

1.2. Low Curie Temperature Materials, The Next Generation of High Energy Density Class II Ceramic Dielectrics?

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1. ABSTRACT

Increase of capacitors' energy density is of prime interest in number of today's applications. High energy density, high voltage capacitors are especially needed in fast-growing segments such as automotive, renewable energy generation and transmission, medical etc.

Film power capacitors are dominating the high voltage segment; however, this technology is limited with lifetime at high temperatures and relatively low energy density level. High capacitance, high energy density MLCC capacitors based on class II dielectric materials offer small, compact size, high reliability, and high temperature range, however it shows significant capacitance (and energy) deterioration with applied voltage that reduces its real energy storage capability as its remarkable disadvantage.

This paper presents a study on suitability of doped BaTiO₃ (BT) based, ferroelectric ceramic materials BCST and BT-11BS with low Curie temperatures as high energy density capacitor dielectrics. Aim of the research was to evaluate key features of these materials and optimize its process parameters to assess potential benefits as a high energy density capacitor dielectric.

Electrical parameters such as permittivity, electrical field strength, temperature dependence and capacitance with voltage dependency were evaluated on lab manufactured samples and benchmarked to the reference-made pure BT material samples.

Key finding on the low Curie temperature materials is that permittivity/capacitance with BIAS voltage does not decrease so rapidly at temperatures above the Curie temperature. This phenomenon increases a total energy storage density across operating voltage and temperature range as demonstrated on BT-11BS material with Curie temperature as low as 37°C. This, so far possibly overlooked behaviour by capacitor manufacturers, could bring a new direction in development of higher energy density and more stable ceramic capacitors.

Both BCST and BT-11BS evaluated low Curie temperature materials showed higher energy density compare to the pure BT reference material, nevertheless BCST's high dielectric losses and low efficiency degrade its dielectric features, thus it may not be a suitable candidate for capacitor dielectric.

The highest energy density on BT-11BS after process optimisation achieved up to 10x higher ED than BT reference material and improved permittivity stability with applied voltage and temperature.

Keywords:

high energy capacitors; high energy density ceramic dielectric materials; high electrical field withstanding ceramic dielectric materials; high energy, high voltage ceramic dielectric materials; low Curie temperature ceramic dielectric materials; high energy density capacitors based on low Curie temperature ceramic dielectric materials.

2. INTRODUCTION

High energy density dielectric materials are subject of prime research for decades. Simple plate capacitance calculation is following the equation:

$$C = \epsilon_0 \epsilon_r \frac{S}{l} \quad \text{where:}$$

ϵ_0 = permittivity of vacuum

ϵ_r = relative permittivity of the dielectric material

S = surface of electrodes

l = thickness of dielectric

In order to achieve maximum capacitance value, ϵ_r relative permittivity of the dielectric material, surface area of electrodes shall be high, and the dielectric shall be as thin as possible. The capacitor must operate reliably at defined voltage in addition, so the dielectric shall feature high electric field strength in order to use a thin dielectric layer at desired working voltage. Surface area of electrodes is also important, and it may be related to the thickness of dielectric layer, as thin dielectric can follow fine structures / pores and thus create large surface area. This is especially important with increase of rated voltage of the capacitors as the thicker, high voltage dielectrics may not follow fine structure of electrodes. Thus, low voltage capacitors may successfully use nano/microstructure electrode materials, while high voltage capacitor electrodes has to be optimized for thicker dielectrics and also handling of much higher charging / discharging currents as the energy increase with voltage squared.

Selection of the right dielectric materials and capacitor construction is influenced also by other requirements such as required operation temperature range, high peak temperature withstanding during PCB mounting, humidity, vibration robustness, long lifetime etc.

Pushkar et.col [1] studied wide range of dielectric materials from the perspective of its relative permittivity versus electrical field strength and concluded that there is a certain limit that was achieved (at the time of his study in 2004) across all capacitor technologies:

$$\epsilon_r \times E_{BR}^2 = 400$$

that he called BOCA (Best of One Can Achieve) line. See Figure 1.:

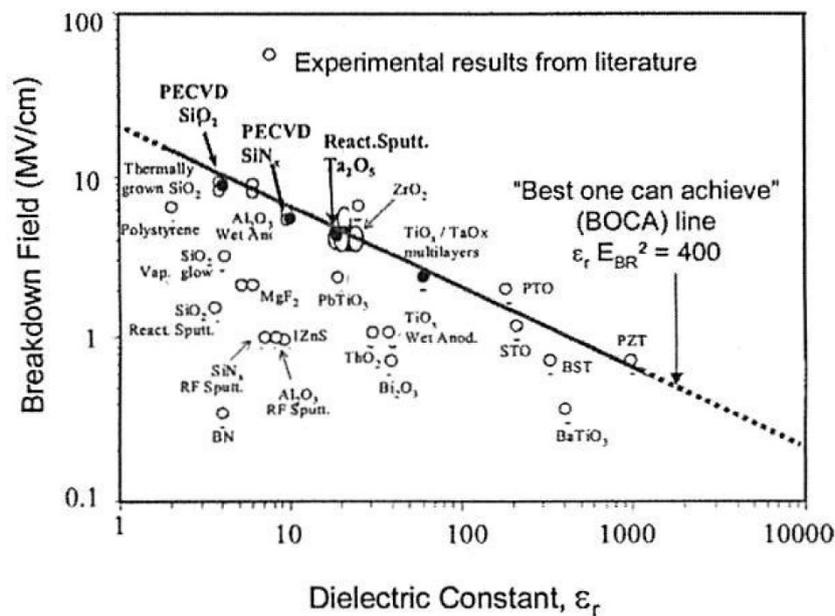


Figure 1. Overview of capacitor dielectrics' dielectric constant vs breakdown voltage; source: Pushkar [1]

3. HIGH ENERGY DIELECTRIC MATERIAL STUDY

3.1. High Energy Dielectric Materials - Overview

There were number of experiments and reported record high permittivity values achieved on various dielectrics since Figure 1. Chart was published by Pushkar in 2004. Nevertheless, the trials on such results achieved in laboratory conditions have not yet brought a breakthrough in practical “stable” and “useful” capacitor technology in mass production on the market yet.

If we look what is a major change on capacitor technology market across past decades, one can notice a major increase of ceramic dielectric technologies that outperformed the other in number of sectors – miniaturization, cost, high voltage, stable parameters and reliability, low leakage current etc. Indeed, there are still some downsides on ceramic capacitor features and application limitations, nevertheless the fact that this technology has seen a major multi-level improvement across the past years and decades can be clearly noticed.

Aim of our research was thus focus to high energy and high voltage ceramic dielectric materials to check how / if we can achieve some improvements over the BOCA line and mass used dielectric types today.

If we look at Figure 1. chart again and highlight domain of the currently most used technologies in mass production we can see that MLCC class II technology may outperform the others on first look into specifications, nevertheless the real application usage has to reflect its capacitance drop with applied voltage that may significantly degrade its energy storage capabilities, especially at high voltages. ... Thus, it is also below BOCA line of max energy achieved. See Figure 2.

Note: the highest energy capacitor dielectric on the market is still tantalum wet electrolytic technology that reach energy density as high as 8J/cc at 250V, nevertheless high cost and higher ESR of this technology limit its use to a specific field such as medical implantable defibrillators.

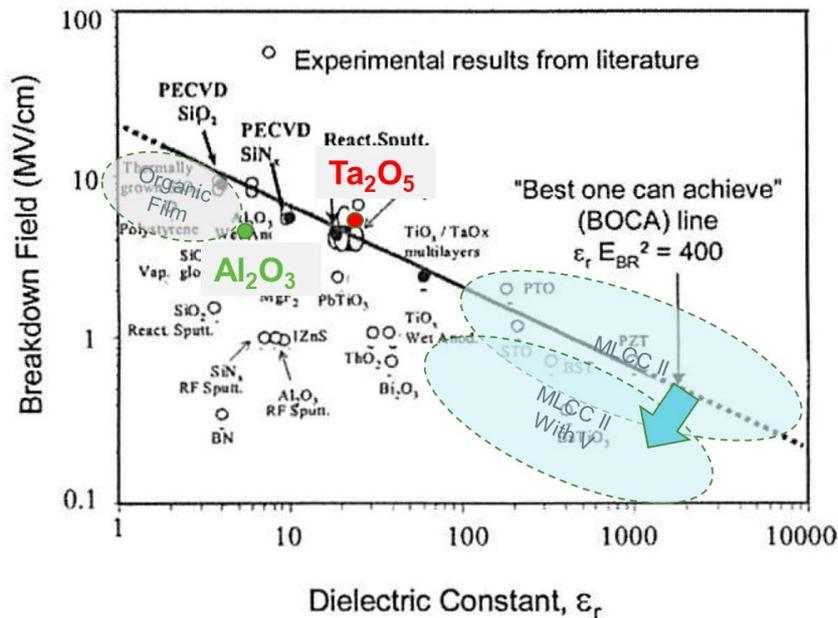


Figure 2. Overview of capacitor dielectrics' dielectric constant vs breakdown voltage from Figure 1. with highlights of major capacitor high energy density technologies.

Unlike tantalum capacitor technology, ceramic dielectric materials offer much higher potential of further development and flexibility to adjust its material characteristics and thus our focused was towards this direction of material research.

3.2. High Energy Ceramic Dielectric Materials

The highest energy density on ceramic dielectric materials is achieved with class II ceramic materials with ferroelectric features usually based on barium titanate BaTiO_3 , where the polarisation (capacitance) is created by its crystal structure.

BaTiO_3 has a cubic crystal structure above the Curie temperature (approx. 125°C or more). It turns into a tetragonal crystal structure that creates a dipole, respectively domains of dipoles with different dipole orientation below the Curie temperature. (see Figure 3., 4 and 5.).

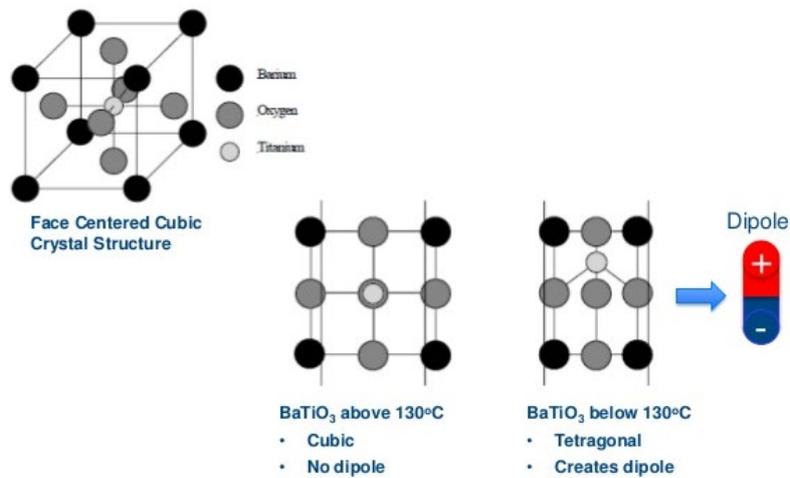


Figure 3. BaTiO_3 dielectric crystal structure above and below Curie temperature; source: Kemet

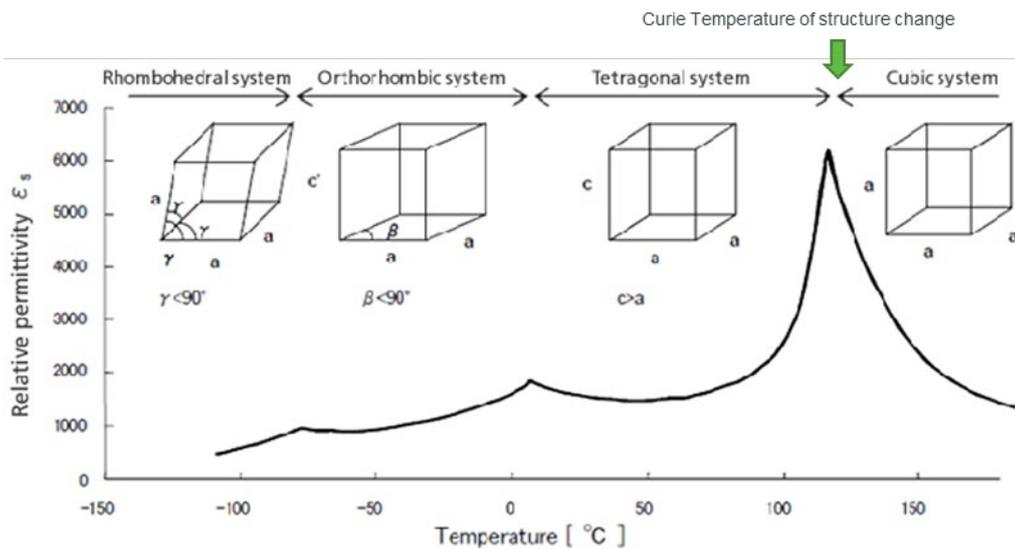


Figure 4. BaTiO_3 dielectric crystal structure versus temperature

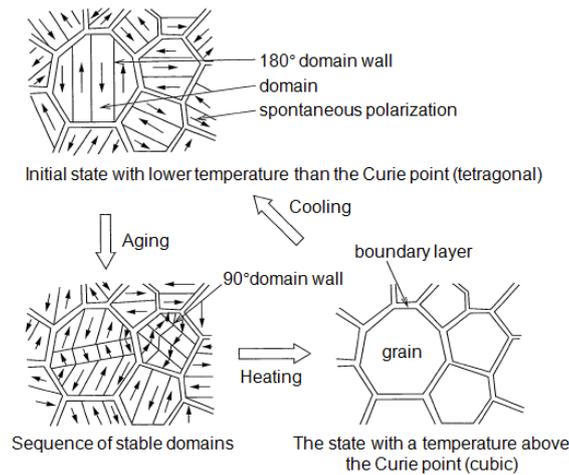


Figure 5. BaTiO₃ dielectric domains; source: Murata

The dielectric material grain size/shape/distribution may impact number of dipoles and domains and thus its features and characteristics.

