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WASIM, Muhammad <<http://orcid.org/0009-0009-0442-068X>>, KORDATOS, Evangelos <<http://orcid.org/0000-0002-5448-3883>>, FETEIRA, Antonio <<http://orcid.org/0000-0001-8151-7009>> and STERIANOU, Iasmi <<http://orcid.org/0000-0002-0983-7603>>

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Article

Tailoring the Electric Field Response of Porous BaTiO₃ Ceramics Fabricated via a Sucrose-Assisted Process

Muhammad Wasim , Evangelos Kordatos , Antonio Feteira * and Iasmi Sterianou

School of Engineering and Built Environment, Sheffield Hallam University, Sheffield S1 1WB, UK; m.wasim@shu.ac.uk (M.W.); e.kordatos@shu.ac.uk (E.K.); i.sterianou@shu.ac.uk (I.S.)

* Correspondence: a.feteira@shu.ac.uk

Abstract

Porous BaTiO₃ (BTO) ceramics with controlled porosity were successfully fabricated using a simple and cost-effective sucrose-assisted processing route. Porosity was introduced by incorporating 10–50 vol% sucrose as a pore-forming agent, followed by sintering at 1350 °C for 2 h. The use of sucrose as an effective pore-forming agent is corroborated by the systematic reduction in bulk density from ~5.92 to ~4.1 g.cm⁻³. X-ray diffraction and Raman spectroscopy analysis revealed the retention of the ferroelectric tetragonal phase across all samples, indicating that the introduction of porosity does not alter either the average crystal or local structure. Microstructural analysis demonstrated well-developed grains with heterogeneously distributed and interconnected porosity upon sucrose addition. Electrical characterisation showed a gradual decrease in maximum polarisation ($P_{\max}$) from ~21 $\mu\text{C.cm}^{-2}$ for dense BTO to ~12 $\mu\text{C.cm}^{-2}$ for 50 vol% sucrose samples. With increased porosity, the electric field-induced strain response exhibited a reduction from ~0.137% to 0.10%, but an enhanced large-signal piezoelectric coefficient, d_{33}^* , of ~468 pm.V⁻¹ for the 20 vol% sucrose sample, whereas the 10 vol% counterpart shows the largest ϵ_{RT} of ~1150 with $\tan \delta = 0.005$. These results demonstrate that sucrose-assisted fabrication enables effective porosity engineering in BTO without compromising its ferroelectric nature, offering a promising approach for the development of porous ferroelectric ceramics with tunable electromechanical properties.

Keywords: BaTiO₃; porous; microstructure; polarisation; strain; d_{33}^*

1. Introduction

Ferroelectric ceramics have attracted considerable attention due to their dielectric and electromechanical properties, making them suitable for applications in capacitors, sensors, actuators and energy-harvesting devices [1,2]. Among these materials, barium titanate (BTO) remains one of the most widely studied ferroelectrics [3,4]. Undoped BTO with a tetragonal crystal structure at room temperature shows a maximum field-induced polarisation up to ~25 $\mu\text{C.cm}^{-2}$ and a bipolar strain of ~0.13–0.24% at 30 kV.cm⁻¹, a direct piezoelectric coefficient (d_{33}) of ~180–430 pC.N⁻¹, a large signal (d_{33}^*) of ~255–400 pm.V⁻¹ and relative permittivity (ϵ_r) ranging from 1000 to 6000 depending on grain size [3,5–7]. In doped BTO-based systems, a range of properties have been reported, such as remanent polarisation, P_r , of ~3–56 $\mu\text{C.cm}^{-2}$ [8–10], high electrostrain of ~0.34–0.58% from 50–130 kV.cm⁻¹ and d_{33} of ~178–348 pC.N⁻¹ in BT, BF-BT and BF-BHT systems [9,11–13]. This range of properties is achieved by doping, as well as control of the defect dipoles and crystal structures. The range of properties allows BTO-based materials to be explored in a



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wide variety of applications ranging from electrostatic capacitors to piezocatalysis [14–16]. However, with the increasing demand for lightweight ceramics [17,18] and energy-efficient devices, there is a growing need to tailor the bulk characteristics of such materials without significantly compromising their functional performance [19,20].

Most ferroelectric ceramics show some residual porosity as a processing defect; however, introduction of controlled porosity has emerged as an effective strategy to enhance the piezoelectric voltage coefficient (g_{33}) and energy harvesting performance [21] and to reduce acoustic impedance $Z = (\rho Y)^{0.5}$, where ρ is the density and Y is the Young's Modulus [22]. Hence, porous ferroelectrics are particularly attractive for sensor applications [23]. Often, the incorporation of porosity is accompanied by reduction in ϵ_r , P_r and P_{max} , primarily due to the reduction in active ferroelectric volume and the development of an inhomogeneous electric field distribution throughout the ceramic. The variation in the coercive field with porosity is more complex [19,24,25].

