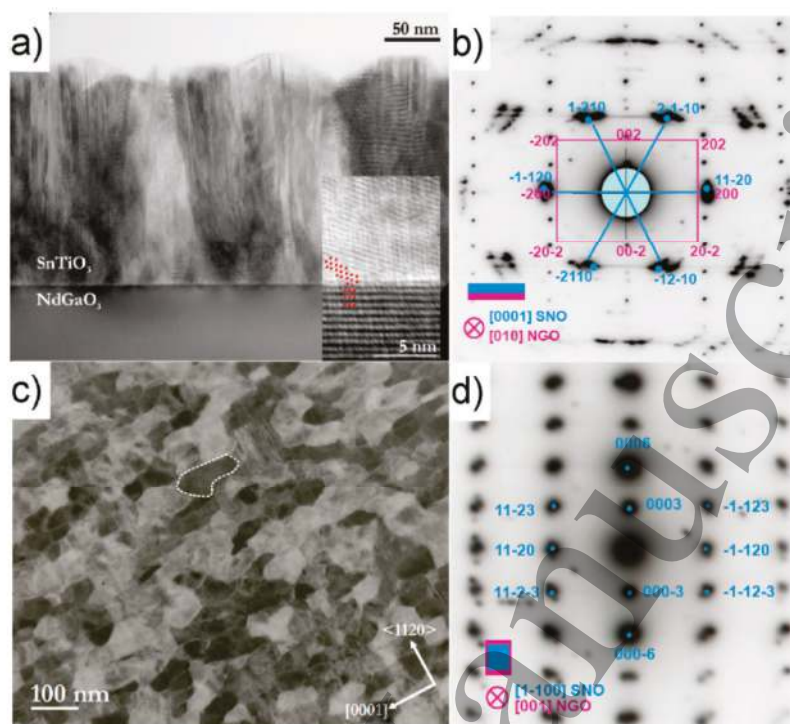


Figure 2: SnTiO_3 films grown by Driscoll et al. showing: (a) HRTEM image of film cross section, (b) diffraction pattern of with NGO [010] zone axis (hexagonal indexing), (c) TEM image (plan-view) of film and (d) diffraction pattern of with NGO [010] zone axis with hexagonal indexing (plan-view). Reprinted with permission from Fix et al. *Cryst. Growth Des.* 2011, 11, 1422. [16] Copyright 2011 American Chemical Society.

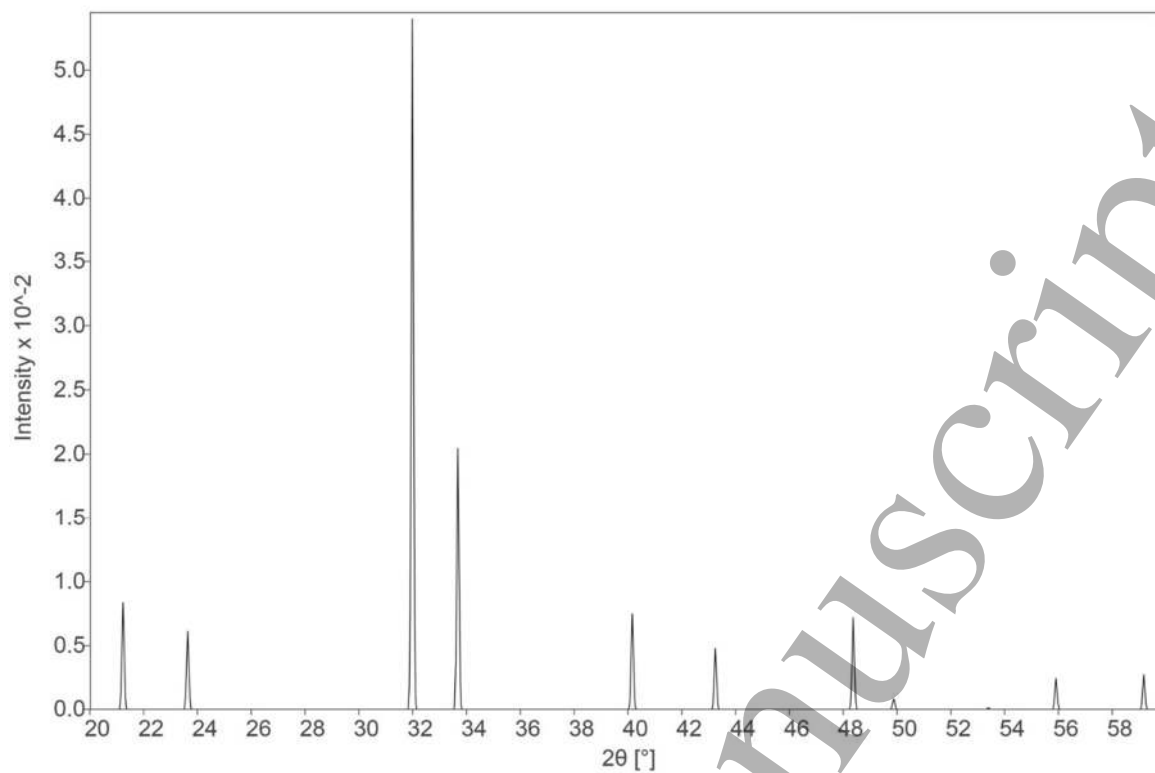


Figure 3: simulated PXRD pattern of perovskite structure (Cu $K\alpha_1$ radiation) using perovskite structural model (space group $P4mm$) and lattice parameters of possible minor perovskite phase from Ref. [16].

