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Enhanced near-ambient temperature energy storage and electrocaloric effect in the lead-free BaTi_{0.89}Sn_{0.11}O₃ ceramic synthesized by sol-gel method

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Abstract

Lead-free perovskite materials with high performance have high potential in clean energy storage applications and developments of electrocaloric devices. In this work, we report structural, dielectric, ferroelectric properties, energy storage and electrocaloric effect near the ambient temperature in barium stannate titanate (BaTi_{0.89}Sn_{0.11}O₃, BTS₁₁) ceramic prepared by a sol-gel method. The formation of a single perovskite structure was confirmed using the X-ray diffraction analysis. An average grain size of 18.5 μm was found by the mean of the SEM micrograph with a density of 5.91 g/cm³. The presence of the multiphase at very near ambient temperature was proved using temperature-dependent micro-Raman measurements and differential scanning calorimetry. The BTS₁₁ ceramic exhibits a high dielectric constant of 15460 and a low dielectric loss (<0.055) with considerable temperature stability. Moreover, a high energy storage density of 122 mJ/cm³ was showed with an efficiency of 79%, and a maximum value of ECE (ΔT) of 0.86 K and finally, an electrocaloric responsivity (ΔT/ΔE) of 0.24 K.mm/kV under the external electric field of 35 kV/cm near ambient temperature. The enhanced dielectric, ferroelectric and electrocaloric properties in BTS₁₁ ceramic makes it a great potential candidate for its uses in solid-state cooling technology and high-energy storage applications near ambient temperature.

Keywords: Lead-free, sol-gel process, energy storage, electrocaloric effect, ambient temperature, barium stannate titanate.

Declarations

Funding

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40 **Conflicts of interest/Competing interests**

41 Not applicable

42

43 **Availability of data and material**

44 Not applicable

45 **Code availability**

46 Not applicable

47

48 **Ethics approval**

49 Not applicable

50

51 **Consent to participate**

52 We confirm that all authors mentioned in the manuscript have participated in, read and approved the manuscript
53 and have given their consent for the submission and subsequent publication of the manuscript.

54

55 **Consent for publication**

56 We confirm that all the authors mentioned in the manuscript have agreed to publish this paper.

57

58 **Relevance Summary**

59 In the submitted manuscript, I am reporting, the successful synthesis of barium stannate titanate ceramics by sol-
60 gel method, and the study of their structural, dielectric, ferroelectric, energy storage, and electrocaloric properties.

61 In addition, we confirm that this work is original and has not been published elsewhere, nor is currently under
62 consideration for publication elsewhere.

63

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68 Higher Education of the Russian Federation, grant agreement No 075-15-2021-953.

69

70 **1. Introduction:**

71 Earlier studies and applications using ferroelectric properties of perovskite structural materials were carried out
72 with lead-based materials such as lead-titanium zirconate (PZT)[1] and magnesium niobate-lead-titanate (PMN-
73 PT)[2]. Unfortunately, due to lead toxicity[3], these lead-based materials can be harmful to the environment or
74 human health, hence the need to develop clean and environmentally friendly lead-free material with improved
75 ferroelectric properties.

76 Barium titanate (BaTiO₃, BT) and its derivatives were the first lead-free perovskite materials studied and used for
77 dielectric capacitors since 1950 [4]. These materials are eco-friendly and can be used to develop new lead-free
78 materials with high piezoelectric, electrocaloric and energy storage properties[5].When doped with isovalent
79 cations, the electrical and dielectric properties of BT tend to improve. Many systems have been studied over the

80 years, including the BCZT ($\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$) system, which consists of calcium cation substitution on the
81 A site and zirconium cation substitution on the B site [6], and BST ($\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$) where the strontium is doped in
82 the A site [7]. The BTS ($\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$) system, on the other hand, is designed by inserting tin cations Sn^{4+} in the B
83 site [5],[8],[9],[10]. Nonetheless, most of these materials tend to achieve significant energy storage and
84 electrocaloric properties only around the Curie temperature when the ferroelectric to paraelectric transition occurs,
85 i.e. in a narrow temperature range, limiting their applications. The emphasis is primarily on lead-free materials
86 with diffuse phase transition that leads to a wider temperature range near ambient temperature, where the energy
87 storage and the electrocaloric properties are improved [11].