The maximum permittivity and capacitance value is achieved at Curie temperature area around 125°C for a standard pure BaTiO₃ material.

Dielectric absorption (DA) and Ferroelectricity

The BaTiO₃ crystalline structure described in previous figures are constituted by dipoles that at the polarizing present a dielectric hysteresis. With pattern from the hysteresis curve of magnetic materials they are called ferroelectric.

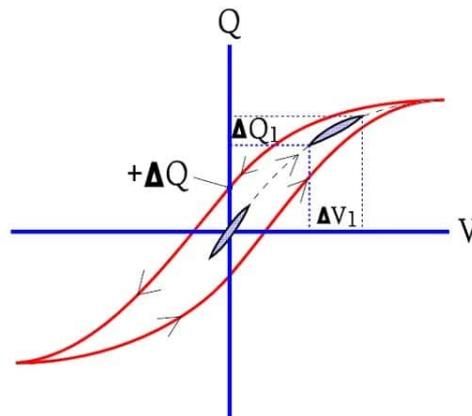


Figure 6. Capacitor with ferroelectric hysteresis. Source [2]

Figure 6 shows how the ferroelectric material locks a residual charge ΔQ on the electrode surface when the voltage over the capacitor recedes to zero (outer circuit short-circuited).

The ferroelectric curve swings to the V axis while the general DA curve looks like a magnified picture of the centre oval. In both cases the bound residual charge ΔQ is time dependent. If the outer circuit is short-circuited ($V = 0$) successively charges on the electrode surfaces are set free while ΔQ decreases. The crystalline structure of ferroelectric materials is maintained up to the Curie temperature.

Specific group of materials are anti-ferroelectric dielectrics. In opposite to ferroelectrics, where permittivity decreases with applied voltage, permittivity of anti-ferroelectric is low at low voltage and increase with electric field / applied voltage. These materials can be used to achieve high CV, high capacitance at high voltage applications

such as energy generation or EV/HEV vehicles in automotive industry. See figure 7. below for comparison of polarisation curves between linear dielectrics (class 1), ferroelectrics (class 2) and anti-ferroelectric materials. Typical antiferroelectric high voltage, high energy density dielectric material is PbLaZrTiO_3 (PLZT). See Figure 7.:

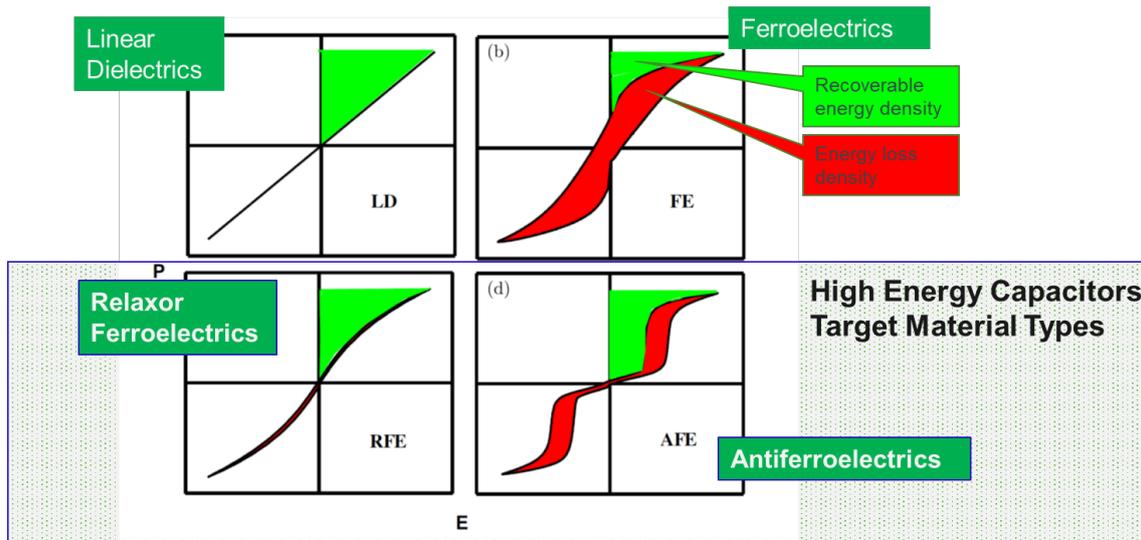


Figure 7. Diagram of hysteresis and energy storage density for various dielectric material types; prepared using source: [3]

Based on the figure 7. overview, the best candidates for high energy density dielectric material shall become from a relaxor ferroelectrics or anti-ferroelectrics group of materials.

Thus, apart of the high permittivity and high electric field strength requirements on dielectric material, we end of for a third high energy density storage condition on ferroelectric material types – **low polarisation losses** – in other words, the material has to have the ability to return the energy stored in the material structure with low losses.

4. EXPERIMENTAL

4.1. Development Task

BaTiO_3 ceramic dielectric material are the most common, proved dielectric material used in mass production of ceramic capacitors today. Due to its structure, the maximum capacitance value is achieved nearby Curie temperature $\sim 125^\circ\text{C}$. There are number of applications with limited requirements on operating temperature range that may not require such wide temperature range – such as wearable electronics. Thus, can we modify BaTiO_3 structure to achieve even higher energy density even at limited temperature range?

Modify BaTiO_3 ceramic dielectric material by doping and optimization of its processing/structure to lower Curie temperature closer to room temperature and obtain suitable ceramic dielectric with high energy density. See Figure 8. and 9.

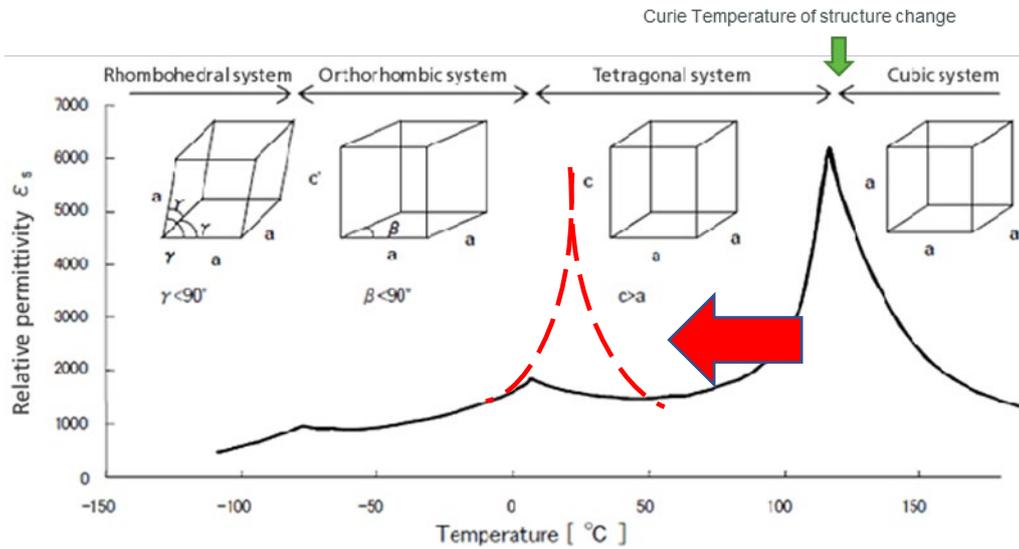


Figure 8. Illustration of development target: Move Curie temperature and maximum of relative permittivity to lower – room temperature range.

Combination of three key parameters of the dielectric will be monitored and targeted for best match: permittivity, electrical field strength and dielectric losses. The dielectrics will be benchmarked using P-E charts that is considered as best for energy storage capability assessment:

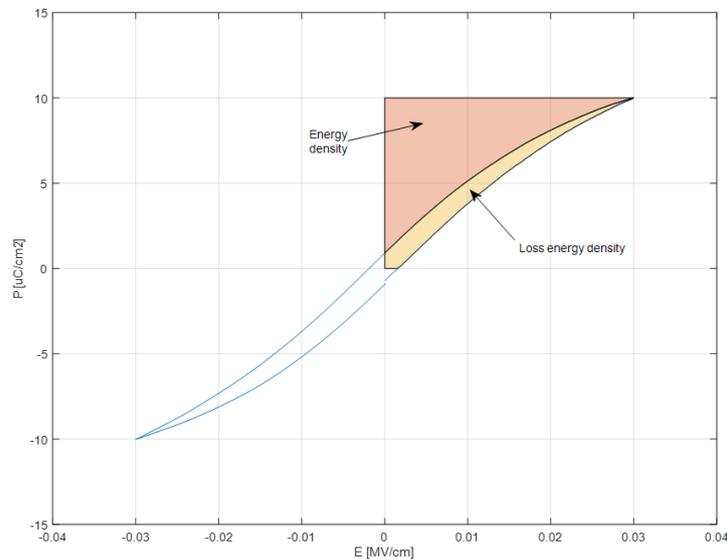


Figure 9. P-E loop chart used as key material assessment benchmark tool

4.2. Calculation of Energy Storage Density and Storage Efficiency

Energy density and a loss energy density can be calculated from areas as shown in P-E loops (Figure 8). Discharge energy density w_1 and Energy storage efficiency η can be calculated as:

$$w_1 = \int_{P_r}^{P_{max}} E dP = \int_0^{E_{max}} (P_{max} - P_L) dE = E_{max} \cdot P_{max} - \int_0^{E_{max}} P_L dE$$

$$\eta = \frac{w_1}{w_1 + w_2} = \frac{E_{max} \cdot P_{max} - \int_0^{E_{max}} P_L dE}{E_{max} \cdot P_{max} - \int_0^{E_{max}} P_R dE}$$

Where w_1 is discharge energy density, w_2 is loss energy density, P_L represents the left loop, P_R represents the right loop.

4.3. Selection of Suitable Ceramic Dielectrics Candidates

The approach to the development of high energy density take advantage of the unique properties of ceramic materials based on BaTiO₃ (barium titanate – BT). These materials exhibit high dielectric as well as piezoelectric constants. Dielectric (and piezoelectric) properties are influenced by the technology of ceramic preparation process (e.g. particle size of starting ceramic powders, calcination and sintering temperature profile, ceramic density/porosity, or fired ceramic grains size), however crucial is also the impact of dopants added to the BaTiO₃ ceramic (e.g. Ca, Sn, Nb, Co) and/or the composition of different barium and titanium based ceramic mixtures.

On the base of the literature search two ceramic materials were chosen for initial research:

- Lead-free ceramic 0.55(Ba_{0.9}Ca_{0.1})TiO₃-0.45Ba(Sn_{0.2}Ti_{0.8})O₃ (further denoted as **BSCT**), where excellent piezoelectric properties in the temperature range about 40°C were expected [4 to 7]. Due to that coincidence of piezoelectric and dielectric properties are observed in most cases, this ceramic was included.
- System BaTiO₃-xBaSnO₃ where the composition with x = 11 was chosen as the most promising one. (further denoted as **BT-11BS**) Here the relative permittivity maximum is observed for the Curie temperature close to 42°C. Reported dielectric constant peak value is about 70 000 at this temperature [8].

4.4. Sample Preparation Methods

Preparation of ceramic dielectric materials consist of two basic steps: (i) material synthesis and (ii) fabrication of the sample disc.

Features and electrical behaviour of ceramic materials are depending to number of structure parameters such as grain size, homogeneity, grain boundaries, material density, purity and other parameters.

Each synthesis and fabrication methods have its advantages and limitations. Selection of the method depends to requirements on dopant type, its quantity, duration of the test etc. and it may result in quite wide range of final parameters.

In our test preparation initial powder was mixed/milled, dried, sieved, calcinated, milled, dried, and sieved as the basic synthesis sequence resulting in a structure with mixed particle sizes. The synthesised material was then fabricated by three different processing methods referred further as: **Process 1**, **Process 2**, and **Process 3**.