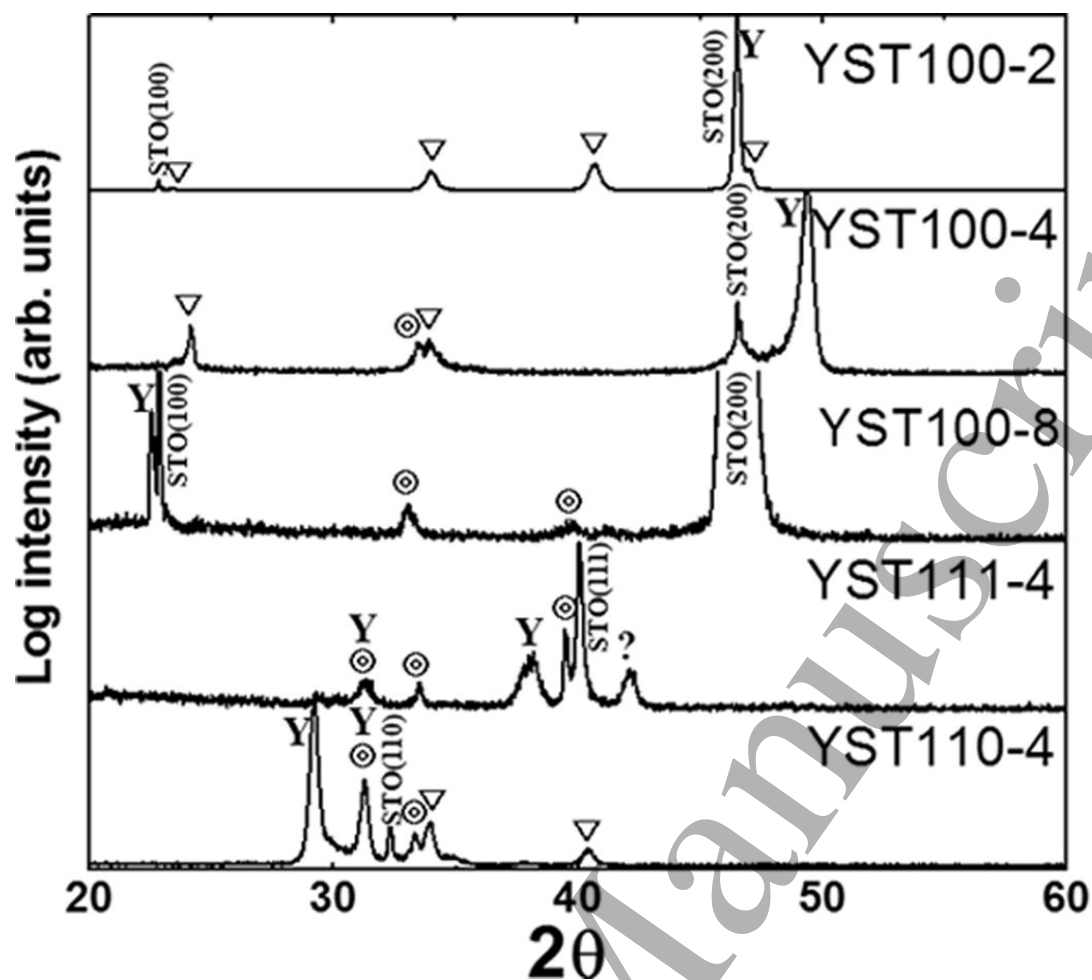


Figure 4: XRD of $\text{YMnO}_3/\text{SnTiO}_{3+x}$ PLD films produced in Ref [19]. Films were deposited on 100, 111 or 110 orientated substrates with 4 or 8 layers - indicated in text on right of figure. Y = YMnO_3 phase, circle = perovskite, and triangle = ilmenite. Reprinted from "A new multiferroic heterostructure of $\text{YMnO}_3/\text{SnTiO}_{3+x}$ ", H Zhao *et al.*, Scripta Materialia 65 (2011) 618, Copyright (2011), with permission from Elsevier and Acta Materialia Inc.