88 In this regard, the Curie temperature has been reported to decrease from 120°C for the undoped BT system, to
89 40°C, 41°C and 37°C in the BTS systems [5,9,12]. As a result of the coexistence of the four phases, cubic,
90 tetragonal, orthorhombic, and rhombohedral (R, O, T, and C) at the quadruple point near the ambient temperature
91 (AT), defined as 25 °C by the International Union of Pure and Applied Chemistry (IUPAC), the BTS_{11} could
92 achieve an extremely high dielectric constant, a high piezoelectric coefficient, enhanced energy storage, and a
93 significant electrocaloric effect [9]. However, the dielectric peak remained noticeably sharp in all studied
94 compositions. Gao et al. [12] conducted the study of the $\text{Ba}(\text{Ti}_{1-x}\text{Sn}_x)\text{O}_3$ ferroelectric material system with various
95 compositions, and came to the conclusion that one aspect that requires to be addressed further is the poor
96 temperature stability of the BTS system properties.

97 The most commonly used method for elaborating dense and performant BTS ceramics is the solid-state method,
98 which produces non-homogeneously doped powders with a high risk of contamination and agglomeration, it also
99 necessitates a high calcination temperature (1250 °C) [8]. However, the sol-gel method, which is also commonly
100 used in thin film synthesis [13][14][15][16], is a simple and precise method that can produce a more uniform and
101 fine powder with better stoichiometry control, resulting in improved dielectric and ferroelectric properties. and it
102 also requires lower heating temperatures [17].

103 In the present study, structural, dielectric, ferroelectric and electrocaloric properties were investigated in
104 $\text{BaTi}_{0.89}\text{Sn}_{0.11}\text{O}_3$ ceramic (BTS_{11}) and found to be enhanced around ambient temperature in a broad temperature
105 range. Therefore, the BTS_{11} ceramic can be a suitable candidate for ambient temperature energy storage and
106 frigorific applications.

107 **2. Experimental details:**

108 **2.1. Chemicals:**

109 In order to prepare the BTS_{11} ceramics, barium acetate $\text{Ba}(\text{CH}_3\text{COO})_2$, titanium isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) and
110 tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) were used as raw materials, whereas acetic acid and 2-Methoxyethanol were used as the
111 solvents. All reagents and solvents were of chemical grade and used without any further purification.

112

113

114 **2.2. Experimental methods:**

115 The XRD patterns were obtained by X-ray diffraction using the Panalytical X-Pert Pro with Cu-K α radiation ($\lambda =$
116 1.54059 Å) at room temperature ranging from 20° to 80°, while the surface morphology of the ceramic was
117 examined using a scanning electron microscope (SEM, VEGA 3-Tescan). The density of the ceramic sample was
118 determined by the Archimedes method. The micro-Raman Raman spectra were excited by the polarized radiation

119 of an argon laser with $\lambda = 514$ nm and were measured using a Renishaw in Via Reflex Raman spectrometer
120 equipped with an Edge-filter. Temperature-dependent micro-Raman measurements were performed by a Linkam
121 THMS600 heating and freezing stage with a temperature stability of 0.1 K. The dielectric properties temperature
122 dependence was measured using an impedance analyzer (HP 4284A) in the temperature range of 20 to 80 °C, and
123 at frequency ranges of 20 Hz-100 kHz. Differential scanning calorimetry (Perkin Elmer Jade DSC) was used to
124 point out the different phase transitions in a temperature range of -20 to 100 °C. The polarization-electric field (P-
125 E) hysteresis loops were performed by CPE1701, PloyK, USA, with a high voltage power supply (Trek 609-6,
126 USA) in a silicone oil bath at 100 Hz in the temperature range of 5-120 °C. Finally, the electrocaloric study was
127 carried out by the indirect method using the previously recorded P-E hysteresis loops. A silver paste was used to
128 electrode the BTS_{11} ceramic pellet for the dielectric and ferroelectric measurements.