Pure BT (BaTiO₃) Reference Samples

Reference pure BT samples were synthesised and then prepared using fabrication **Process 1** method. The **Process 1** method allows preparation of thin film ceramic layers and thus the material properties is similar to Tape Casting MLCC mass production process type.

Ferroelectric properties like polarization versus field loops of poled samples were measured at 1 Hz and 10 Hz frequencies using piezoelectric evaluation system (aixPES, aixACCT systems GmbH, Germany).

disc test sample of the ceramic dielectric material



Calculated value of energy storage density varies with applied electric field (see Figure 10.: P - E dependences measured for electric field 1kV/mm, 2kV/mm and 3kV/mm) and with measuring frequency (see Fig. 11: P - E dependences were measured at frequency 1 Hz and 10 Hz, respectively)

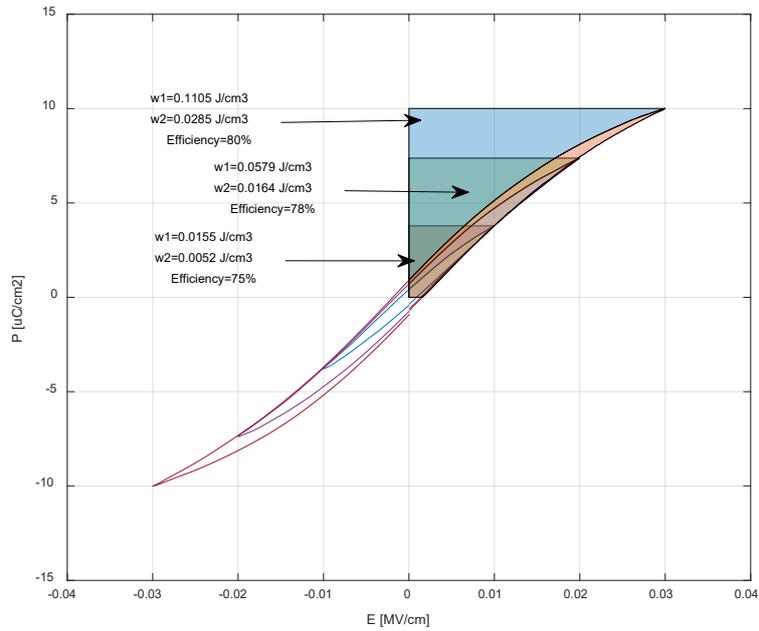


Figure 10.: P-E dependences measured at sample BT prepared by **Process 1**. technique and sintered at 1300°C for electric field 1kV/mm, 2kV/mm and 3kV/mm.

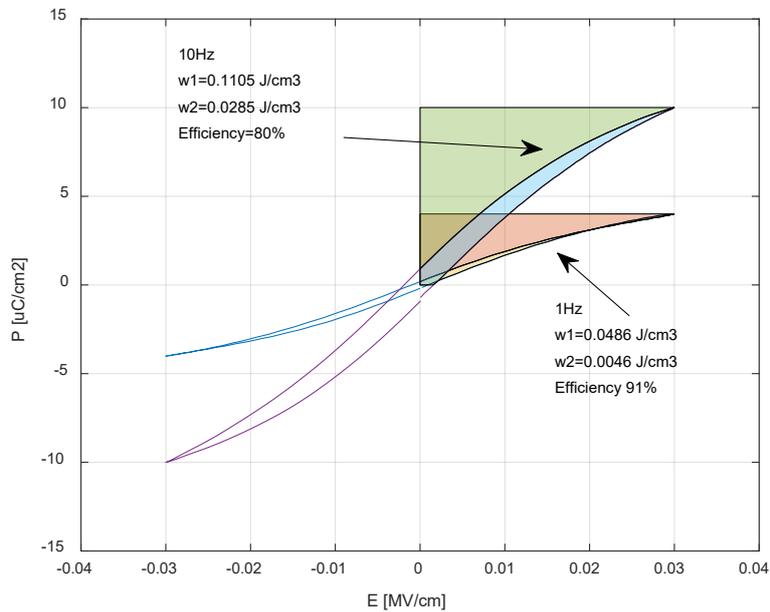


Figure 11.: P-E dependences measured at sample BT prepared by **Process 1**. technique and sintered at 1300°C. The P-E loops are measured for frequencies 1 Hz and 10Hz

5. TEST RESULTS

Test results are presented for ceramic disc samples made of three different ceramic dielectric materials:

1. **BT** - pure BaTiO₃
2. **BCST** - 0.55(Ba_{0.9}Ca_{0.1})TiO₃-0.45Ba(Sn_{0.2}Ti_{0.8})O₃
3. **BT11BS** - BaTiO₃-11BaSnO₃

P - E dependences were measured for frequencies 1 Hz and 10 Hz and are evaluated for BT ceramic disc samples. P - E dependences measured for frequency 1 Hz are evaluated for BCST and BT11BS system ceramic disc samples (measurements at 10 Hz frequency were unfeasible for these samples due to the measurement system limitation).

5.1. BT – Pure BaTiO₃ – Reference Ceramic Material Evaluation

P - E loops measured at frequency **10 Hz** for BT samples prepared at different sintering temperatures are shown in Figure 15.

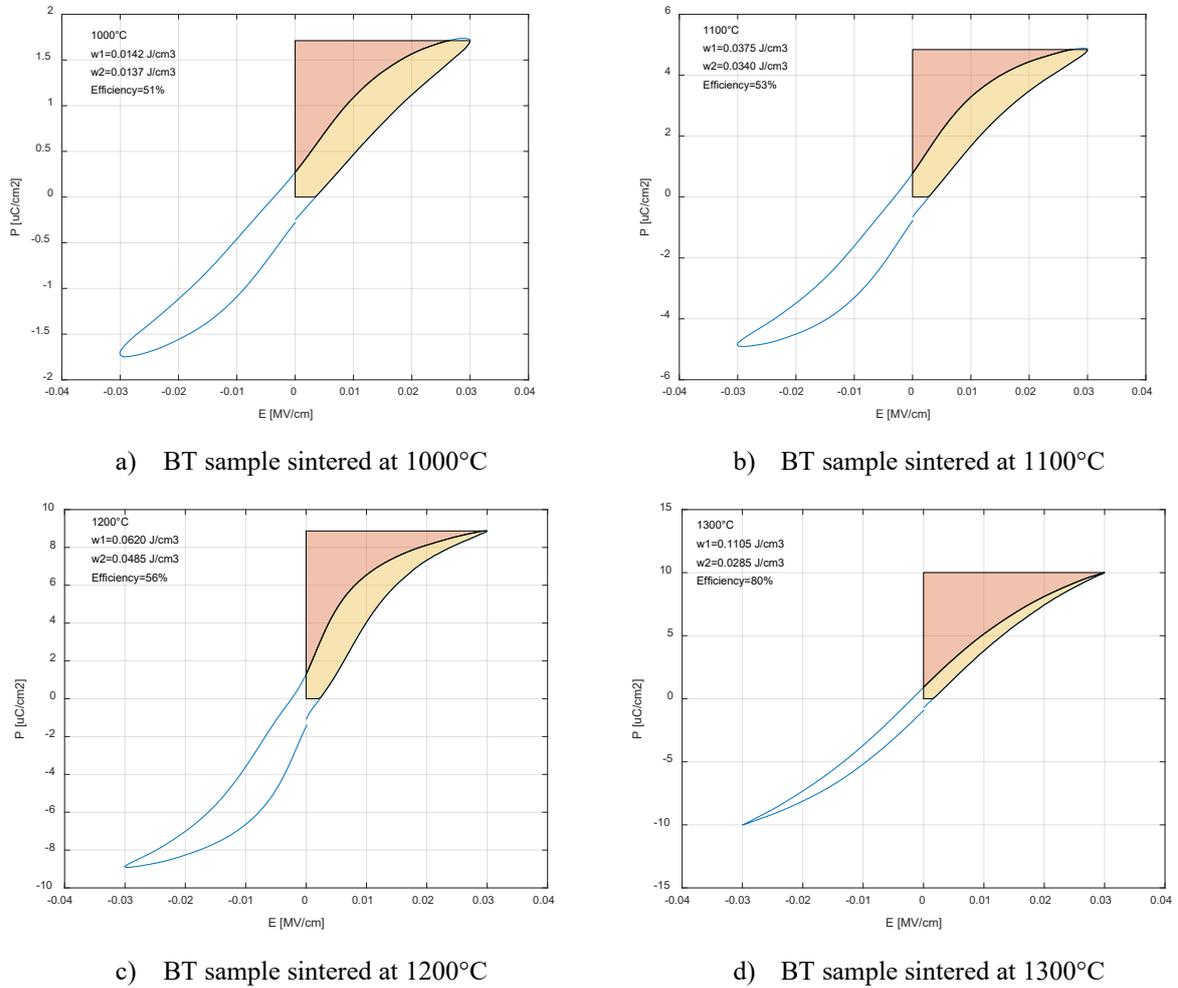


Figure 15: P - E loops measured at 10 Hz for sample BT prepared by Process 1. Highlighted area represents energy storage density and a loss energy density.

Figure 16. shows the dependence of dielectric constant on the electric field for different sintering temperature of BT prepared by **Process 1**. We can see that the dielectric constant value increases with sintering temperature, which is a result of higher density achieved within the sintering.

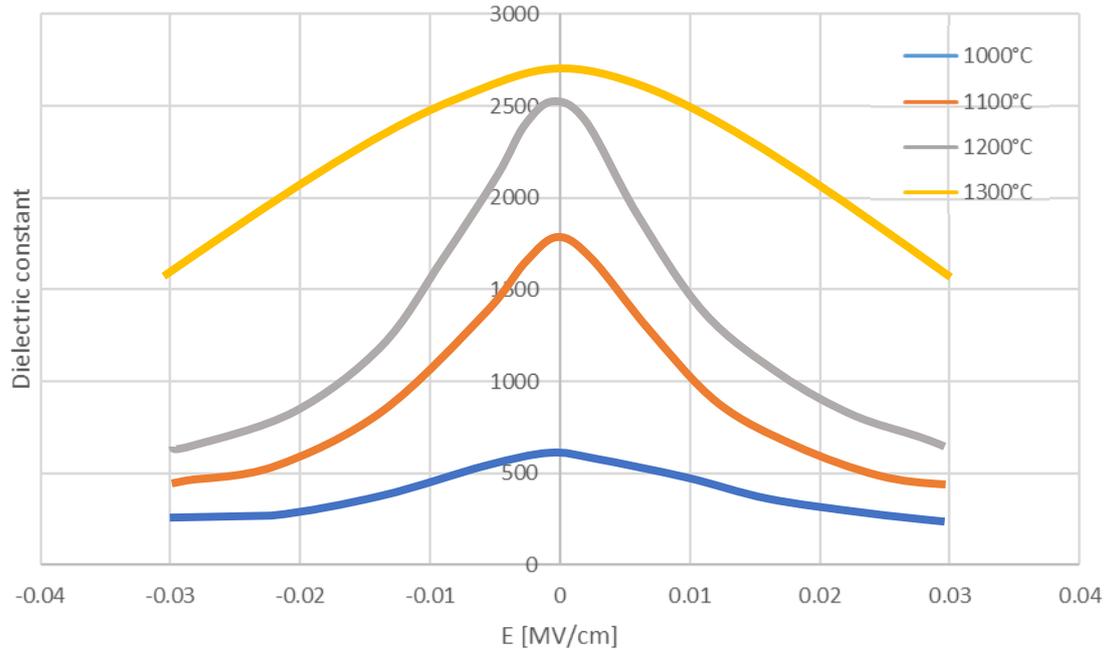


Figure 16: Dielectric constant vs. electric field measured for BT ceramics prepared by Process 1. technique at different sintering temperatures.

The summary of results measured on reference samples of barium titanate ceramics is given in Table 1.

Here the Energy storage density, Loss energy density, Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz and 10 Hz, and ϵ_r and $\tan \delta$ measured at frequency 1 kHz is shown. Sintering temperature 1300C showed the best results with high efficiency above 90% @1Hz.

Sample	Sintering Temp. [°C]	ϵ_r	$\tan \delta$	Energy Density 10Hz [J/cm ³]	Loss energy Density 10Hz [J/cm ³]	η 10Hz [%]	Energy Density 1Hz [J/cm ³]	Loss energy Density 1Hz [J/cm ³]	η 1Hz [%]
BT1	1000	492	0.0078	0.0142	0.0137	51	0.0062	0.0215	22.4
BT2	1100	1471	0.0111	0.0375	0.0340	53	0.0134	0.0420	24.1
BT3	1200	2123	0.0255	0.0620	0.0485	56	0.0284	0.0302	48.5
BT4	1300	2534	0.0137	0.1105	0.0285	80	0.0486	0.0046	91.3

Tab 1.: Energy storage density, Loss energy density and Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz and 10 Hz; ϵ_r and $\tan \delta$ measured at frequency 1 kHz for BT prepared by Process 1. with different sintering temperatures.

The BT capacitance dependency with voltage at different temperatures 25°C(RT), 130°C(Curie Temperature) and 160°C (above Curie Temperature) see Figure 17.