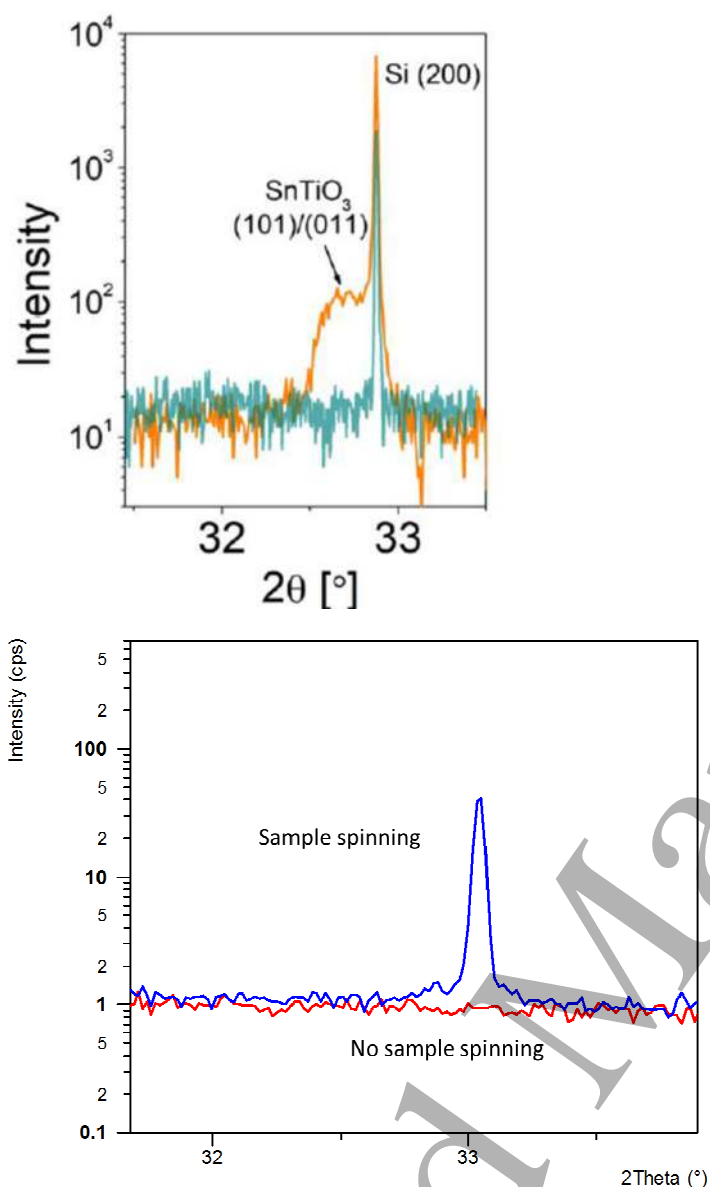


Figure 5: Powder X-ray diffraction patterns of: (a) Si(100) substrate (green) and deposited ALD film on substrate (orange); with the forbidden Si(200) and overlying peak, proposed to originate from perovskite SnTiO₃, indicated (Reproduced from Ref [17], R. Agarwal, et al., Phys. Rev. B 2018, 97, 054109; (b) loss of forbidden Si(200) peak when sample sample is not spun.