129

130 ***2.3. Synthesis procedure:***

131

132 BaTiSn_{11} ceramic was prepared via a sol-gel route. A suitable amount of barium acetate ($\text{Ba}(\text{CH}_3\text{COO})_2$) was
133 dissolved in glacial acetic acid, while tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) was dissolved separately in 2-methoxyethanol.
134 The two solutions were then mixed at room temperature. The mixture was then stirred for 1 hour after a
135 stoichiometric volume of titanium isopropoxide was added. The solution was then poured drop by drop with
136 ammonia until it formed a clear gel, which was dried overnight before being calcined at 1000 °C for 4 hours. The
137 resulted powder was then pressed under uniaxial compression in pellets of 8 mm diameter and 0.4 mm thickness
138 that were sintered at 1350 °C for 7 h. All chemicals are of analytical grade and used without further purification.

139

140 **3. Results and discussion:**

141 ***3.1. Structural and microstructural analysis:***

142

143 The XRD of the BTS_{11} calcined powder and the sintered ceramic are displayed in figure 1(a, b). Both spectra show
144 a pure perovskite structure with no heterogeneous peaks, indicating that Ti^{4+} has been completely replaced by Sn^{4+}
145 in the BTS_{11} solid solution. The enlarged view of the calcined powder's 45° peak reveals a distinct splitting,
146 indicating the presence of the tetragonal phase (Figure 1-c). The presence of the orthorhombic phase is indicated
147 by the formation of a triplet at 65° (Figure 1-d) [18][19][20]. However, the enlarged views of the XRD peaks centred
148 at $2\theta=45^\circ$ and $2\theta=65^\circ$ of the sintered BTS_{11} ceramic presented in figure 1-e and figure 1-f respectively, indicate
149 the presence of a single characteristic peak with a small shoulder towards lower angles. The merger of (200) and
150 (002) peaks at $2\theta=45^\circ$, and (202) and (220) peaks at $2\theta=65^\circ$ indicates the dominant cubic phase in the BTS_{11}
151 ceramic at room temperature. Given the similarity of the total energies between the cubic phase (nonpolar phase)
152 and the tetragonal, rhombohedral, and orthorhombic phases (polar phases), polar phases can be randomly
153 generated, formed and embedded in the cubic phase matrix [21]. Thus, the Rietveld refinement of the dominant
154 cubic phase with the space group $\text{Pm}\bar{3}\text{m}$ was performed using Fullprof suite software (figure 2-a). Table 1 compares
155 the refined structural parameters of BTS_{11} ceramic at room temperature to those reported in the literature. As one
156 can see in the table 1, the BTS_x ceramics exhibit different phase structures depending on the tin composition (x),
157 usually the cubic phase is remarked when x exceeds 10% [13],[19],[17], and the tetragonal or the

158 orthorhombic phase is remarked when x takes a value below 10% [24],[25],[10]. Thus, a dominant phase of cubic
 159 is found in our BTS_{11} ceramic, which can be further demonstrated by Raman and DSC measurements.