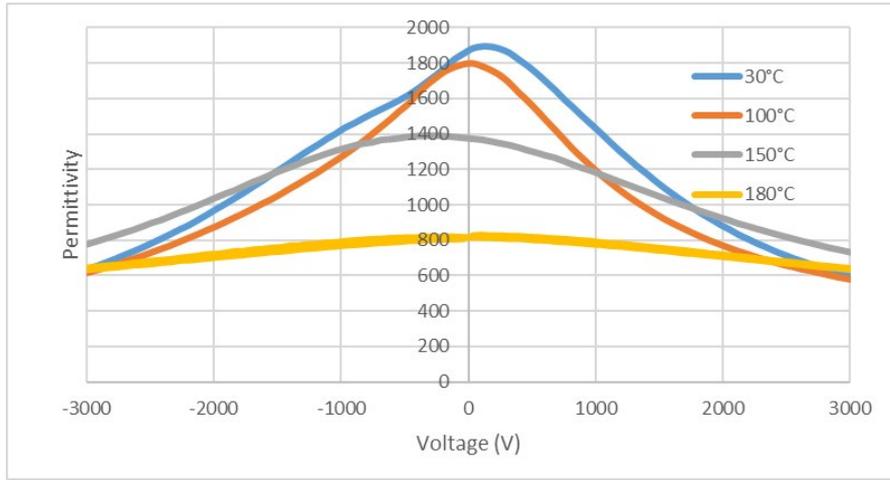
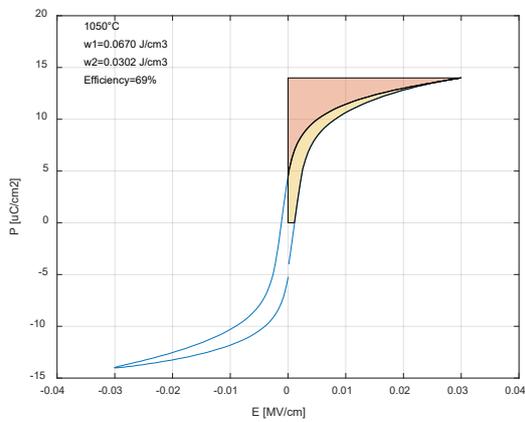


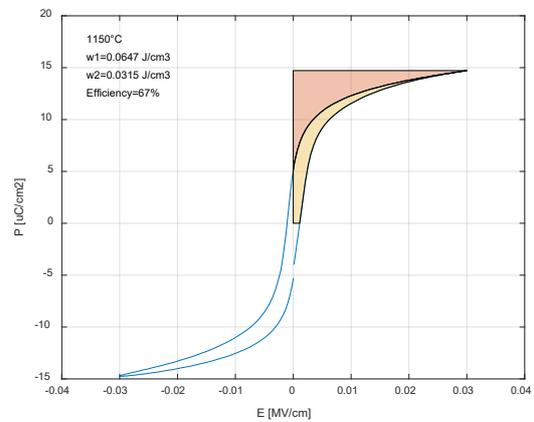
Figure 17. Capacitance vs. BIAS voltage measured for BT ceramics (Curie Temperature $\sim 135^{\circ}\text{C}$) prepared by Process 1. technique at different temperatures.

5.2. BCST 0.55(Ba_{0.9}Ca_{0.1})TiO₃-0.45Ba(Sn_{0.2}Ti_{0.8})O₃ Ceramic Material Evaluation

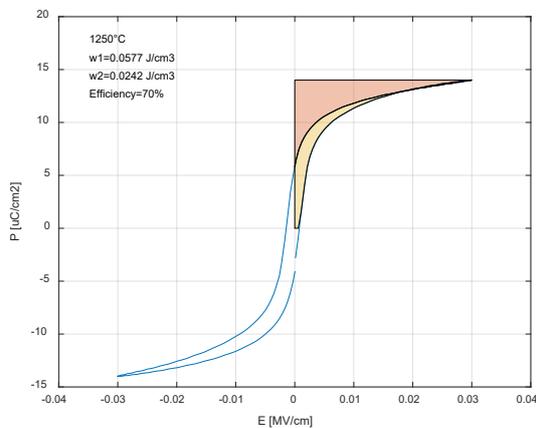
P - E loops measured at frequency 1 Hz for BCST samples prepared at sintering temperature 1480°C with different calcination temperatures in the range 1050 to 1350°C are shown in Figure 18. Due to the S-shape of measured characteristic the increase of energy storage density with electric field is small. The efficiency of charge/discharge process is below 70 %.



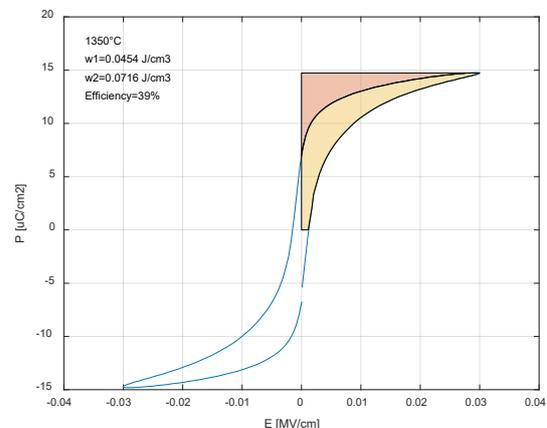
a) BCST sample sintered at 1050°C



b) BCST sample sintered at 1150°C



c) BCST sample sintered at 1250°C



d) BCST sample sintered at 1350°C

Figure 18: P - E loops measured at 1 Hz for sample BCST. Highlighted area represents energy storage density and a loss energy density.

The dependences of dielectric constant on the temperature in the range -30 to 120°C is shown in Figure 19 for different calcination temperatures of BCST ceramic. We can see the shift of dielectric constant peak value on the Curie temperature with calcination temperature. The lower is the calcination temperature, the lower is Curie temperature. The Curie point is between 60 and 68°C in this case.

Figure 20 shows the dependence of dielectric constant on the electric field at room temperature for different calcination temperatures of BCST ceramic. We can see that the dependence of dielectric constant value on the calcination temperature is weak, however still there is visible the optimal value for the calcination at the temperature about 1150°C .

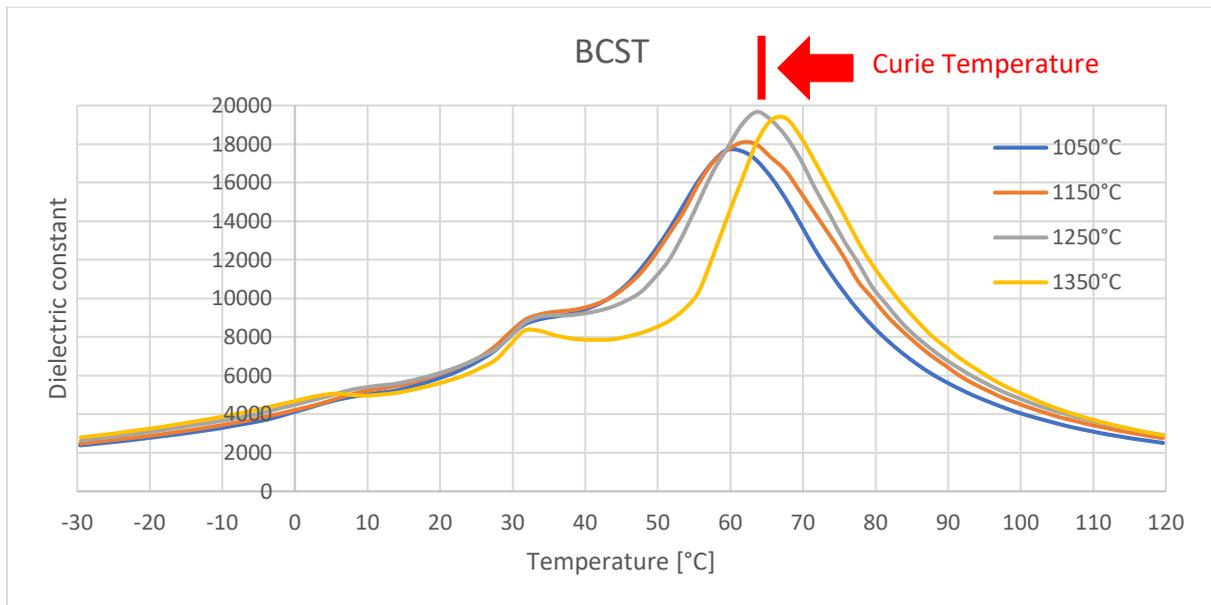


Figure 19: Temperature dependence of dielectric constant for BCST ceramics sintered at 1480°C and calcinated at different temperatures.

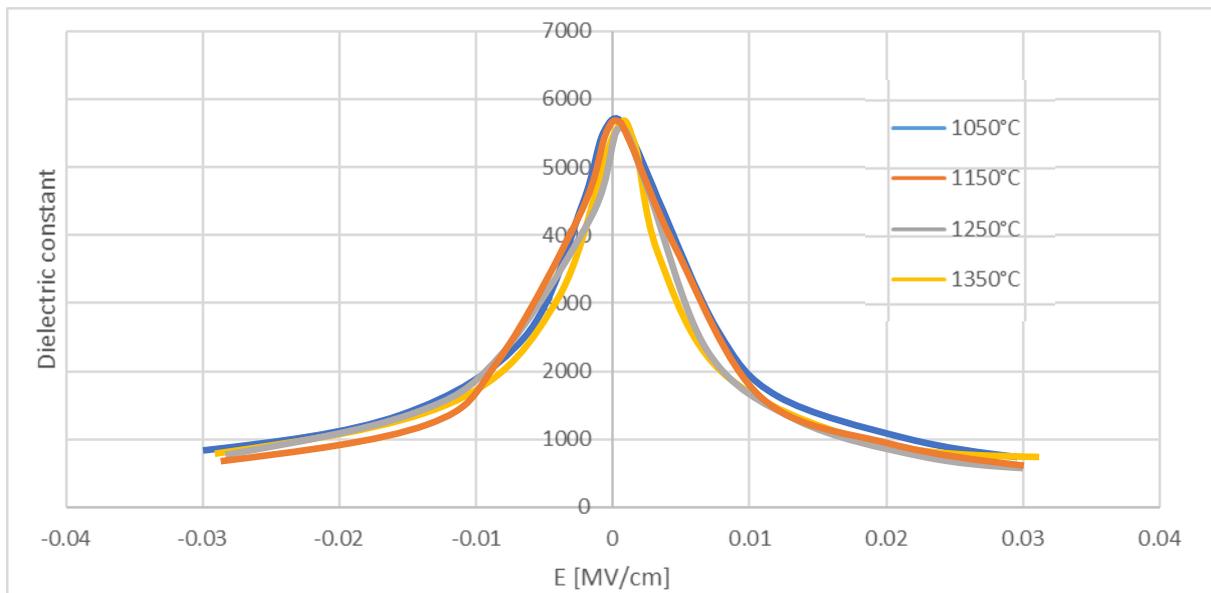


Figure 20: Dielectric constant vs. electric field for BCST ceramics sintered at 1480°C and calcinated at different temperatures.

The summary of results measured on reference samples of BCST ceramics is given in Table 2. Here the Energy storage density, Loss energy density, Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz, and ϵ_r and $\tan \delta$ measured at frequency 1 kHz is shown.

Tab 2.: Energy storage density, Loss energy density and Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz; ϵ_r and $\tan \delta$ measured at frequency 1 kHz for BCST prepared with different calcination temperatures.