Various processing approaches have been developed to introduce controlled porosity in ferroelectric ceramics. Among the so-called sacrificial approaches, the burn-out of plastic spheres (BURPS method) reported early by Rittenmyer et al. [26] enables large fractions of porosity, though randomly distributed with a wide variety of pore sizes. J. I. Roscow et al. [27] used the BURPS method to fabricate porous BaTiO₃ ceramics with a range of porosities ranging from 10 to 72 vol%, and these ceramics exhibited macro-pores with sizes ranging from 50 to 400 μm , due to not only possible variation in sphere sizes but also their agglomeration. Another sacrificial method reported by Lukacs et al. [28] is suitable for conventional ceramic processing and offers flexibility in the pore morphology (>50%) by varying the type and size of the template, with pore sizes below 15 μm , but the electrical properties are adversely affected, showing a decrease in ϵ_r and P_{max} and high E_c due to the reduction in the active ferroelectric component. However, freeze casting produces aligned anisotropic pore channels, which can be controlled and form an aligned structure. This technique is favourable with a minor effect on dielectric properties; as reported by Roscow et al. [29], undoped BTO and 45% porous have comparable d_{33} of 144.5 and 134.5 pC.N^{-1} , respectively. Cracium et al. [30] reported the use of tape casting for scalable fabrication of thin, multilayered or graded porous ceramics (up to 60% porosity) with a controlled thickness and an increased piezoelectric voltage constant g_h ; furthermore, tape casting is also widely used for fabrication of different types of porosity, as shown in reported work by Nishihora et al. [31], by adjusting particle size, sacrificial pore formers, sintering conditions and combined techniques (phase inversion and freeze casting). Roscow et al. [32] reported the fabrication of “sandwich porosity” between two dense layers of BTO using the BURPS method, where they show an increasing trend of average d_{33} in the range of ~ 43 – 125 pC.N^{-1} and a decreasing trend of average permittivity ϵ_r in the range of 167–1500 as the thickness of the porous layer and the total porosity level of the layered structure increased, with the reduction in permittivity related to the presence of a low permittivity air phase. Aerogel-based processing reported by Khansur et al. [33] produces an open porosity of $\sim 12\%$ on thick films with enhanced relative permittivity and low losses related to the lower extent of internal residual stress. While these methods enable control over pore architecture, they are often associated with increased processing complexity, limited scalability or restricted porosity ranges and, most importantly, high processing costs. In addition, much of the existing work has focused on complex or doped systems [24,34], whereas comparatively fewer studies have addressed porosity engineering in undoped BTO while maintaining its intrinsic ferroelectric characteristics [27,35–37].

In this context, the use of sacrificial pore-forming agents such as sucrose offers a simple, cost-effective and scalable route for introducing controlled porosity. Although sucrose has previously been employed as a pore-forming agent in compositionally modi-

fied BZT–0.5BCT ceramics [24], its application in undoped BaTiO₃ remains comparatively unexplored. Therefore, the present work presents a simple approach to investigate how controlled porosity affects the electrical (ferroelectric and electromechanical) properties of BaTiO₃. In terms of health and environmental effects, sucrose undergoes non-hazardous thermal decomposition and can generate well-distributed pore structures without introducing secondary phases. The reported sucrose decomposition temperature of ~190 °C [38] proved by TGA/DSC makes it more reliable as the densification process of the mostly ceramic material starts after 1000 °C, which allows the complete burning process of sucrose. Although such approaches have been explored in related ferroelectric systems, a systematic understanding of pore shape and how porosity influences the electromechanical response of undoped BTO [27,39], particularly in terms of maintaining or enhancing strain and large-signal piezoelectric behaviour, remains limited [40]. Previous studies have reported contrasting effects of porosity in ceramics. In some cases, increasing porosity reduces the active amount of ceramic material and leads to decreased ferroelectric and electromechanical performance [24,41]. However, other studies suggest that a moderate level of porosity can improve the electromechanical response by altering the local electric field, mechanical constraint and domain switching within the ceramics [21,33,42]. In the present work, porous BTO ceramics with controlled porosity were fabricated using a sucrose-assisted route by conventional sintering. The study focuses on the relationship between porosity, microstructure and functional properties, with particular emphasis on polarisation, strain, large-signal piezoelectric response (d_{33}^*) and dielectric permittivity. Structural analysis confirms that the introduction of porosity does not alter the crystal structure, while the electromechanical response is maintained and, in some cases, slightly enhanced at moderate porosity levels. These findings highlight the potential of porosity engineering as an effective strategy for developing lightweight ferroelectric ceramics with stable electromechanical performance.

2. Materials and Methods

Porous BaTiO₃ (BTO) ceramics were prepared using BTO powder (200 nm; KCM Corporation (Nagoya, Japan)). Controlled porosity was introduced by mixing the BTO powder with sucrose as a sacrificial pore-forming agent at volume fractions of 10, 20, 30, 40 and 50 vol%. The powders were homogenised using a conventional mortar and pestle with isopropanol was used as the mixing medium, followed by drying to remove the solvent. The mixed powders were uniaxially pressed into disc-shaped pellets under an ~125 MPa pressure with a diameter of 10 mm and a thickness of approximately 1.5 mm. The green pellets were sintered at 1350 °C for 2 h in air using a heating and cooling rate of 5 °C.min^{−1} in covered crucible to obtain porous BTO ceramics. The radial shrinkage and bulk density were determined by measuring the diameter and thickness of the sintered pellets, and the weight was measured using a digital scale. Phase purity and crystal structure of the sintered samples were examined using X-ray diffraction (XRD) with Co K α radiation ($\lambda = 1.789 \text{ \AA}$) in the 2θ range of 10–90°. Rietveld refinement of the XRD data was performed using HighScore 4.9 (PANalytical B.V., Almelo, The Netherlands) to determine crystal structure and lattice parameters. Raman spectroscopy was performed using a Thermo Scientific DXR2 Raman microscope (Thermo Fisher Scientific, Madison, WI, USA) equipped with a 532 nm laser to further examine their local structure. Microstructural analysis was carried out using tungsten filament in a scanning electron microscope (FE-SEM, Quanta 650, FEI, Brno, Czech Republic).

For electrical measurements, platinum electrodes were applied by painting on both faces of the polished pellets and heat-treated at 600 °C for 30 min to ensure good electrical contacts. Polarisation–electric field (P–E) hysteresis loops, strain–electric field (S–E) loops and large-signal piezoelectric response (d_{33}^*) were measured at room temperature using a TF

Analyzer-2000E ferroelectric tester (aixACCT Systems GmbH, Aachen, Germany) operated at a frequency of 1 Hz. The large-signal piezoelectric coefficient (d_{33}^*), was determined from unipolar measurement by linear regression from point $N/2$ to below N , where N is the total number of measurement points. In other words, it was calculated for the non-switching branches of the butterfly loop which correspond $V_{\max}$ to below zero. The first point of the displacement loop was set to 0 by definition. Dielectric permittivity was measured at room temperature at a frequency of 100 kHz using an HP 4284A Precision LCR Meter (Agilent Technologies, Santa Clara, CA, USA).