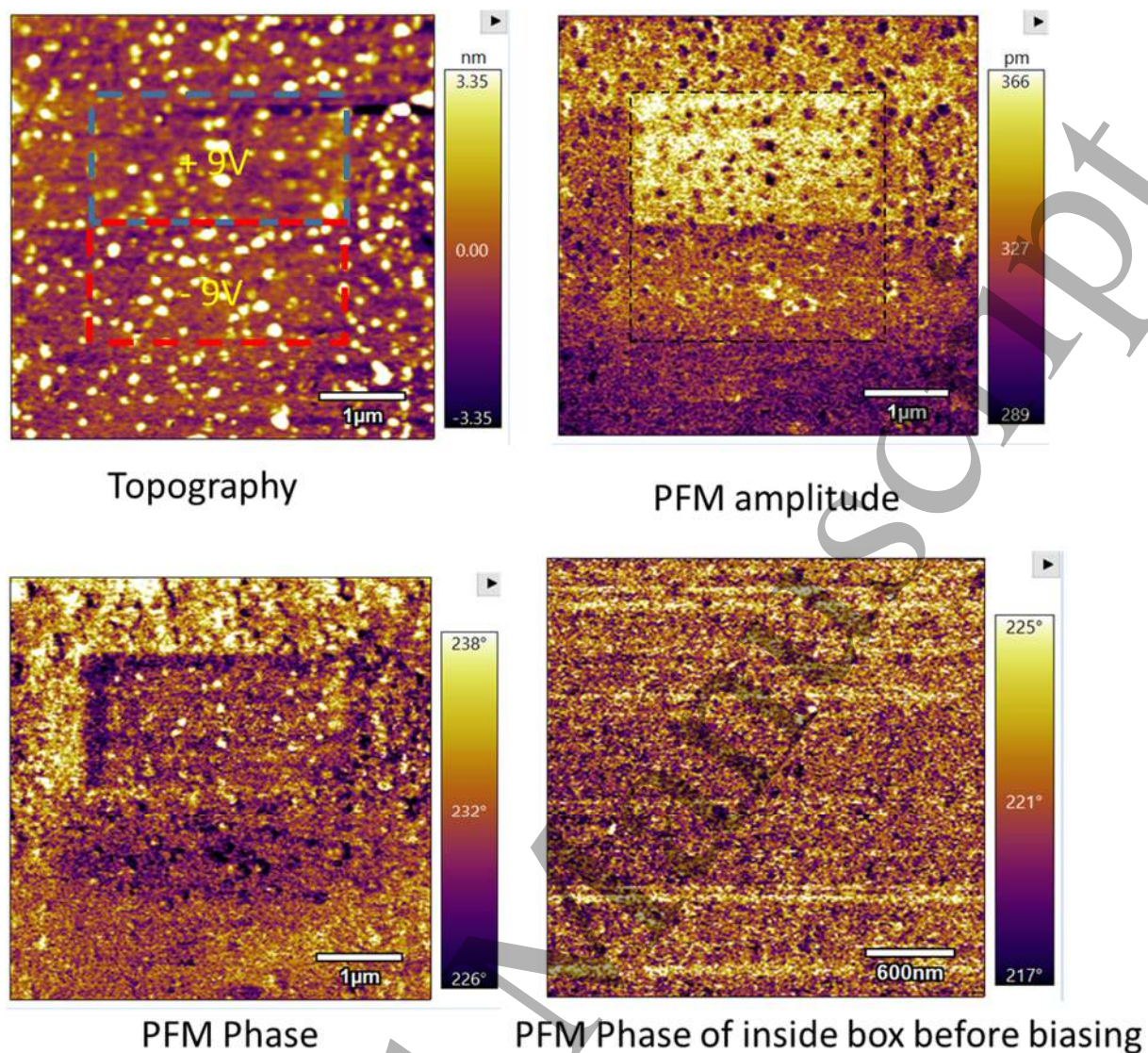


Figure 6: Piezoresponse force microscopy of ALD film. Contrast in phase and amplitude show contrast suggestive of bias writing.

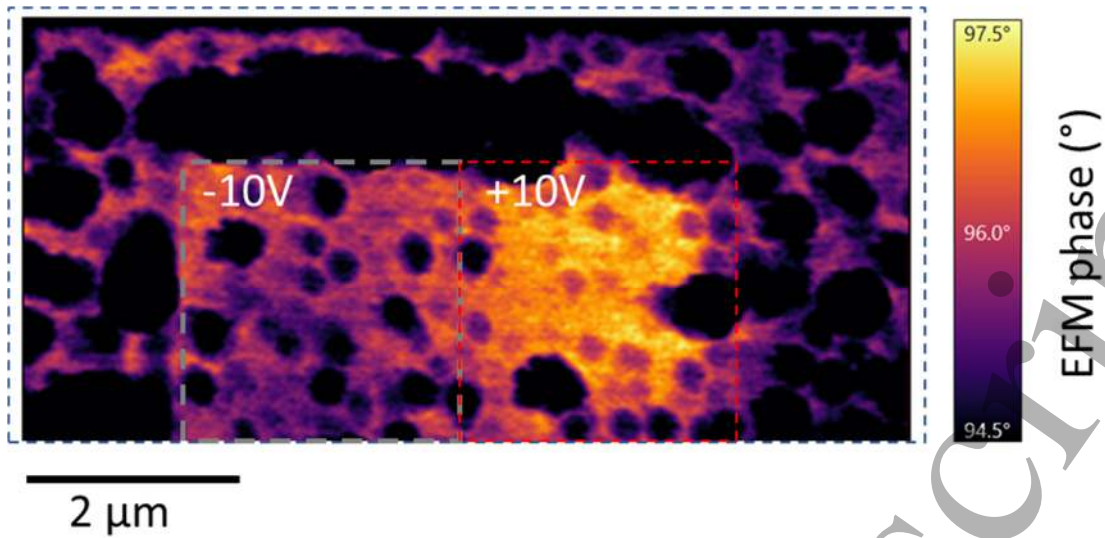


Figure 7: Electrical force microscopy of ALD film.