Sample	Calcination Temp. [°C]	ϵ_r	$\tan \delta$	Energy Density 1 Hz [J/cm ³]	Loss energy Density 1 Hz [J/cm ³]	η 1 Hz [%]
BCST1	1050	5507	0.0278	0.0670	0.0302	69
BCST2	1150	5402	0.0291	0.0647	0.0315	67
BCST3	1250	5627	0.0307	0.0577	0.0242	70
BCST4	1350	5305	0.0297	0.0454	0.0716	39

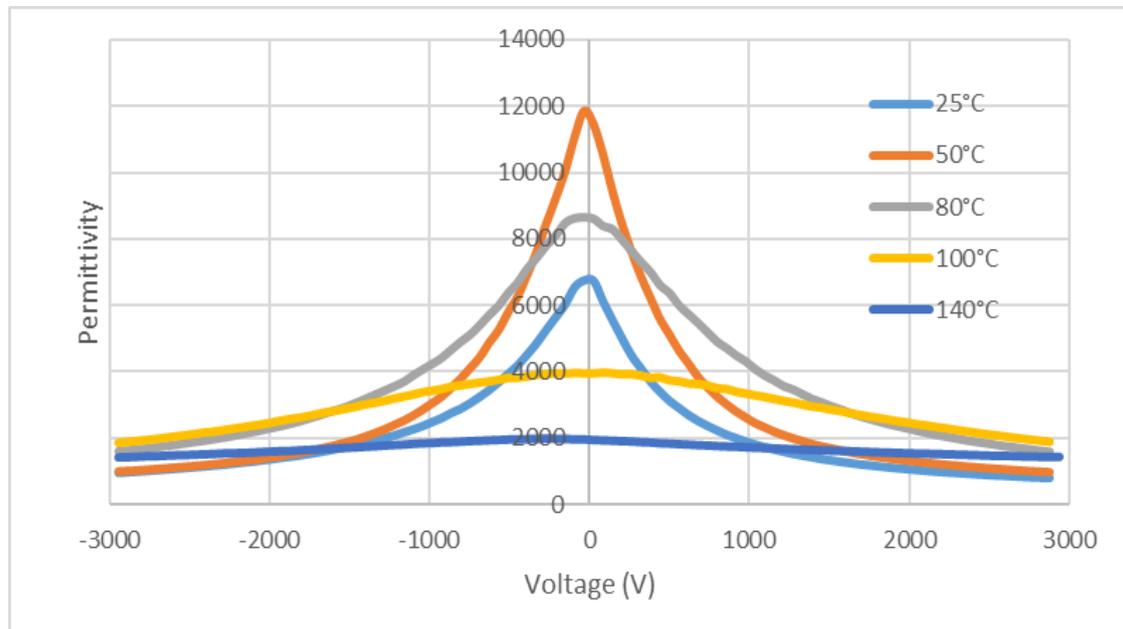


Figure 21. Capacitance vs. BIAS voltage measured for BCST ceramics (Curie Temperature $\sim 65^\circ\text{C}$) prepared by Process 1. technique at different temperatures.

BCST results vs pure BT

The BCST dielectric key parameter differences versus pure BaTiO₃:

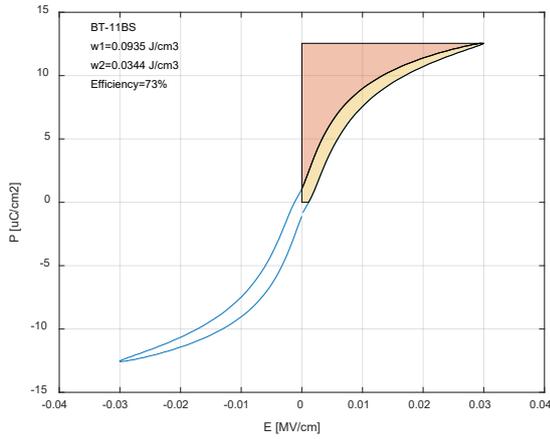
- Curie temperature lowered from $\sim 130^\circ\text{C}$ to $\sim 65^\circ\text{C}$
- Higher dielectric constant (2x in relative comparison to our reference samples)
- 40% increase of energy density vs reference BT sample
- Higher dielectric losses, efficiency below 70%

BCST evaluation summary

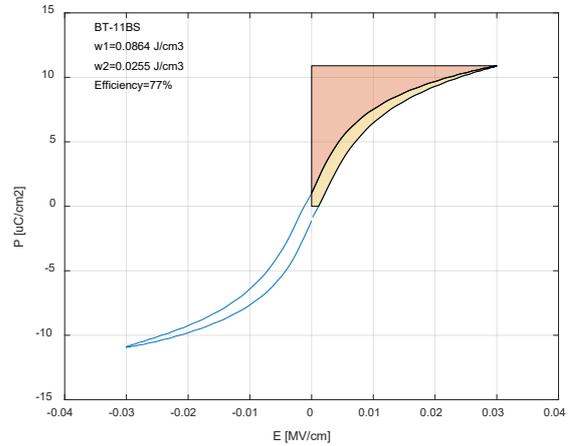
The BCST dielectric material shows increase of dielectric constant and energy density versus reference pure BT material, however **the material shows high level of dielectric losses that disqualify this ceramic material as suitable capacitor dielectric.**

5.3. BT-11BS BaTiO₃-11BaSnO₃ Ceramic Material Evaluation

P-E loops measured at frequency **1 Hz** for two BT-11BS samples prepared at calcination temperature 1150°C and sintering temperature 1400°C are shown in Figure 22. The efficiency of charge/discharge process is in the range 73 to 77% for the samples within a batch.



a) Sample 03 of BT-11BS ceramics



b) Sample 07 of BT-11BS ceramics

Figure 22: *P-E* loops measured at 1 Hz for sample BT-11BS prepared by solid state reaction. Highlighted area represents energy storage density and a loss energy density.

Curie temperature of BT-11BS material, where the peak of dielectric constant value is obtained, is slightly above 37°C – see Figure 23, that may find a benefit for wearable applications operating at human body temperature.

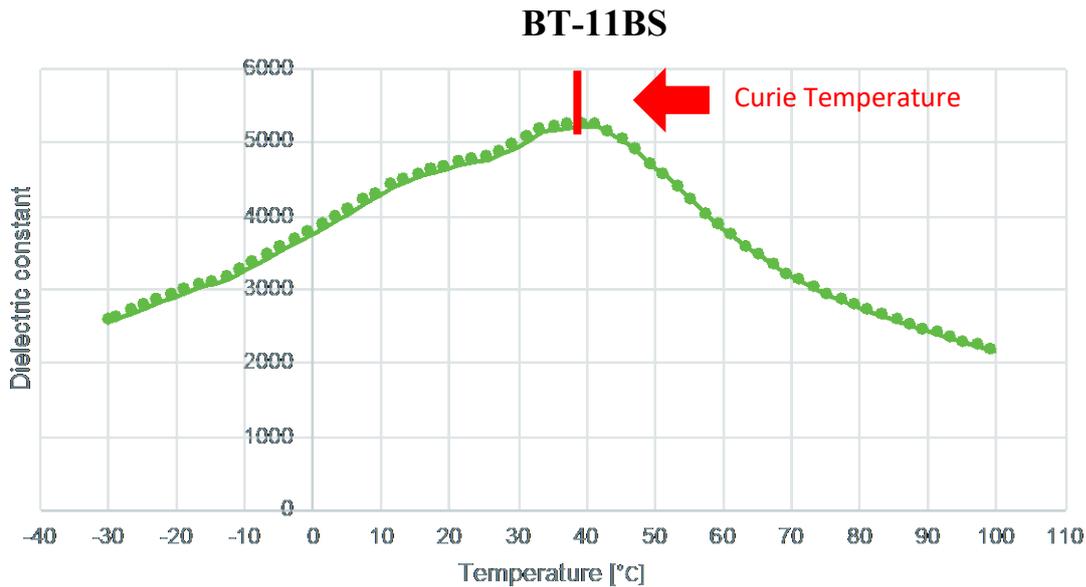


Figure 23. Temperature dependence of dielectric constant of BT-11BS ceramic

Figure 24 shows the dependence of dielectric constant on the electric field at room temperature for BT-11BS ceramic at sintering temperature 1400°C. The difference between the parameters of the samples within the batch is within $\pm 10\%$.

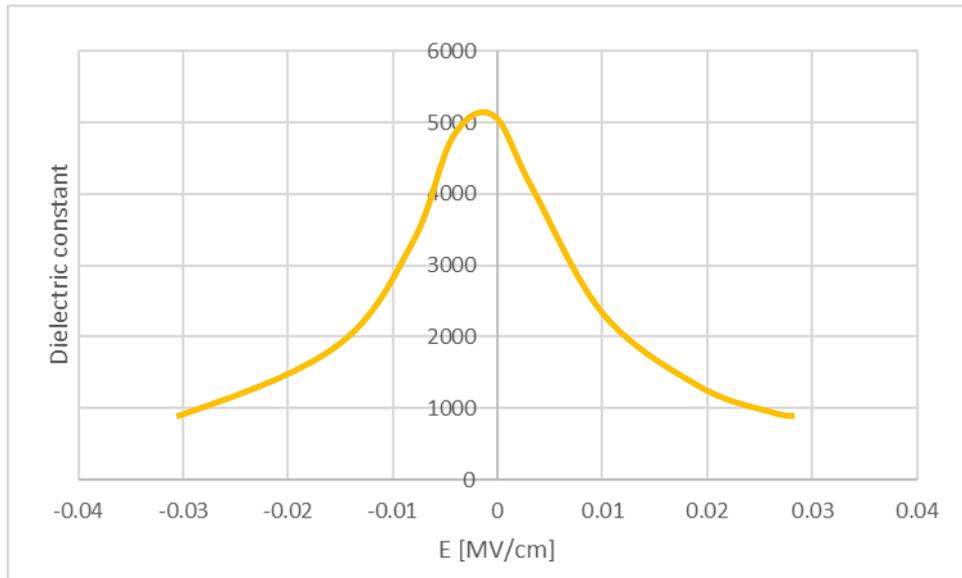


Figure 24. Dielectric constant vs electric field at room temperature of BT-11BS ceramic

The summary of results measured on reference samples of BT-11BS ceramic is given in Table 3. Here the Energy storage density, Loss energy density, Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz, and ϵ_r and $\tan \delta$ measured at frequency 1 kHz is shown.

Tab3.: Energy storage density, Loss energy density and Efficiency of charge/discharge cycle determined from P - E loops measured at frequency 1 Hz; ϵ_r and $\tan \delta$ measured at frequency 1 kHz for BT-11BS

Sample	Sintering Temp. [°C]	ϵ_r	$\tan \delta$	Energy Density 1 Hz [J/cm ³]	Loss energy Density 1 Hz [J/cm ³]	η 1 Hz [%]	Breakdown field [V/□m]
BT-11BS1	1400	5314	0.0232	0.0935	0.0344	73%	25*
BT-11BS2	1400	4249	0.0327	0.0864	0.0255	77%	25*

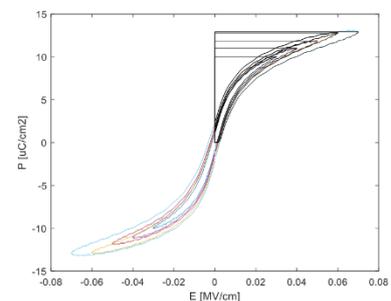
Notes: *measured on the sample from batch until destructive breakdown

Energy density vs Electrical Field

Samples of the BT-11BS were also subjected to evaluation of impact of high electrical field to obtained energy density values – see Tab 4 and illustration impact to P - E characteristics.

Tab 4.: Electrical field versus energy density and its impact to P - E loops (right) for BT-11BS material

E_{max} [MV/cm]	Energy Density [J/cm ³]	Loss energy Density [J/cm ³]	η [%]
0.03	0.0800	0.0243	77
0.04	0.1055	0.0432	71
0.05	0.1272	0.0678	65
0.06	0.1923	0.0646	75
0.07	0.1626	0.1402	54



The highest energy densities achieved was 0.19J/cc at 6V/mm electric field, and 75% efficiency. P-E loop of this sample is shown in Figure 25.

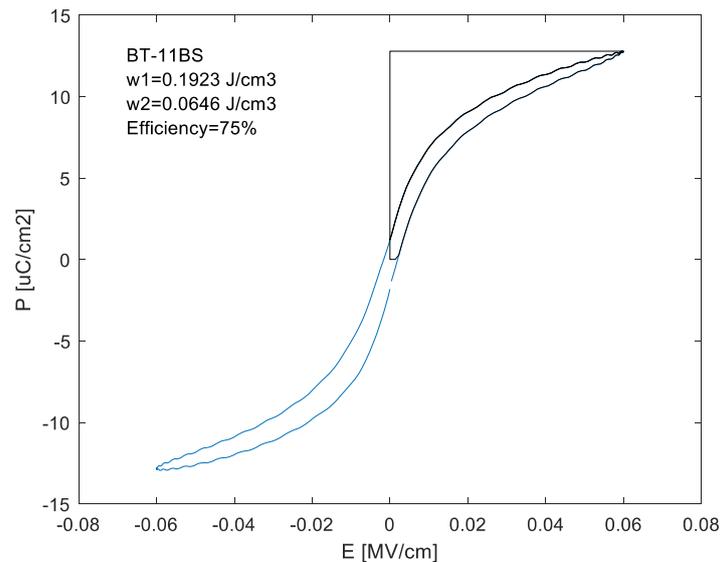


Figure 25: P-E loops measured at 1 Hz for the highest energy density of BT-11BS at 6V/mm

BT-11BS results vs pure BT

The BT-11BS dielectric key parameter differences versus pure BaTiO₃:

- Curie temperature lowered from ~130°C to ~37°C
- **Higher dielectric constant** (2x in relative comparison to our reference samples)
- **High electrical field strength above 7V/mm**
- **Up to 4x higher energy density vs reference BT sample**
- High efficiency above 75%

BT-11BS evaluation summary

The BT-11BS dielectric material shows increase of dielectric constant and energy density versus reference pure BT material while efficiency is also kept at high level. **The BT-11BS material shows high potential for further evaluation as a high energy, high electrical field capacitor dielectric material.**

6. BT-11BS OPTIMISATION as CERAMIC DIELECTRIC MATERIAL

BaTiO₃-xBaSnO₃ ceramic system permittivity and its piezo characteristics have been already studied in scientific papers [8], however the main scope was to maximize its permittivity to achieve best piezo-electric features. Figure 26 is showing its crystal structure changes versus temperature and confirms that BT-11BS feature the highest permittivity among the BT-xBS system according to [8].