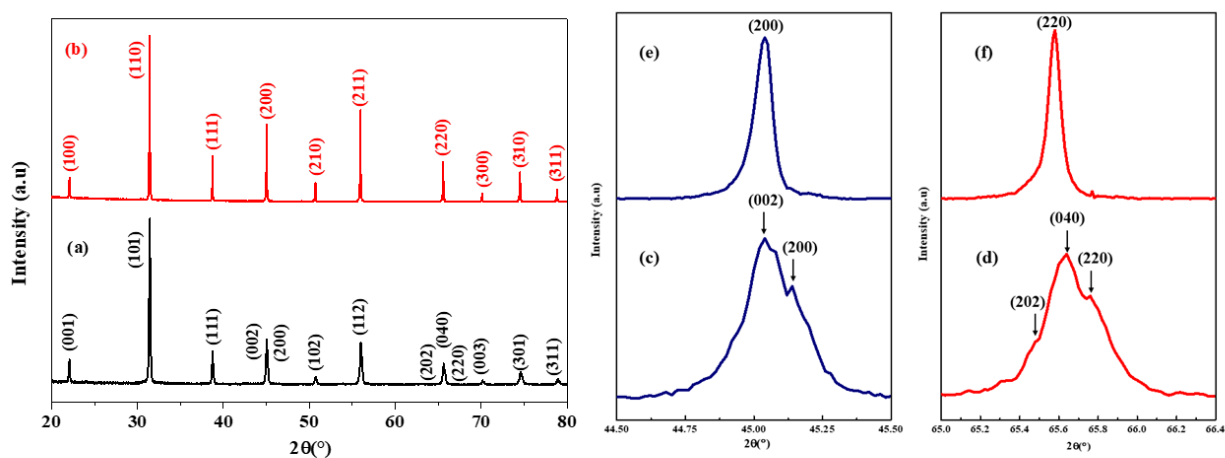


Fig.1 XRD patterns of (a) the calcined BTS_{11} powder and its the enlarged views of 45° XRD peak (c) and 65° peak (d), (b) XRD patterns of the sintered BTS_{11} ceramic, and its enlarged views of 45° XRD peak (e) and 65° peak (f).

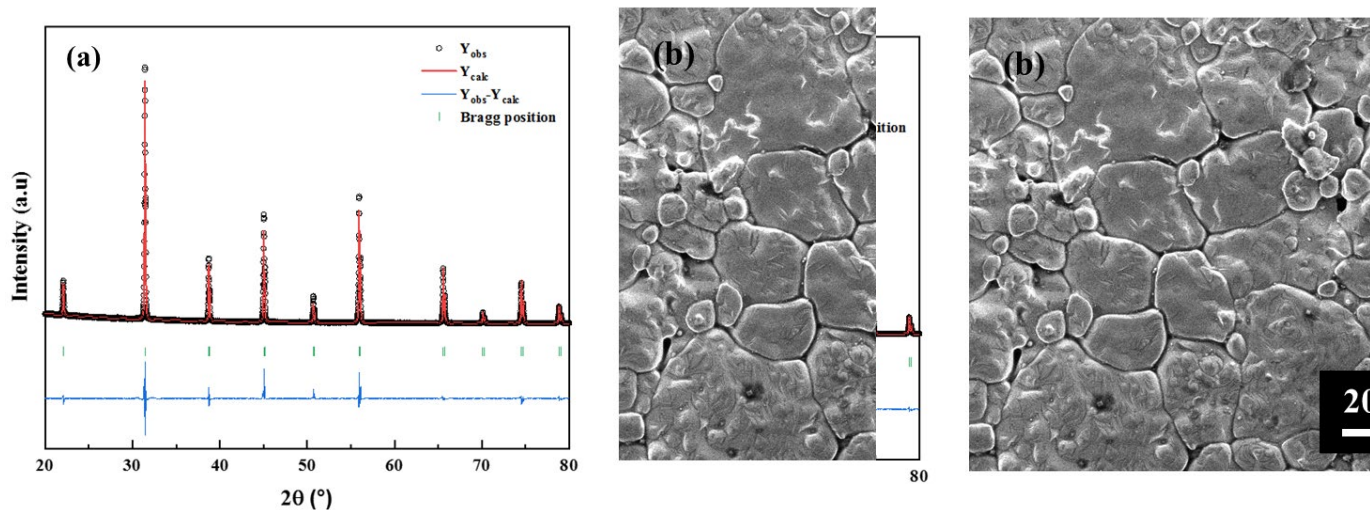


Fig.2 (a) Refined XRD patterns of the sintered BTS_{11} ceramic and (b) SEM micrograph the BTS_{11} sintered ceramic.

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Table 1 Refined structural parameters for the BTS₁₁ ceramic at room temperature in comparison with other BTS_xceramics.