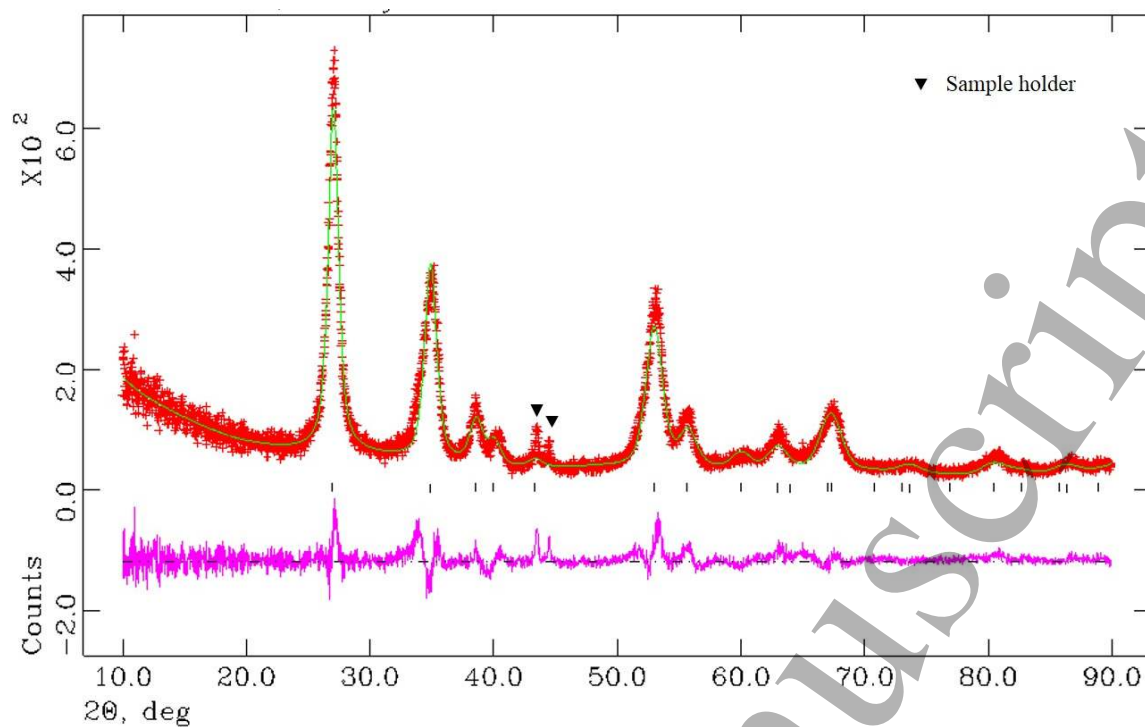


Figure 8: powder x-ray diffraction pattern of new sol-gel tin titanate. Bragg peaks are consistent with the rutile structure. Red crosses indicate observed data, vertical bars indicate reflection positions of rutile structure. The continuous line through the data represents the calculated structure from the Rietveld refinement; difference curve below this.