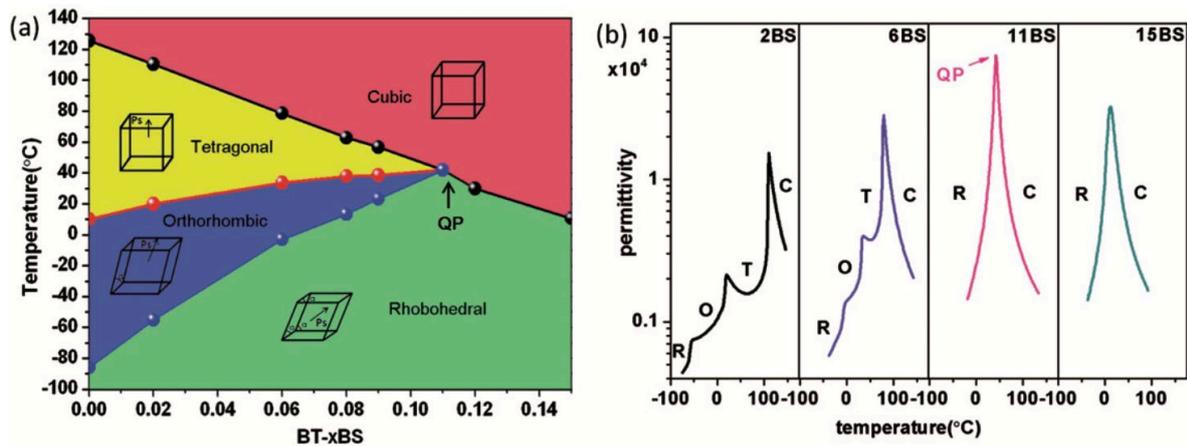


Figure 26. Crystal structure (left) and permittivity values of BT-xBS ceramic material; source [8]

The BT-11BS material has a cubic crystal structure in temperatures above 37°C and rhombohedral structure in lower temperatures according to the source. It shall be noted that the peak high relative permittivity on BT-11BS in reference around 70K may achieve a good feature for piezo-electric applications, but it may not be optimized for capacitor dielectric where electrical field strength and dielectric losses may degrade its high energy storage capabilities.

The maximum of the BT-11BS dielectric constant was found to be ~ 17K at 41 °C on material prepared in reference [9]. The recovered energy density was 0.08 J/cm³ and 91% efficiency at 60 °C and the BT-11BS was considered as a potential material for further energy storage capability study.

Our next task for BT-11BS optimization as capacitor dielectric material included:

- preparation of the ceramic material by different techniques to achieve homogeneous microstructure with good functional properties.
- preparation of the ceramic material using different particle size to evaluate its impact to the material features.
- perform capacitance measurements and characterization

6.1. BT-11BS Samples Preparation

BT-11BS Particle Size Structure Optimization

For the optimization of this ceramic system, we studied the impact of particle size and sintering temperature for samples synthesized by **Process 2.** and **Process 3.** methods. Particle size of the ceramic powder was 100nm and 5µm, respectively. Four different sintering temperatures were chosen: 1380°C, 1400°C, 1420°C and 1440°C. This technology tuning resulted in eight different samples, which were further evaluated.

6.2. BT-11BS Process 2. Test Results

The dependences of dielectric constant on the temperature in the range 20 to 70°C is shown in Figure 27 for samples BT-11BS prepared by **Process 2.** with particle sizes 100nm and 5 µm and sintering temperatures 1380°C, 1400°C, 1420°C and 1440°C. Curie temperature, where the peak of dielectric constant value is obtained, is at temperature 42°C for samples of particle size 5 µm and at temperature 46°C for samples of particle size 100 nm, respectively.

Dielectric constant peak value varies with sintering temperature and particle size. For samples of particle size 100 nm the value is in the range approx. 18600 to 21000, while the value is in the range approx. 25700 to 41000 is achieved for samples of particle size 5 µm. The highest dielectric constant value is observed for sintering

temperature 1440°C in the case of samples of particle size 5 μm , and for sintering temperature 1420°C in the case of samples of particle size 100 nm.

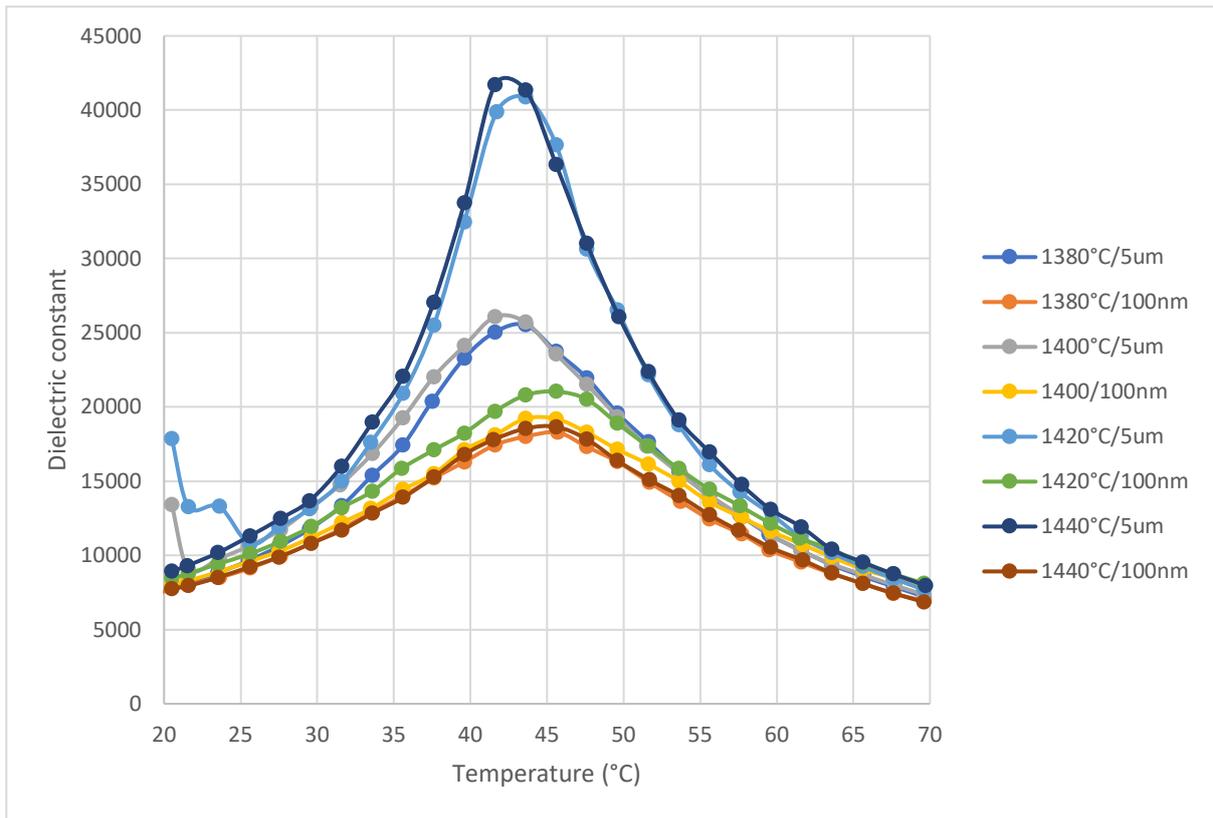


Figure 27. Temperature dependence of dielectric constant for samples BT-11BS prepared by Process 2. – particle sizes 100nm and 5 μm , sintering temperatures 1380°C, 1400°C, 1420°C and 1440°C

Tables 5 and 6 show the dimensions of prepared disk samples, measured capacitance and $\tan \delta$ values (at room temperature) and calculated value of dielectric constant for all BT-11BS samples prepared by Process 2.

Tab 5.: Sample thickness t , electrode diameter d , capacitor active area A ; Capacitance C_T and $\tan \delta$ measured at frequency 1 kHz and calculated dielectric constant ϵ_r for BT-11BS samples prepared by Process 2. – particle size 100nm, different sintering temperatures.

Sample No.	sintering temperature [°C]	t [mm]	d [mm]	A [mm ²]	C_T [nF]	$\tan \delta$	ϵ_r
100 1380 1	1380	0.90	10.89	92.75	7.12	0.048	7803
100 1380 2	1380	1.03	10.56	88.70	6.42	0.052	8420
100 1400 1	1400	0.86	10.89	91.00	7.30	0.055	7792
100 1400 2	1400	0.87	10.89	92.70	7.93	0.054	8406
100 1420 1	1420	0.94	10.91	93.00	7.68	0.056	8767
100 1420 2	1420	0.87	10.81	93.00	5.54	0.055	5853
100 1440 1	1440	0.86	10.70	92.00	7.60	0.058	8024
100 1440 2	1440	0.94	10.80	89.00	6.32	0.059	7539

Tab 6.: Sample thickness t , electrode diameter d , capacitor active area A ; Capacitance C_T and $\tan \delta$ measured at frequency 1 kHz and calculated dielectric constant ϵ_r for BT-11BS samples prepared by Process 2. – particle size 5 μm , different sintering temperatures.

Sample No.	sintering temperature [°C]	t [mm]	d [mm]	A[mm ²]	C _T [nF]	tan δ	ε _r
5 1380	1380	1.08	11.29	94.00	6.08	0.056	7890
5 1400	1400	1.05	11.29	97.00	6.49	0.055	7935
5 1420	1420	1.10	10.89	91.00	6.25	0.061	8533
5 1440	1440	1.10	10.77	88.00	6.45	0.06	9106

Energy density comparison determined from P-E loops at room temperature for all *Process 2*. samples is shown in Figure 28. Higher energy density values are observed for samples with particle size 100 nm for all sintering temperatures. The efficiency of charge/discharge process is about 70% for 100 nm samples, while efficiency from 60% (sintering temperature 1380 to 1420°C) to 70% (sintering temperature 1440°C) is determined for 5 μm samples. Impact of sintering temperature on the energy storage properties is smaller comparing to the impact of the ceramic particle size. For smaller particle size, higher energy density is achieved.

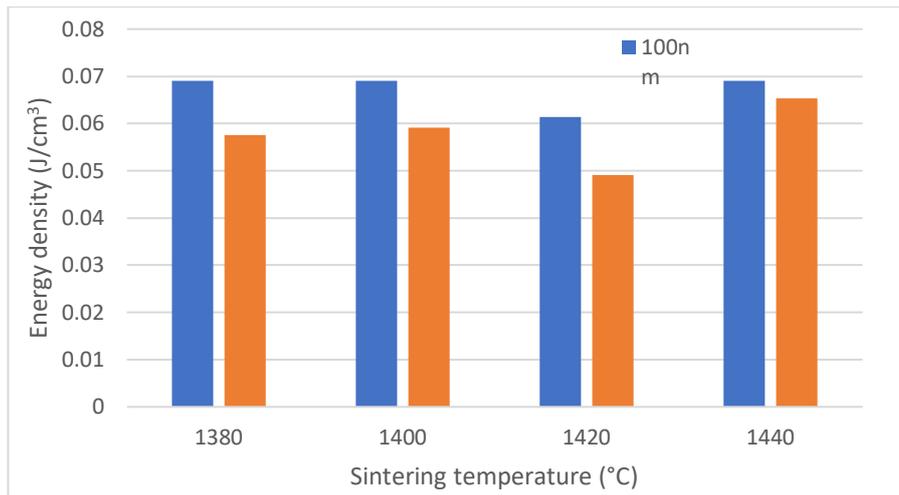


Figure 28: Energy density determined from P-E loops (1 Hz, room temperature) for samples BT-11BS prepared by *Process 2*. n – particle size 100nm (blue), particle size 5 μm (red), different sintering temperatures.

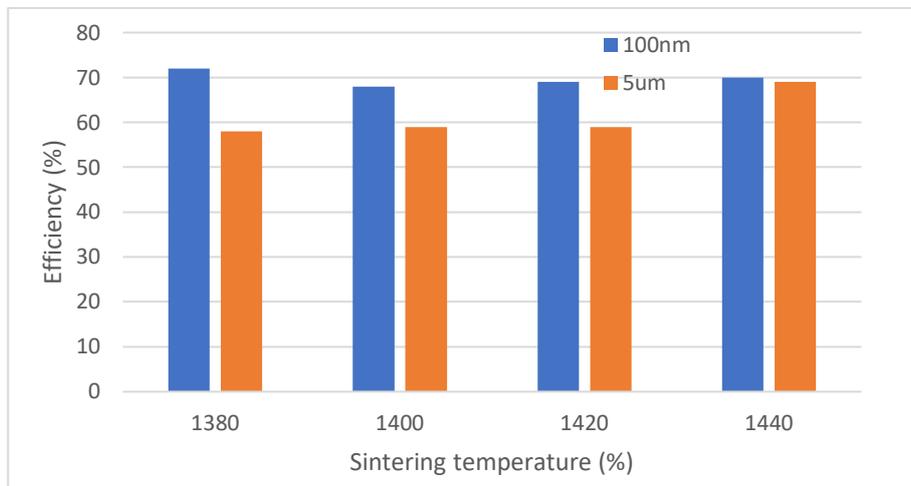


Fig. 29: Efficiency of charge/discharge cycle determined from P-E loops (1 Hz, room temperature) for samples BT-11BS prepared by *Process 2*. – particle size 100nm(blue), particle size 5 μm (red), different sintering temperatures.