3. Results and Discussion

3.1. Bulk Density and Porosity

The bulk density and corresponding porosity of BTO ceramics as a function of sucrose content are presented in Figure 1a,b, respectively. The BTO sample exhibits a high bulk density of $\sim 5.92 \text{ g.cm}^{-3}$, indicating effective densification under the applied sintering conditions, considering that the theoretical density of BTO is 6.02 g.cm^{-3} . Upon the introduction of sucrose, the reduction in density is not strictly linear at low concentrations. In particular, the sample with 10 vol% sucrose shows only a marginal decrease in bulk density, which may be attributed to the partial role of sucrose in enhancing particle packing or acting as a temporary binder during compaction, as reported in previous studies [43]. Nevertheless, the decomposition of sucrose during heat treatment still leads to the formation of a limited amount of porosity, resulting in a slightly lower density compared to BTO.

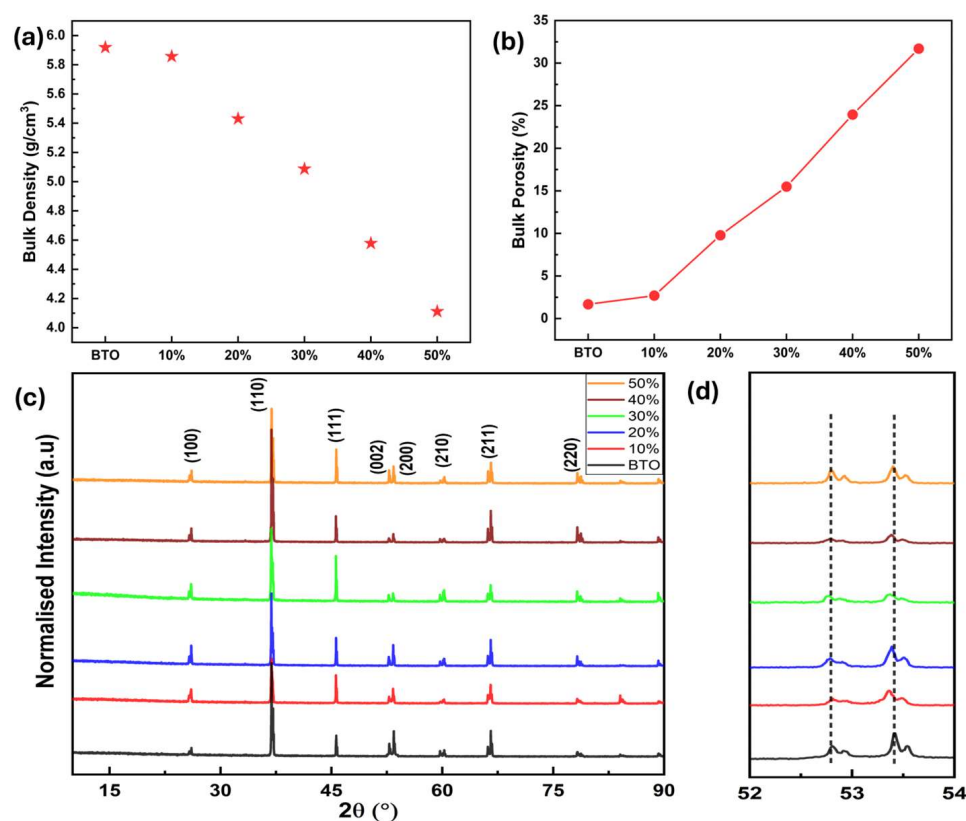


Figure 1. Bulk density (a), bulk porosity (b), and XRD data and a zoomed region of 52 to 54° 2θ (c,d) show the 002 and 200 peaks for BTO and BTO + Sucrose ceramics sintered at 1350 °C, respectively, (d) dashed lines are visual guides for peak positions.

With further increase in sucrose content (20–50 vol%), a clear decreasing trend in bulk density is observed, reaching $\sim 4.1 \text{ g.cm}^{-3}$ for the 50 vol% sample. This behaviour reflects

the dominant effect of pore formation at higher pore-former concentrations, where the increasing volume fraction of decomposed sucrose leads to a more significant reduction in the effective ceramic density. However, as the sucrose content increased to 50 vol%, a significant decrease in density (~30%) was recorded, confirming the effective formation of porosity within the BTO matrix.

The corresponding porosity (P) values, calculated using Equation (1), increased from ~1.7% for dense BTO to ~31.7% for the highest sucrose content.

$$P = \left(1 - \frac{\rho_{BD}}{\rho_{TD}} \right) * 100 \quad (1)$$

where ρ_{TD} is the theoretical density of BTO (6.02 g.cm⁻³) and ρ_{BD} is the measured bulk density obtained using the geometric method.

It is important to note that the measured porosity does not show a direct linear relationship with the initial sucrose volume fraction. This deviation can be attributed to the combined effects of pore formation and sintering-induced densification. During heat treatment, sucrose undergoes thermal decomposition, generating voids that act as pore former. However, at elevated temperatures, partial densification of the ceramic matrix, along with shrinkage and coalescence of pores, reduces the final pore volume relative to the initial sucrose content [17]. As a result, the effective porosity remains lower than the nominal pore-former fraction across all compositions.

3.2. Phase Purity and Crystal Structure

The X-ray diffraction (XRD) patterns of BTO ceramics with varying sucrose content (Figure 1c,d) show a well-defined tetragonal phase with space group P4mm [44,45], consistent with the standard reference pattern (ICDD #01-085-9527) [46]. The clear splitting of the {002}/{200} reflections confirms the presence of the ferroelectric tetragonal structure at room temperature [44]. No additional diffraction peaks corresponding to secondary phases are observed for any sample (0–50 vol% sucrose), indicating that the phase purity is preserved and the tetragonal structure is retained despite the introduction of porosity.