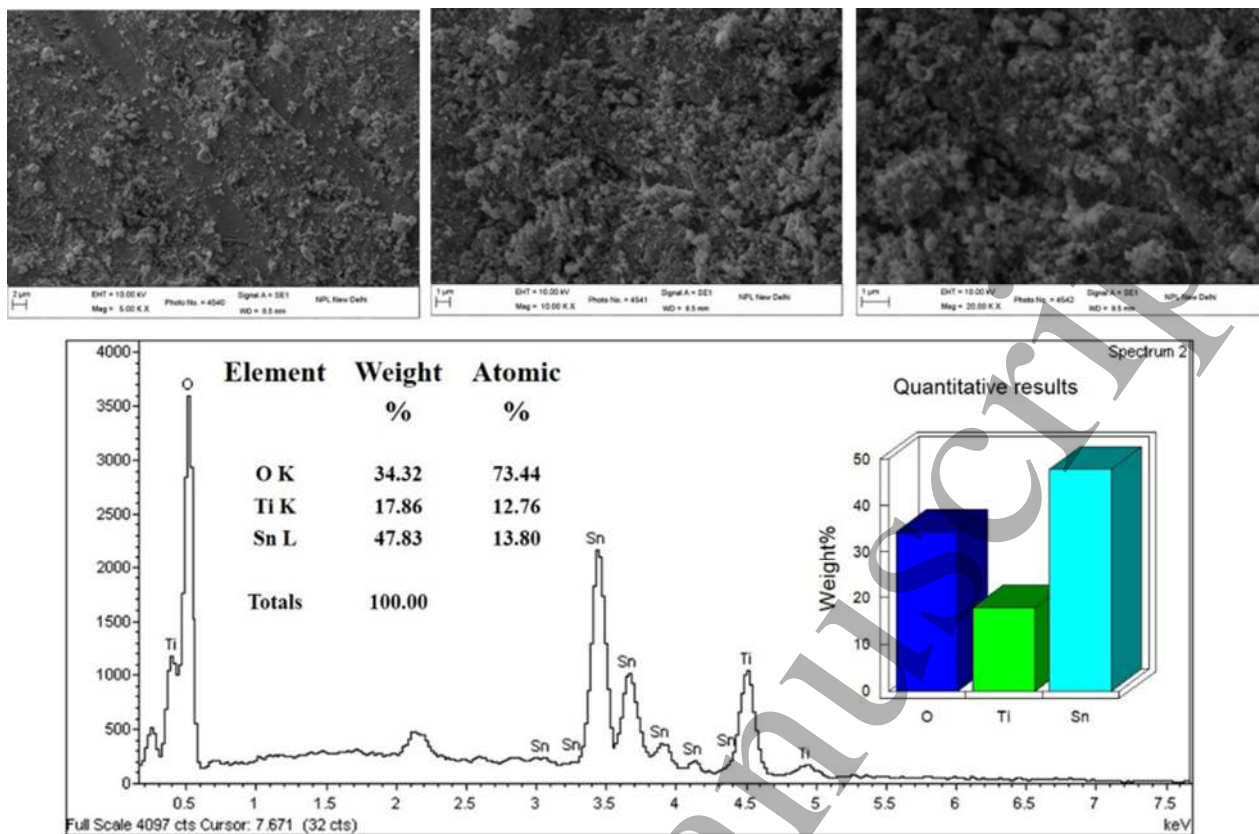


Fig. 9: illustrates the SEM/EDAX data, which demonstrate a 1.1:1 ratio of Sn/Ti in the new sol-gel samples, with 12.8% (atomic) Sn and 13.8% Ti and 73% oxygen.

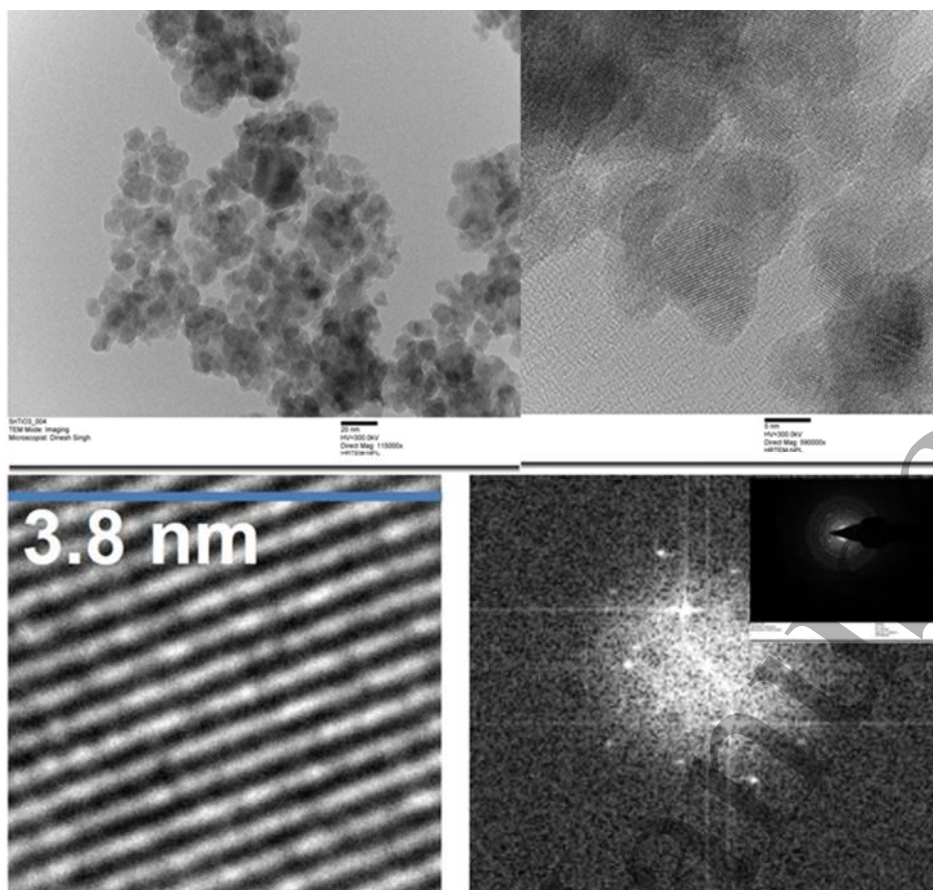


Fig. 10 depicts the high resolution TEM image of SnTiO₃ nanocrystals.

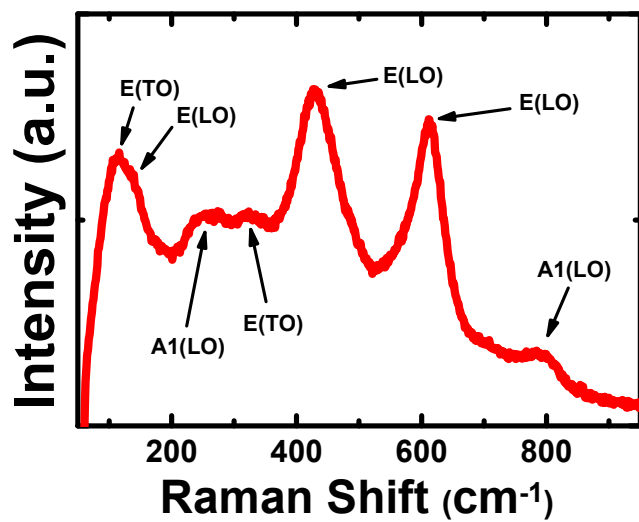


Fig. 11 Raman spectrum of tin titanate sample synthesised via sol gel route.