Preparation method of BTS _x	Composition (x)	Structure	Calcination Temperature T°C/time (h)	Sintering temperature (°C) and time (h)	Cell volume (Å ³)	Density	References
Sol-gel	11	Cubic <i>Pm-3m</i>	1000/4	1350/7	65.122 4	5.91	This work
Low-temperature aqueous synthesis	13	Cubic	800/2	1300/2	-	-	[23]
Solid-state	5	Tetragonal <i>P4mm</i>	1130/2	1330/2	-	5.7	[24]
Solid-state	6.5	Orthorhombic <i>Amm2</i>	1050/4	1350/4	-	5.2	[25]
Solid state	10	Tetragonal <i>P4mm</i>	1100/4	1350/4	64.68	-	[10]
Sol-gel	20	Cubic	1000	1350/2	-	5.43	[17]
Solid state	12	Cubic	1100/2	1370/5	64.76	-	[22]

167

168 The SEM micrograph of the sintered BTS₁₁ ceramic is presented in figure 2-b. The sintered ceramic exhibits coarse
169 and large grains along with some small particles, resulting in a high density of 5.91 g/cm³ and an average grain
170 distribution of 18.5 μm. The small particles found in the BTS₁₁ ceramic fill the gaps between the larger grains,
171 improving densification and, eventually, enhancing the dielectric and ferroelectric properties [26].

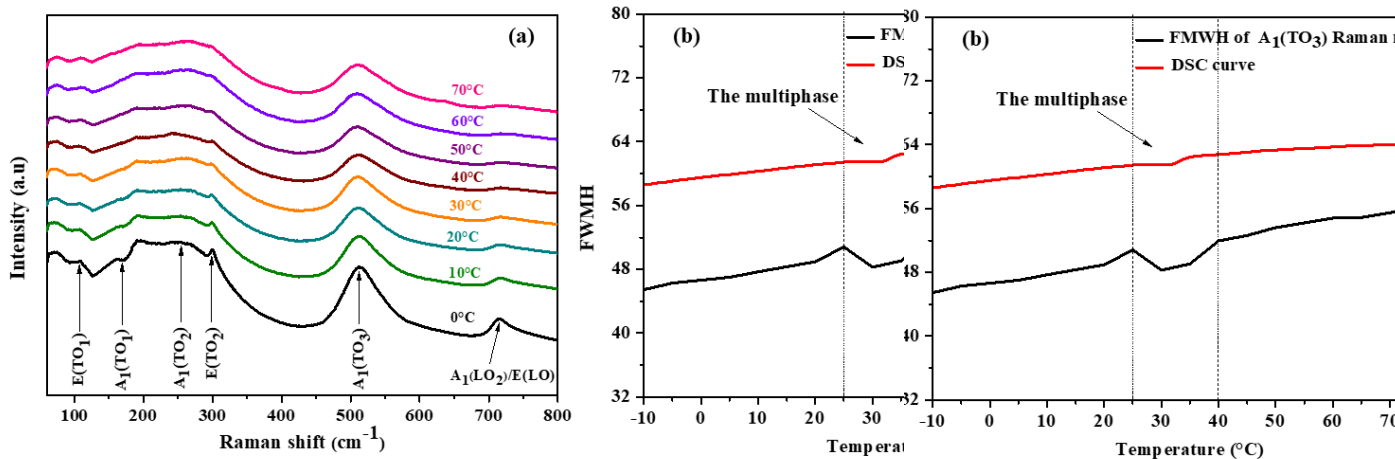
172 The DSC and the temperature dependence of Raman spectroscopy were performed for the BTS₁₁ sintered ceramic
173 to acquire more information about the phase transitions.

174 The DSC curve of our sample presented in figure 3-b shows a unique, small and large endothermic peak near
175 ambient temperature between 28°C and 41°C. Indeed, as reported by Gao et al. [12], when the composition x of Sn
176 dopant increases in BTS_x, the transition enthalpy at the Curie temperature decreases gradually, and when it changes

177 to the multi-phase point ($x=10.5$), the heat flow peak becomes nearly invisible, indicating that first-order transition
 178 changes to the near second order. Thus, the presence of only one small endothermic peak indicates that the three
 179 phase transitions (T_{R-O} , T_{O-T} and T_{T-C}) are all overlapped in this large temperature range. Hence, due to the
 180 characteristics of the multi-phase boundary, high dielectric constant and ultra-high piezoelectric properties can be
 181 expected in this temperature range [9,12].