Lattice parameter refinements were performed to further examine possible structural variations, and those are summarized in Supplementary Table S1. The results show that the lattice parameters and unit cell volume exhibit only very minor variations across the compositional range. The tetragonality (c/a ratio) remains close to that of BTO for all samples, with only a slight reduction observed for the 10 vol% composition. Across the full series, the tetragonality (c/a) is 1.0103 ± 0.0002 . Considering the small magnitude of these variations and the associated refinement uncertainty, no systematic trend in lattice distortion is evident.

Overall, these results indicate that the introduction of porosity via the sucrose-assisted route does not induce any detectable phase transformation or significant modification of the crystal structure. Therefore, the changes observed in the dielectric and electromechanical properties are primarily attributed to microstructural effects associated with porosity rather than alterations in the intrinsic crystal structure.

3.3. Raman Spectroscopy Analysis

Raman spectroscopy was employed to further examine the local structure of BTO ceramics with varying sucrose content, and the corresponding spectra are presented in Figure 2a–c. The dense BTO sample exhibits the characteristic Raman-active modes of the tetragonal phase, confirming the presence of long-range ferroelectric order [47,48]. No additional modes associated with secondary phases are observed across all compositions, which is consistent with the XRD results and indicates that the incorporation of porosity

does not alter the phase purity of the material. The prominent Raman modes observed at approximately $\sim 305\text{ cm}^{-1}$ and $\sim 720\text{ cm}^{-1}$ correspond to the $E(\text{TO}_2)$ and $A_1(\text{LO}_2)$ vibrations, respectively, which are well-known signatures of tetragonal BTO. The $E(\text{TO}_2)$ mode is commonly associated with the ferroelectric nature of BTO and is often considered a fingerprint of spontaneous polarisation, while the $A_1(\text{TO}_2)$ mode of Ti-O is sensitive to local lattice vibration and internal strain [49]. A closer inspection of the spectra in the regions of $225\text{--}325\text{ cm}^{-1}$ and $450\text{--}600\text{ cm}^{-1}$, as shown in Figure 2b,c respectively, reveals there are not even minor variations in mode frequency with increasing sucrose content.

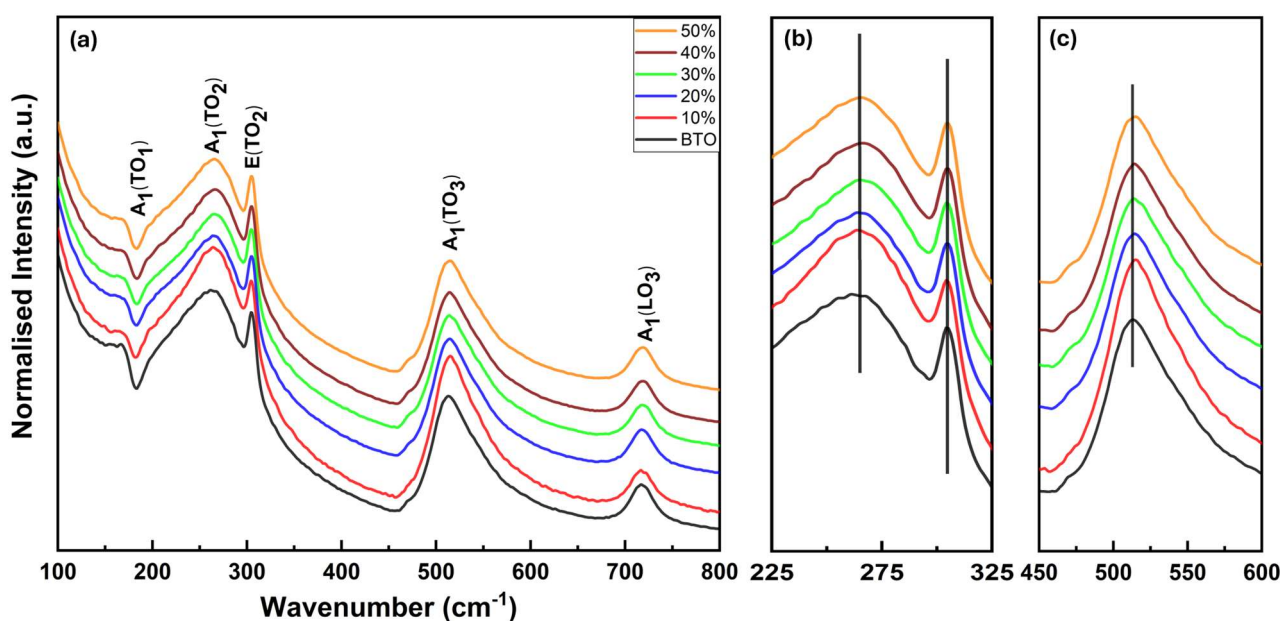


Figure 2. (a) Raman spectra of BTO and BTO + Sucrose ceramics sintered at $1350\text{ }^{\circ}\text{C}$; (b,c) enlarged view of Raman spectra of BTO and BTO + Sucrose ceramics sintered at $1350\text{ }^{\circ}\text{C}$ in the regions of 225 to 325 and 450 to 600 cm^{-1} , respectively; (b,c) vertical lines are visual guides for peak positions.

Overall, the retention of all characteristic Raman modes, along with the absence of any additional features, confirms that the local structure of BTO is preserved without stresses acting on grains of ceramics with different levels of porosity. These results are in good agreement with the XRD analysis, demonstrating that the sucrose-assisted process to create controlled porosity neither affects the crystallographic structure nor creates local lattice distortions [50].

3.4. Microstructure Analysis

The surface morphology of BTO ceramics with varying sucrose content is shown in Figure 3a–f. The BTO sample (Figure 3a) exhibits well-defined, polyhedral grains with an average grain size of $\sim 75\text{--}100\text{ }\mu\text{m}$. The grains are closely packed with well-developed grain boundaries, indicating effective densification and minimal porosity, which is consistent with the bulk density. Furthermore, energy-dispersive X-ray (EDX) analysis (Supplementary Figure S1) confirms, as expected, that the elemental composition remains unchanged with the introduction of porosity, indicating that the sucrose-assisted process does not alter the chemical stoichiometry of the BTO ceramics.