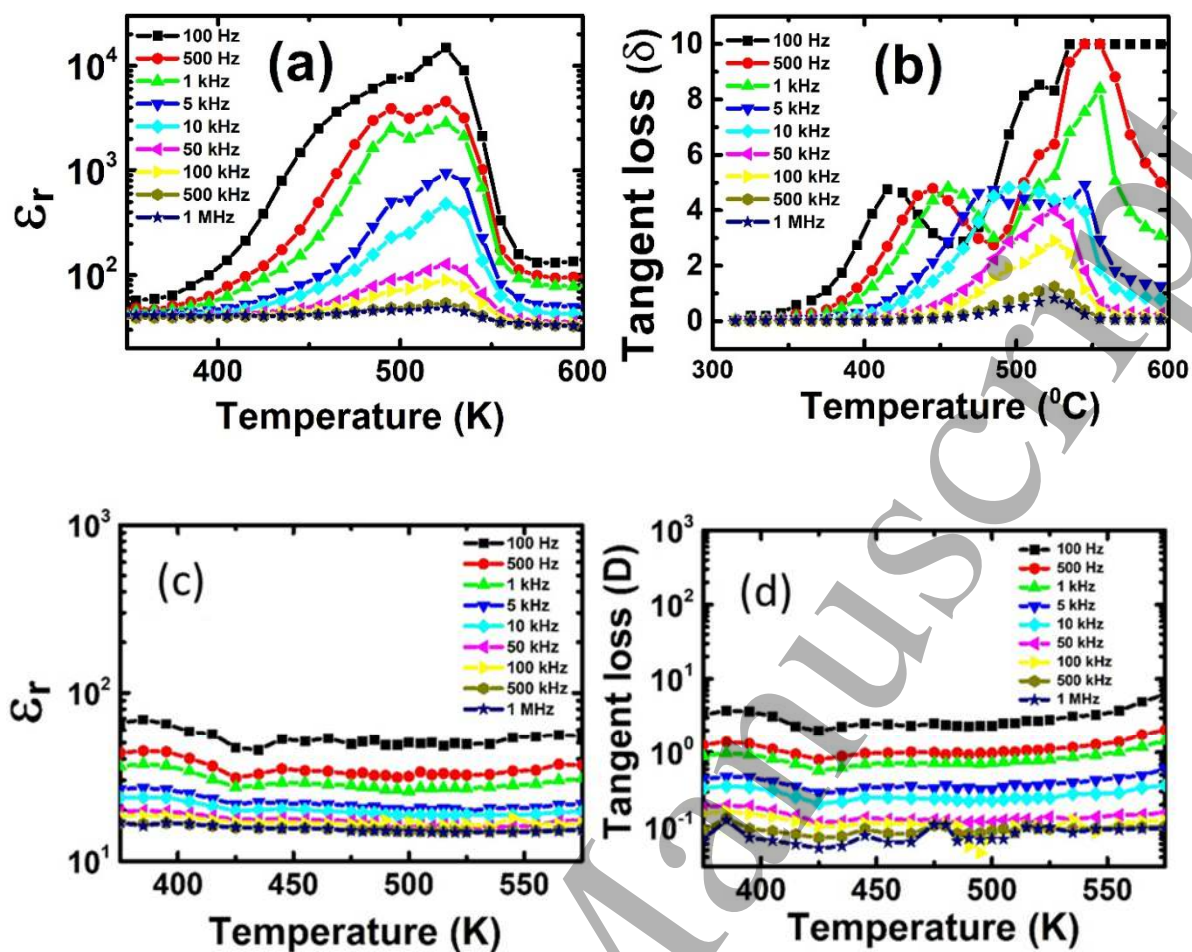


Figure 12: Relative permittivity, ϵ_r and normalised loss, $\tan \delta$, for tin titanate sol-gel pellets with Ag electrodes for: (a) and (b) initial heating and (c) and (d) subsequent cooling showing diminished peak.