Energy density (see Figure 30) and Efficiency of charge/discharge cycle (see Figure 30) was determined from P-E loops for temperatures 21°C, 37°C, 45°C and 55°C. We can see that Energy density increases with temperature in the whole temperature range. Efficiency of charge/discharge cycle increases up to the Curie

temperature (about 46°C) and remains stable with additional temperature increase. It seems that **optimal properties** with respect to the **energy storage** are reached when **operating the ceramic samples at temperature just above the Curie point**. The increase of Energy density between the room temperature and 55°C is about 30%.

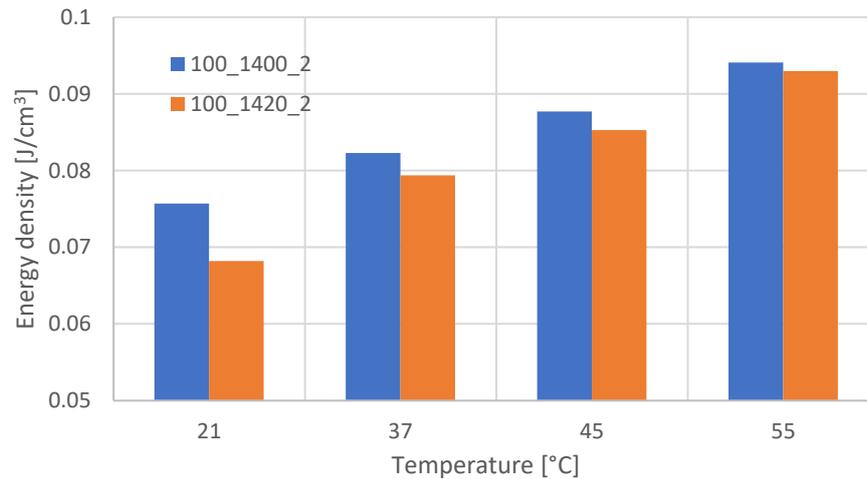


Figure 30: Energy density determined from P-E loops measured at temperatures 21°C, 37°C, 45°C and 55°C for sample No. 100_1400_2 – particle size 100nm, sintering temperature 1400°C (blue), and sample No. 100_1420_2 – particle size 100nm, sintering temperature 1420°C (red)

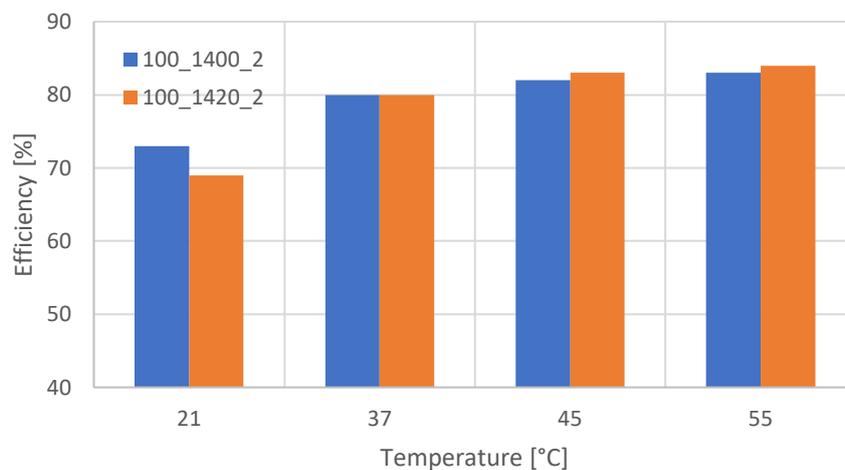


Figure 31: Efficiency of charge/discharge cycle determined from P-E loops measured at temperatures 21°C, 37°C, 45°C and 55°C for sample No. 100_1400_2 – particle size 100nm, sintering temperature 1400°C (blue), and sample No. 100_1420_2 – particle size 100nm, sintering temperature 1420°C (red)

The reason for the increase of energy density and Efficiency of charge/discharge cycle can be determined from the dependence of the dielectric constant on the applied voltage (electric field on the sample). Figure 32 shows the dependence of dielectric constant on the applied voltage in the range -800 to +800 V for five different temperatures in the range approx. 25°C to 70°C.

Peak Electric field calculated as maximum applied voltage over sample thickness is in the range 0.82 to 0.92 kV/mm for samples with particle size 100 nm (all sintering temperatures). Dielectric constant decreases with increased electric field for all temperatures, but the closer we are to the Curie temperature (about 46 °C for these samples), the higher is both peak value of dielectric constant as well as the dielectric constant value for maximum applied voltage. However, for temperature above the Curie point the decrease of dielectric constant with electric field is considerably slower – see Figure 32. and Figure 33.

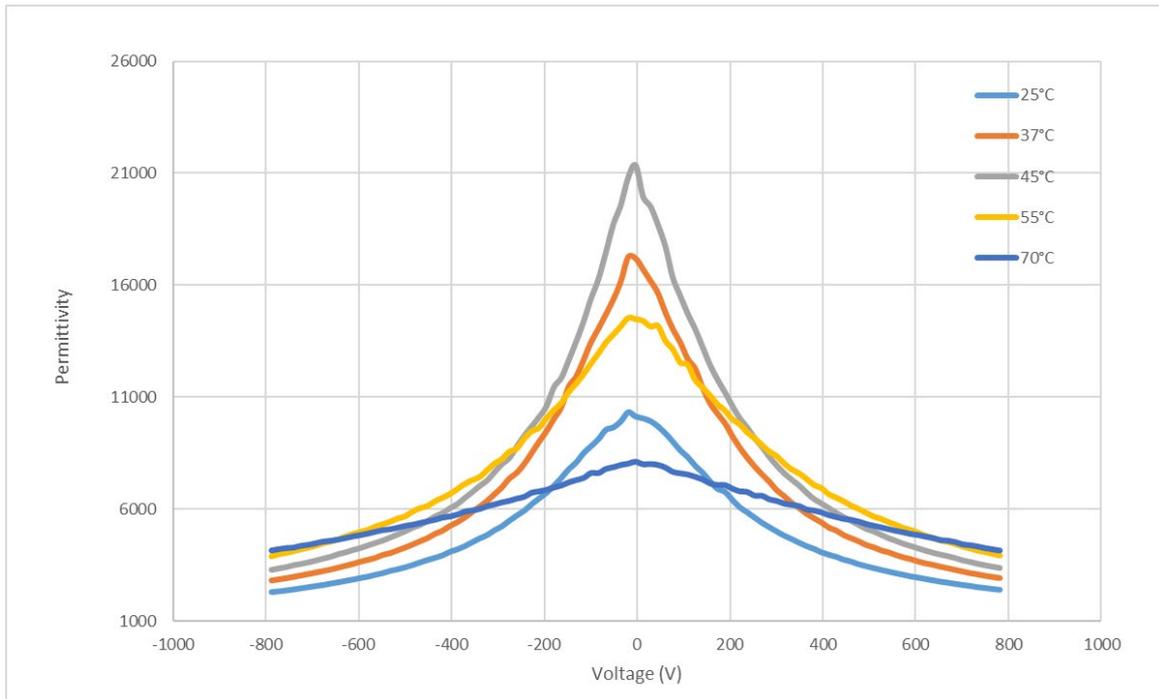


Figure 32: Capacitance vs. BIAS voltage measured for BT-11BS ceramics sample 100nm_1420°C/4h (Curie Temperature ~ 37°C) prepared by Process 1. technique at different temperatures.

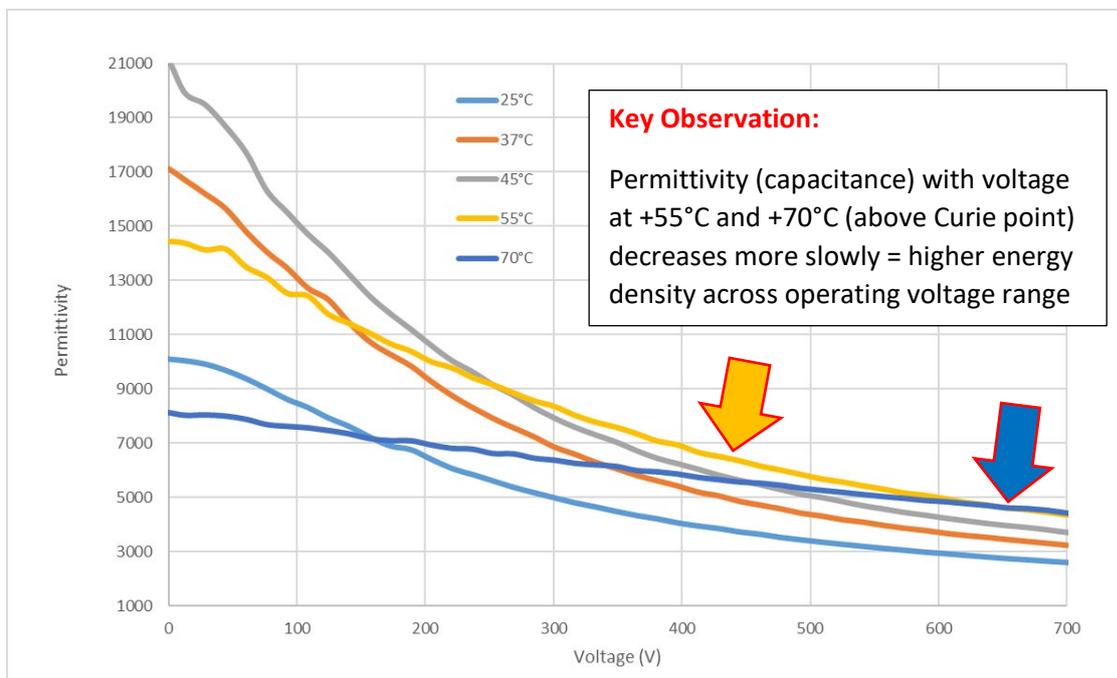


Figure 33: Zoom

from Figure 32. dielectric constant vs applied voltage.

This phenomenon has been observed also in the case of pure BT reference material – see Figure 17., and BCST material – Figure 21, where capacitance dependence with voltage was flatter for temperatures above the Curie Temperature. Based on this observation we can assume that this behaviour is not specific to the BT-11BS material, but common for ferroelectric ceramic dielectrics.

6.3. BT-11BS Process 3. Test Results

The dependences of dielectric constant on the temperature in the range 22 to 50°C is shown in Figure 33 prepared by Process 3. Curie temperature, where the peak of dielectric constant value is obtained, is at temperature approximately 42°C. Dielectric constant varies in the range 2760 to 2870 within the studied temperature range. Comparing to the SSR technology the dielectric constant variation with temperature is negligible.

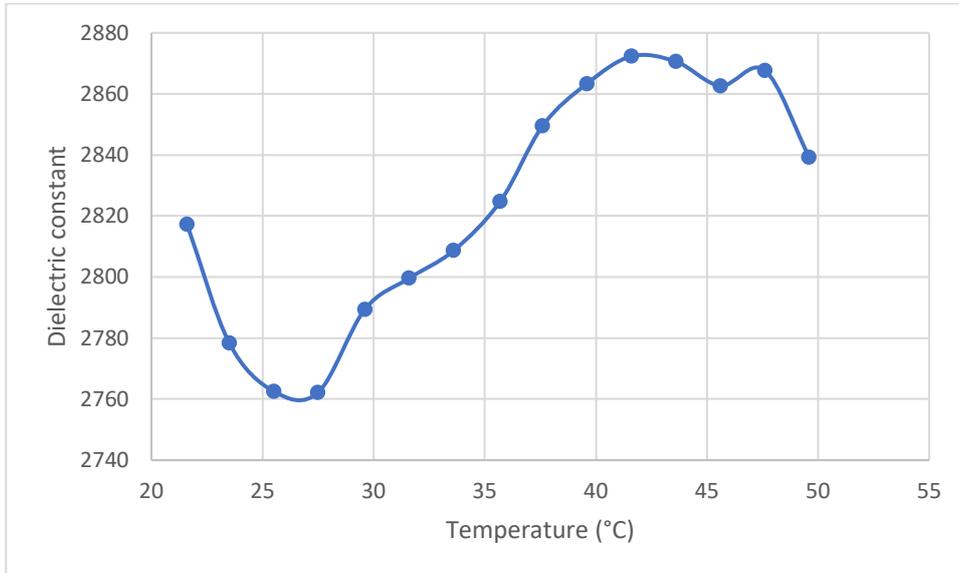


Figure 33. Temperature dependence of dielectric constant on BT-11BS prepared by Process 3.