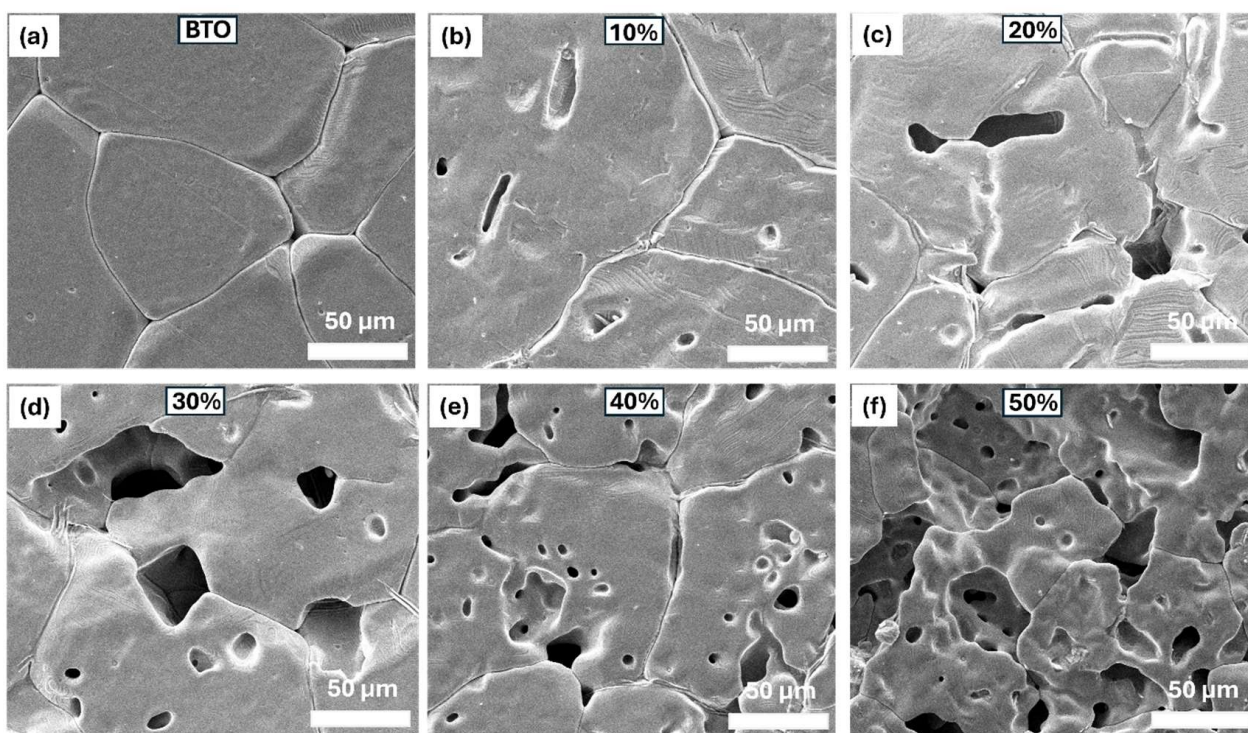


Figure 3. Microstructures of BTO and BTO + Sucrose ceramics sintered at 1350 °C for 2 h: (a) BTO without sucrose; (b) BTO with 10 vol% sucrose; (c) 20 vol% sucrose; (d) 30 vol% sucrose; (e) 40 vol% sucrose; and (f) 50 vol% sucrose.

With the introduction of sucrose (Figure 3b–f), a gradual evolution in microstructure is observed, characterised by the progressive formation and growth of pores. At lower concentrations, pores appear as isolated features within grains and along grain boundaries as shown in Figure 3b,c, while increasing sucrose content leads to a higher pore density and enlargement of pore size. At higher concentrations, the pores become more irregular in shape and more non-uniformly distributed, resulting in the formation of a well-developed porous network across the surface shown in Supplementary Figure S2. The average grain size is around 146 ± 71 , 135 ± 64 and 121 ± 44 for BTO to the 20 vol% sucrose sample, respectively. Precise evaluation of the grain size is difficult for high porosity samples, 30 to 50 vol%, due to the non-homogeneous distribution of the porosity across the grain boundaries, as shown in Supplementary Figure S3.

To further examine the pore connectivity, cross-sectional SEM images are presented in Figure 4 at different magnifications (from ~1 mm to ~0.05 mm in scale). The cross-sectional analysis reveals that the pores are not limited to the surface but are distributed throughout the bulk of the material. At higher magnifications, a clear interconnected pore network can be observed, confirming that the porosity extends across the entire sample. This interconnected structure suggests the formation of continuous pathways within the ceramic matrix, which is consistent with the observed reduction in density and supports the effectiveness of the sucrose-assisted processing route. Importantly, despite the significant increase in porosity, the grains remain well connected across all compositions. This indicates that the ceramic matrix maintains structural continuity even at high porosity levels, which is essential for preserving functional pathways for polarisation and strain response.