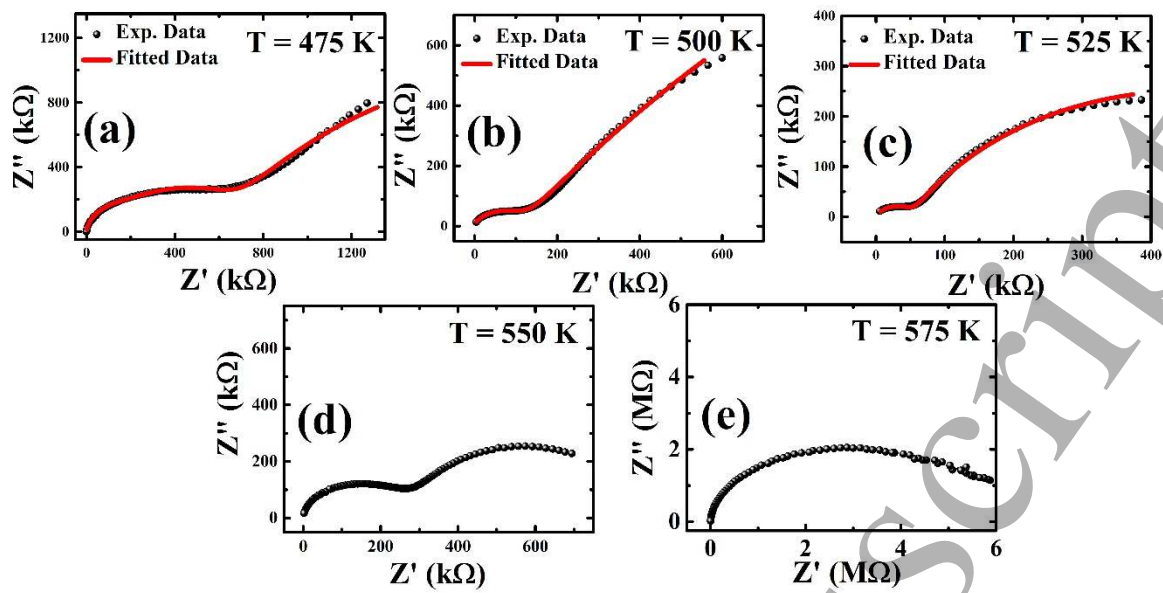


Figure 13: Impedance complex plane plots measured from tin titanate sol gel sample at different temperatures with equivalent electrical circuit model fitting.

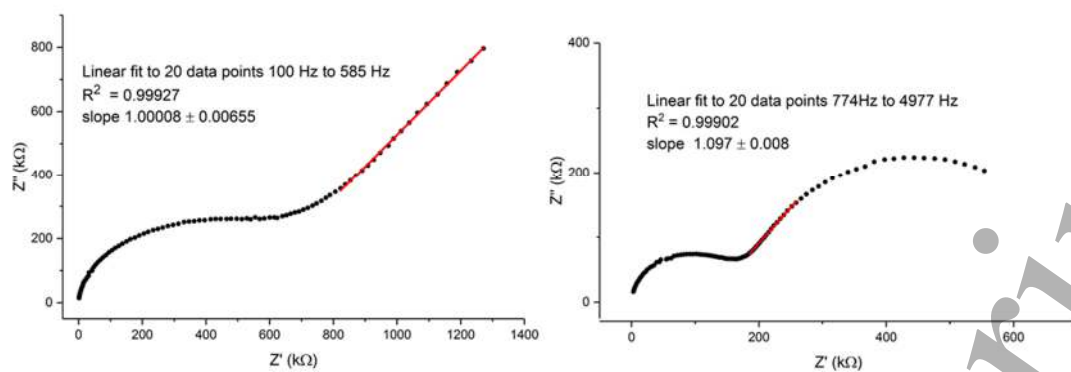


Figure 14: linear fit to low frequency data indicating Warburg element behaviour (gradient of fitted line ≈ 1) at 475 K and (right) apparent linearity present at higher temperatures (gradient of fitted line ≈ 1.1) at 540 K.

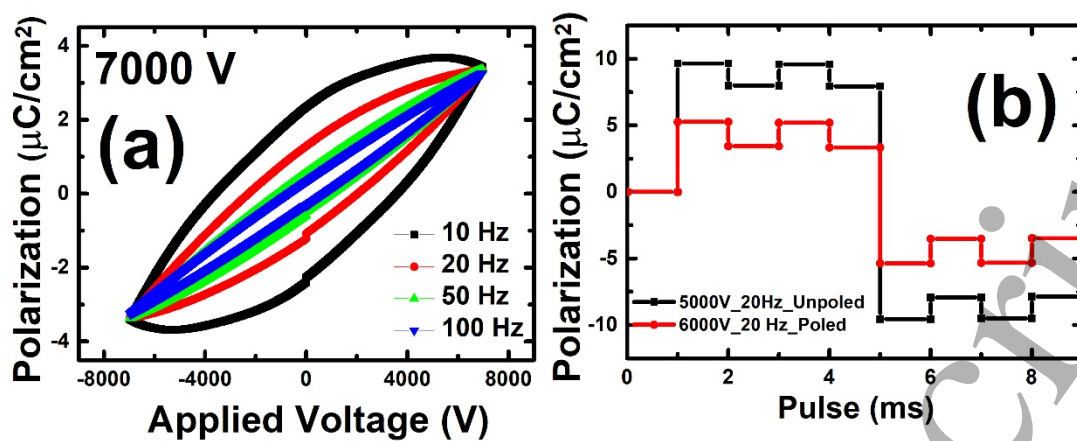


Figure 15: (a) Polarisation vs. applied voltage plot of the tin titanate sol gel sample, (b) PUND data of the bulk sample in unpoled and poled situation.