P - E loops measured at frequencies 1 Hz and 10 Hz at temperature 24°C are shown in Figure 34 for maximal electric field $E_{max} = 7$ kV/mm. Energy density determined from P - E loops for frequency 1 Hz is about 0.28 J/cc and increases for about 15% to 0.33 J/cc. Similarly, Efficiency of charge/discharge cycle determined from P - E loops for frequency 1 Hz is 87% and increases to 89% for measuring frequency 10 Hz.

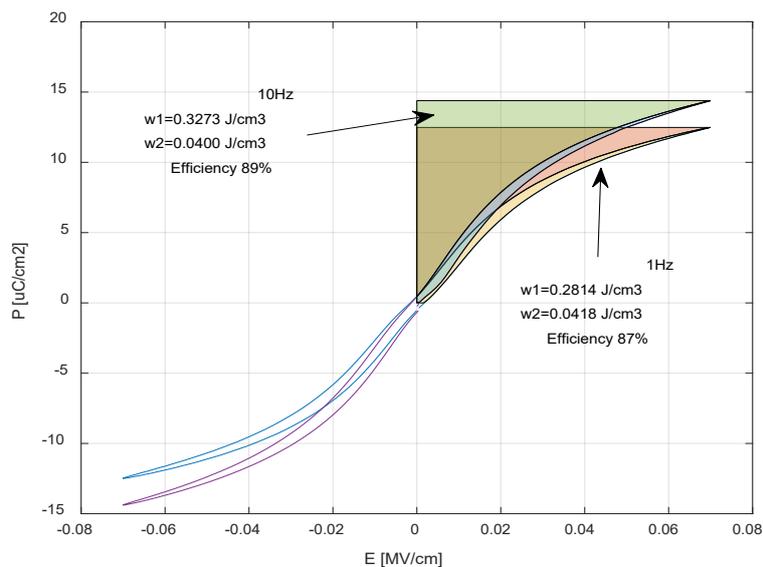


Figure 34: P - E loops measured at frequencies 1 Hz and 10 for maximal electric field $E_{max} = 7$ kV/mm, measured at temperature 24°C on BT-11BS prepared by Process 3.

P - E loops measured at frequency 1 Hz at temperature 24°C are shown in Figure 35 for maximal electric field $E_{max} = 9$ kV/mm. Energy density determined from P - E loops for frequency 1 Hz is about 0.42 J/cc.

The dependence of dielectric constant on electric field at temperature range from 25°C to 100°C is shown in Figure 36. Dielectric constant decreases with electric field just for about 30% at electric field 3 kV/mm and permittivity

decrease within the temperature range is just below 10%. This decrease is reasonably lower than that observed for 11BST samples prepared by solid-state reaction process with about 80 to 90% drop at comparable electric field value.

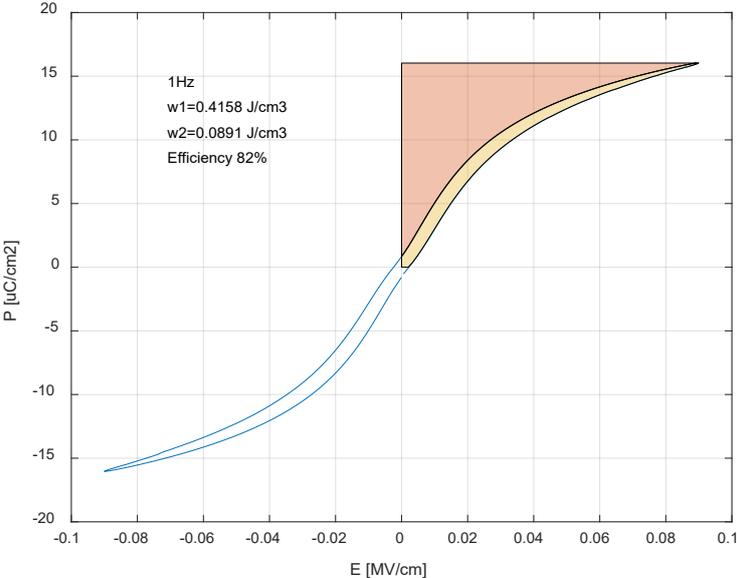


Figure 35: P-E loop measured at 1 Hz for maximal electric field $E_{max} = 9 \text{ kV/mm}$ on BT-11BS prepared by Process 3., measured at temperature 24°C

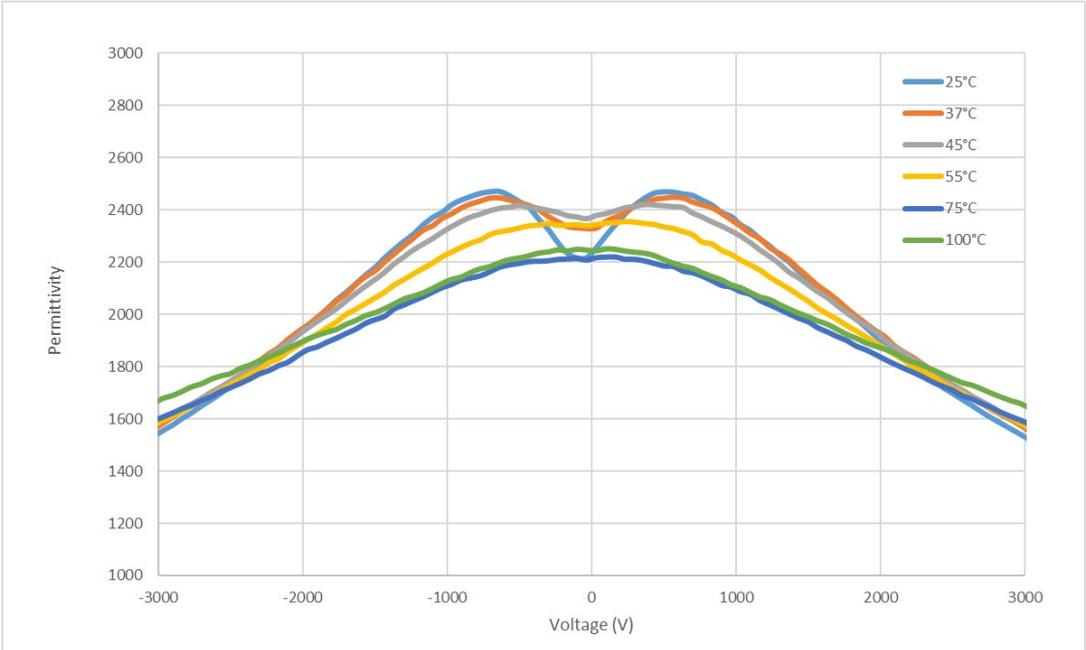


Figure 36. Capacitance vs. BIAS voltage measured for BT-11BS ceramics (Curie Temperature $\sim 37^\circ\text{C}$) prepared by Process 3. technique at different temperatures.

6.4. BT-11BS Optimization Results and Discussion

6.4.1. BT-11BS Process 2. Test Summary

BT-11BS material in its first evaluation showed some potential benefits with promising shape of E-P loop and efficiency above 75%. The impact of particle size and sintering temperature was studied on eight samples synthesized by the conventional solid-state method.

The optimized material prepared by conventional solid-state method showed increase of efficiency >80% and the permittivity up to 16K at 37°C temperature (~8K at room temperature) with overall energy densities around **twice higher compared to pure BT reference sample** (~0.1 J/cc @1Hz).

The increase of energy density as well as energy efficiency when operating the structure above the Curie temperature is an interesting finding illustrated in figures 30 and 31. **The permittivity at temperatures above the Curie point is more stable with voltage.**

The energy density may increase further with higher frequencies such as 100Hz and ED may increase in thin layers – for example prepared by tape casting MLCC manufacturing process.

6.4.2. BT-11BS Process 3. Test Summary

BT-11BS material prepared by Process 3. technique resulted in fine particle size, dense, homogenized structured material with different features compare to the materials prepared by Process 2. method.

The Process 3. material shows **lower permittivity** in range of ~ 3K at room temperature but **increased electrical strength** that allowed application of electrical field up to 0.09 MV/cm (vs 0.03 MV/cm in the case of conventional solid-state method).

Capacitance of Process 3. prepared samples drops at maximum voltage by ~50% vs ~80% drop on conventional methods (for comparable electric field). This results in significantly **lower dependence of its permittivity / capacitance to applied voltage and increase of energy density at higher electrical fields.**

The maximum energy density achieved was **0.4 J/cc** at 82% efficiency, that is **~10x higher energy density** compared to the reference pure BT material at 1Hz.

The Process 3. samples in our lab scale preparation had a limitation in too high thickness of test samples with very high breakdown voltage. Thus, to be able to analyse the sample disks in our test devices we had to grind and polish the sample to enable the measurement. These processes may degrade the pure material capabilities by some degree, thus in reality performance of the BT11-PS material prepared by Process 3. method may be even higher compare to the test results presented herein.

The energy density may increase further with higher frequencies such as 100Hz and it may present state of the art energy density in ceramic dielectric materials.

7. SUMMARY

- Methodology of using E-P hysteresis loop for dielectric material characterisation have been applied as the best suitable method for the first efficient evaluation at the existing lab scale environment.
- Ferroelectric BT-11BS known from its use in piezo devices was proved as the best candidate for high energy density ceramic dielectrics.
- BT-11BS material particle size and sintering temperatures have been subjected to optimization resulting in improvement of the material prepared by conventional solid-state synthesis method exceeding energy density of currently mass use pure BaTiO₃ material.
- An interesting finding is that lowering Curie temperature of ferroelectric materials may increase electric density even further as the permittivity does not drop with voltage so rapidly when operating above the Curie temperature. This has been demonstrated on low Curie Temperature BT-11BS, BCST but also on pure BT material (at temperature of 160°C above CT). This behaviour is also not dependant to the fabrication process – observed in the same materials prepared by both Process 1., Process 2. and Process 3. methods, thus it can be considered as a **general feature of ferroelectric materials.**

- Advanced method of material preparation using Process 3. method yielded into a sample with fine, dense particle structure and further improved ED values in range of 10x versus reference pure BT samples. BT-11BS samples prepared by the Process 3. method were too thick that was difficult to analyse, and it had to be grinded that may impact on the final performance. Thus, further room present for the process optimisation to achieve even better results.
- Other preparation technologies such as Tape Casting or Cold Sintering may be more suitable to prepare thinner layer of the BT-11BS material to fully evaluate its potential for MLCC technology.

8. CONCLUSIONS

The research presented in this report identified BT-11BS ceramic ferroelectric material as a potential candidate for high energy density storage dielectric material with advantages of use especially as a high voltage, high energy capacitor with a stable capacitance vs BIAS and temperature performance.

Particle size, sintering temperature and use of different manufacturing methods to prepare BT-11BS layer were subjected to our lab optimization to maximize its energy density and capacitance stability. The maximum achieved energy density in our lab was **~4-10x higher energy density compared** to the reference pure BT material depending to the manufacturing process.

The highest energy density on BT-11BS (10x higher ED than BT reference) was achieved using **Process 3.** method that produced very fine, dense ceramic dielectric structure with lower permittivity **~3K** at room temperature but increased electrical strength that allowed application of **very high electrical field up to 0.09 MV/cm** (vs 0.03 MV/cm in the case of conventional solid-state method). Permittivity/capacitance drop with DC voltage has been also much lower (~ 30% at high electric field) compare to conventional methods (~ 90%). Permittivity/capacitance is also very stable with temperature – see Fig.36 – within 10% change between 25°C and 100°C. Process 3. method may be especially suitable for high voltage SLCC single layer ceramic capacitors to further increase its energy density at high operating voltages over kV range.

Interesting finding of the research is that permittivity/capacitance of general ferroelectric ceramic materials operated above Curie temperature decrease less with BIAS voltage and thus its overall energy density is higher as demonstrated on all tested materials pure BT, BCST and BT-11BS. This may be especially beneficial at high voltage field i.e., high energy density and high voltage capacitors.

These findings present a potential focus for development of the next generation capacitor ceramic materials with low Curie temperature featuring higher energy densities compare to the current state of the art.

BT-11BS is readily available material used and known for its piezoelectric features in piezo devices. It can be prepared and processed into a standard paste form used in mass ceramic capacitor manufacturing today such as screen printing and tape casting, thus it can be considered as compatible with the existing ceramic capacitor high manufacturing volume process and equipment.

The presented results of our research may pose a potential for further domination and growth of ceramic technology over the other capacitor technologies in wide range of higher energy density capacitor applications from ultraminiature smartphones through automotive to renewable energies and medical.

9. ACKNOWLEDGEMENT

Authors would like to express thanks to Bernd Pretzlaff, Janosch Lichtenberger, and Volker Lang for their support and advise for this scientific result.

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