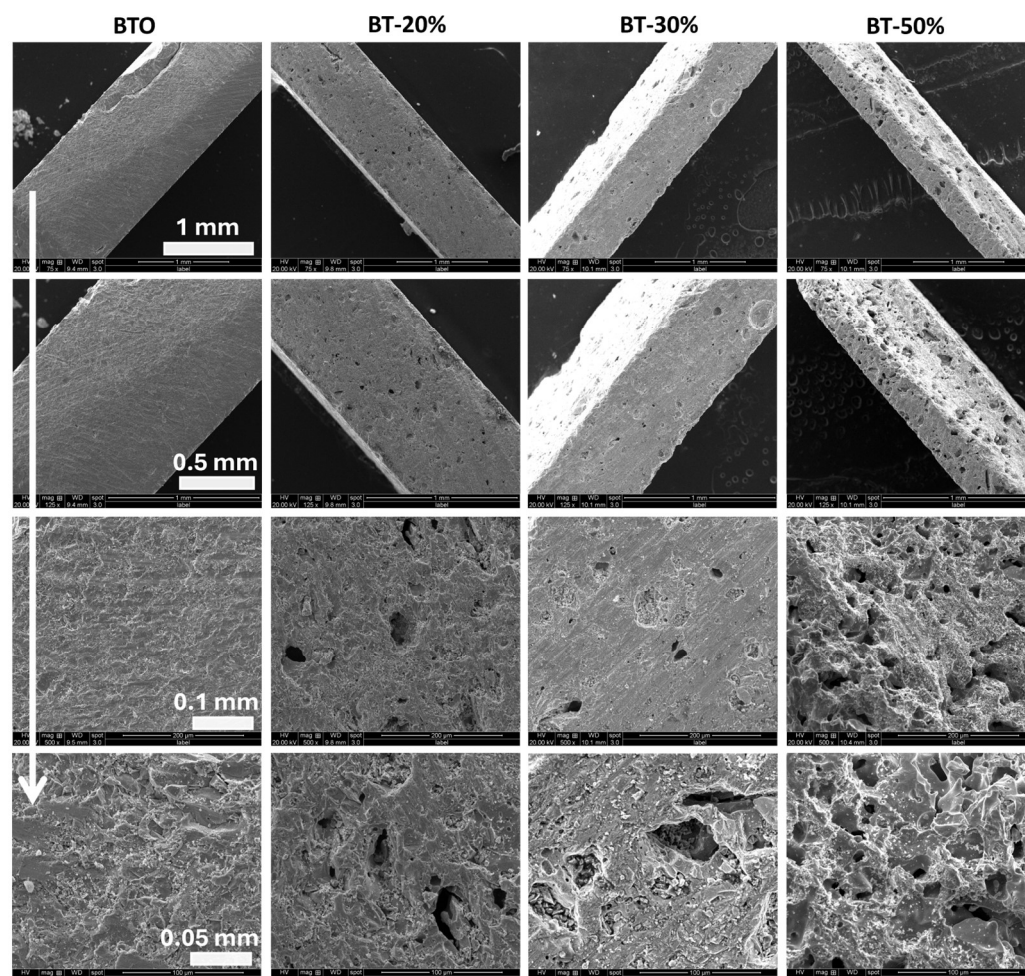


Figure 4. Microstructure of the cross-sections of BTO and BTO + Sucrose (20, 30 and 50 vol%) ceramics sintered at 1350 °C for 2 h at different magnifications.

3.5. High Field Electrical Measurements

The bipolar polarisation–electric field (P–E), strain–electric field (S–E) and switching current responses of BTO ceramics with varying porosity were measured at room temperature under an applied field of 30 kV.cm^{-1} and a frequency of 1 Hz, as shown in Figure 5a–c. The dense BTO sample exhibits a well-defined ferroelectric hysteresis loop with a maximum polarisation (P_{max}) of $\sim 21 \mu\text{C.cm}^{-2}$, a remanent polarisation (P_r) of $\sim 13 \mu\text{C.cm}^{-2}$ and a coercive field (E_c) of $\sim 5 \text{ kV.cm}^{-1}$, consistent with typical ferroelectric behaviour [51].

The evolution of polarisation with increasing porosity does not follow a strictly linear trend. While an overall decrease in P_{max} is observed with increasing porosity, the rate of reduction varies across compositions. In particular, the difference in P_{max} between intermediate porosity levels (20–30 vol% nominal) is relatively small, and a similar behaviour is observed between higher porosity samples (40–50 vol% nominal). This indicates that the influence of porosity on polarisation is not proportional to the nominal pore volume fraction. Such behaviour can be attributed to the inhomogeneous distribution of pores and the resulting local electric field variations within the ceramic matrix [50]. At low to moderate porosity, the ferroelectric regions remain sufficiently connected, allowing effective polarisation switching, and thus, only a gradual reduction in P_{max} is observed [19,24]. As the porosity increases further, the reduction becomes more pronounced; however, beyond a certain level, the change tends to stabilise due to the already reduced active ferroelectric volume. Therefore, the observed behaviour reflects a progressive but non-linear dependence of polarisation on porosity.

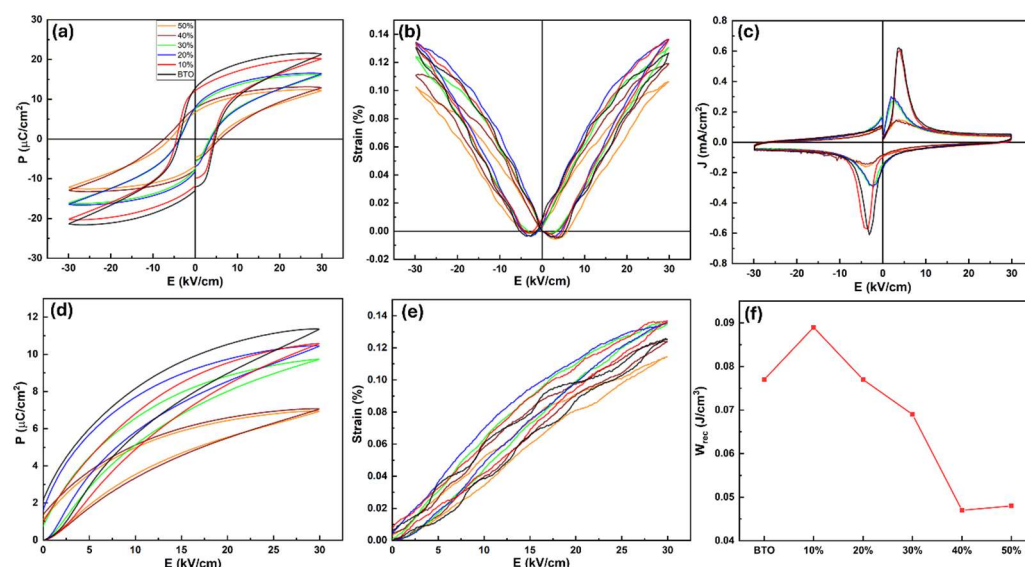


Figure 5. (a–c) Bipolar electrical polarisation, strain (%) and current loops at $30 \text{ kV}\cdot\text{cm}^{-1}$, respectively, for BTO and BTO + Sucrose ceramics sintered at 1350°C for 2 h; (d–f) unipolar polarisation, strain (%) and W_{rec} (%) at $30 \text{ kV}\cdot\text{cm}^{-1}$, respectively, for BTO and BTO + Sucrose ceramics sintered at 1350°C for 2 h.

In contrast to the polarisation behaviour, the strain response exhibits a different trend. The dense BTO sample shows a maximum strain of $\sim 0.125\%$, while the samples with a 10–20 vol% nominal porosity display a slight enhancement, reaching $\sim 0.137\%$, as shown in Figure 5e. This behaviour can be attributed to reduced mechanical constraint within the porous structure, which facilitates domain switching under the applied electric field. To note, the magnitude of strain (%) for positive and negative applied fields is different due to the internal bias, as corroborated by comparing E_c with S_{max} , which are inversely proportional, as shown in Supplementary Table S2. At higher porosity levels (30–50 vol% nominal), the strain shows a gradual decrease; however, it remains relatively stable (~ 0.12 – 0.10%) compared to the corresponding reduction in polarisation. This indicates that the electromechanical response is less sensitive to porosity than the polarisation behaviour. It suggests that the porous structure facilitates deformation despite the reduction in active material.

The current density (J – E) loops (Figure 5c) further support the observed switching behaviour. The dense and low-porosity samples exhibit relatively sharp current peaks near the coercive field, corresponding to domain switching. With increasing porosity, the peaks become broader and less pronounced, indicating wider distribution of local electric fields within the porous structure and distribution of domain switching events.

The unipolar P – E and S – E responses (Figure 5d,e) show progressively slimmer hysteresis with increasing porosity, reflecting reduced hysteresis losses. The recoverable energy density (W_{rec}), calculated from the unipolar loops (Figure 5f), shows a slight enhancement for the 10 vol% sample ($\sim 0.09 \text{ J}\cdot\text{cm}^{-3}$) compared to dense BTO, followed by a gradual decrease at higher porosity levels. This behaviour is consistent with the reduction in polarisation and the change in loop shape. However, the overall magnitude of W_{rec} remains relatively low, and thus, energy storage is not the primary focus of the present study.

3.6. Relative Permittivity and Large-Signal Piezoelectric Coefficient, d_{33}^*

The dielectric properties measured at room temperature and 100 kHz are presented in Figure 6a. The dense BTO sample exhibits a relative permittivity of ~ 1010 with a dielectric loss of ~ 0.019 , which is consistent with typical values reported for large grained

BTO ceramics [3]. With the introduction of 10 vol% sucrose, the permittivity increases to ~1175, accompanied by a significant reduction in dielectric loss (~0.005). This improvement correlated with the easing of domain switching (decreasing E_c) suggests that a small degree of porosity can enhance dielectric response while maintaining low energy dissipation [25,50,52]. At 20 vol% sucrose (~10% porosity), the permittivity remains relatively high (~1075) with low dielectric loss (~0.008). Ceramics with similar levels of porosity have been reported to exhibit increased relative permittivity. Khansur et al. [33] reported ceramics with ~12% porosity and a low dielectric loss (~0.012), while Padurariu et al. [25] reported ceramics with 9% porosity, both of which showed an increase in the relative permittivity as compared to the undoped BTO. Further increases in porosity (30–50 vol% nominal) lead to a gradual reduction in permittivity (~650 at 50 vol%), primarily due to the decreasing volume fraction of the active BTO content [19]. The relative permittivity at room temperature, direct piezoelectric coefficient (d_{33}) and large signal coefficient (d_{33}^*) of previous works are shown in Table 1.

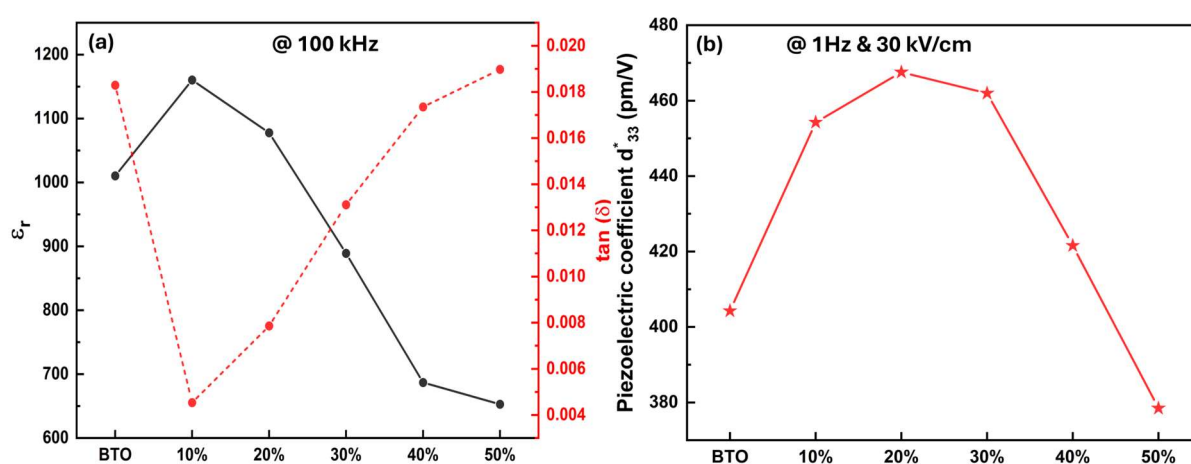


Figure 6. Relative permittivity and loss at room temperature (a) and piezoelectric coefficient, d_{33}^* , at room temperature and a high field of $30 \text{ kV}\cdot\text{cm}^{-1}$ (b) for BTO and BTO + Sucrose ceramics sintered at 1350°C for 2 h.

The large-signal piezoelectric coefficient (d_{33}^*), derived from the unipolar strain–electric field response at $30 \text{ kV}\cdot\text{cm}^{-1}$ and 1 Hz, is shown in Figure 6b. The dense BTO sample exhibits a d_{33}^* of $\sim 404 \text{ pm}\cdot\text{V}^{-1}$. With increasing porosity, d_{33}^* increases to $\sim 454 \text{ pm}\cdot\text{V}^{-1}$ (10 vol% sucrose) and reaches a maximum of $\sim 468 \text{ pm}\cdot\text{V}^{-1}$ at 20 vol% sucrose, while remaining high ($\sim 462 \text{ pm}\cdot\text{V}^{-1}$) at 30 vol%. This enhancement at moderate porosity is consistent with the decreasing E_c (Supplementary Table S2) and can be attributed to reduced mechanical constraint and ease of switching within the porous structure, allowing more effective electromechanical deformation under an applied field. At higher porosity levels, d_{33}^* decreases to ~ 422 and $\sim 378 \text{ pm}\cdot\text{V}^{-1}$, respectively, due to the reduced active material volume and increased structural discontinuity. There is a point to note that undoped BTO prepared by Roscow et al. [29] using freeze casting with 45% porosity shows a reduction of d_{33} of 6.9%, while the undoped BTO with 32% porosity by the conventional method in this work shows a reduction of d_{33}^* of $\sim 6.4\%$.

Overall, the electrical results demonstrate that while polarisation decreases with increasing porosity, the strain response and large-signal piezoelectric behaviour are preserved and even enhanced at moderate porosity levels. This highlights the potential of porosity engineering as an effective approach to achieving lightweight BTO ceramics with stable electromechanical performance.

Table 1. Dielectric properties of BTO porous reported in the literature (different routes, porosity, d_{33} , d_{33}^* and ϵ_{RT}). (TW—this work).

Composition	Porosity (%)	d_{33} (pC/N)	d_{33}^* (pm/V)	ϵ_{RT}	Ref.
Undoped BTO (grain size-dependent)	~1–5	~180–430		~1000–6000	[3,6]
BTO (BURPS)	~10–72	~40–160	-	-	[27]
BTO (freeze casting)	45	~129	-	~580	[29]
BTO (sandwich layer) Average porosity	~5–72	~43–125	-	~167–1500	[32]
BTO (hydrothermal nanocubes)	~33–37	-	-	~280–320	[41]
BTO (sacrificial soft polymeric additives)	~4–26	-	-	~850–2300	[25]
BTO (polymethyl methacrylate)	~3–29	~120–30	-	-	[40]
BTO (sacrificial template)	~50	-	-	~750	[28]
BTO	~2	-	~404	~1010	TW
BTO Suc 10 vol%	~3	-	~454	~1175	TW
BTO Suc 20 vol%	~10	-	~468	~1075	TW
BTO Suc 30 vol%	~16	-	~462	~890	TW
BTO Suc 40 vol%	~24	-	~421	~687	TW
BTO Suc 50 vol%	~32	-	~378	~650	TW

4. Conclusions

Porous barium titanate (BTO) ceramics were successfully fabricated using a simple sucrose-assisted route, enabling regulated porosity in the range of ~2% to ~32%. Crystal structure analysis confirmed that the tetragonal P4mm phase is retained across all compositions, indicating that the introduction of porosity does not significantly affect the crystal structure. The incorporation of porosity leads to a systematic reduction in polarisation due to the decrease in effective ferroelectric volume and the presence of local electric field inhomogeneities. In contrast, the strain response and d_{33}^* are preserved and even enhanced at moderate porosity levels (2–10%), reaching a maximum d_{33}^* of ~468 pm.V^{−1}. This behaviour is attributed to reduced mechanical constraint within the porous structure, which facilitates electromechanical deformation under an applied electric field. Dielectric measurements further show that low levels of porosity (2–10%) can improve permittivity while maintaining low dielectric loss, whereas higher porosity leads to a gradual decline due to the increasing contribution of the pore phase. Overall, these results demonstrate that controlled porosity can effectively tailor the structure–property relationships in BTO without compromising its ferroelectric phase stability. This study highlights porosity engineering as a viable strategy for developing lightweight ferroelectric ceramics with stable electromechanical performance, particularly in applications where reduced density and reliable strain response are required.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst16100604/s1>, Figure S1. Area EDX spectra and corresponding SEM images of BTO ceramics prepared with different sucrose contents and sintered at 1350 °C for 2 h: (a) BTO without sucrose; (b) BTO with 10 vol% sucrose; (c) 20 vol% sucrose; (d) 30 vol% sucrose; (e) 40 vol% sucrose; and (f) 50 vol% sucrose. The white rectangles indicate the analysed areas, and the insets show the corresponding atomic percentages of O, Ti, and Ba; Figure S2. BTO + Sucrose 50% sample for magnified view of microstructure and grain size; Figure S3. Low-magnification (300×) SEM micrographs of BTO ceramics prepared with different sucrose contents and sintered at 1350 °C for 2 h: (a) BTO without sucrose; (b) BTO with 10 vol% sucrose; (c) 20 vol% sucrose; (d) 30 vol% sucrose; (e) 40 vol% sucrose; and (f) 50 vol% sucrose. All scale bars represent 400 µm;

Table S1. Refined lattice parameters, c/a ratio, unit cell volume and goodness-of-fit (GOF) of all compositions; Table S2. Bipolar applied field maximum strain (%) and coercive field of BTO and BTO + Sucrose ceramic samples, respectively.

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Abbreviations

The following abbreviations are used in this manuscript:

BTO	barium titanate/BaTiO ₃
XRD	X-ray diffraction
SEM	scanning electron microscopy
EDX	energy-dispersive X-ray spectroscopy
P–E	polarisation–electric field
S–E	strain–electric field
J–E	current density–electric field
P _{max}	maximum polarisation
P _r	remanent polarization
E _c	coercive field
W _{rec}	recoverable energy density
d ₃₃ [*]	large-signal piezoelectric coefficient
ICDD	International Centre for Diffraction Data
GOF	goodness of fit
LCR	inductance–capacitance–resistance meter

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