182 Raman spectroscopy is a versatile method to probe the short range modes since its structural information refers to
 183 a single TiO_6 octahedra, whereas the symmetry from XRD is due to a group of unit cells of more than 10 nm^3 [27].
 184 Thus, to confirm the multiphase co-existence in the BTS_{11} , the temperature dependence of Raman spectroscopy
 185 was performed and presented in figure 3-a. Note that at 0°C , the spectral response contains the polar modes with
 186 E and A_1 -symmetries typical for the tetragonal phase of the BaTiO_3 ceramics. Although the spectra change rather
 187 gradually with temperature, we observe several important features that are interpreted as the coexistence of
 188 different phases characteristic for the BaTiO_3 in a narrow temperature range. Below 30°C , we note the presence
 189 of both bands $A_1(\text{TO}_1)$ at 150 cm^{-1} and $A_1(\text{TO}_3)$ at 250 cm^{-1} , characteristic of the tetragonal and cubic
 190 symmetries. Moreover, the relative intensities of E(TO_2) and $A_1(\text{LO}_2)/\text{E}(\text{LO})$ bands at 305 and 715 cm^{-1} ,
 191 respectively, which are more intense below 30°C , indicate the presence of the tetragonal phase. The band at 190
 192 cm^{-1} assigned to the orthorhombic phase is also visible up to 30°C [28]. Besides, the three modes $A_1(\text{TO}_1)$, $A_1(\text{TO}_3)$
 193 and E(TO_1) that identify the rhombohedral structure are also present up to 30°C . The disappearance of the
 194 characteristic modes of all ferroelectric phases at 180 cm^{-1} $A_1(\text{TO}_1)$, 305 cm^{-1} E(TO_2), and 715 cm^{-1} $A_1(\text{LO}_2)/\text{E}(\text{LO})$
 195 above 30°C confirms that the ferroelectric-paraelectric phase transition happens around this temperature. Thus, the
 196 BTS_{11} ceramic above 30°C starts transitioning into cubic paraelectric phase.

197 For additional support of the latter conclusion, the thermal variation of FWHM of the $A_1(\text{TO}_3)$ Raman mode has
 198 also been investigated and displayed in figure 3-b. This figure shows only one abrupt variation observed at a
 199 temperature range of $25\text{--}40^\circ\text{C}$, which can be associated with the three phase transitions, and confirmed the
 200 existence of the multiphase at near ambient temperature [29].



201

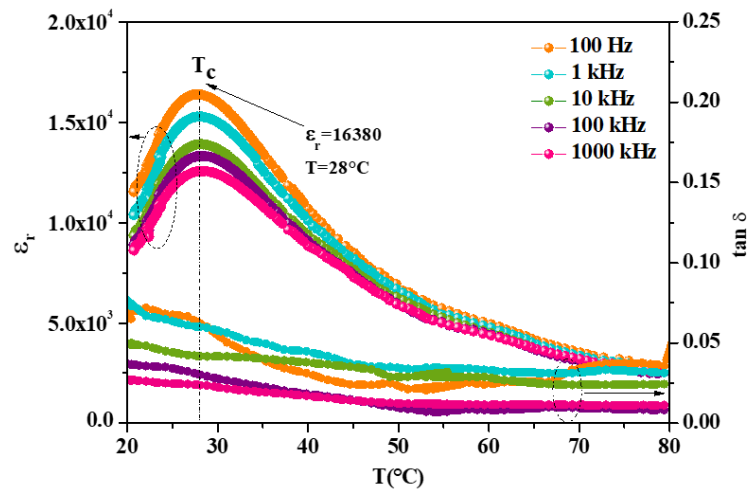
Fig.3 (a) Temperature dependence of Raman spectra (b) FWHM of the $A_1(\text{TO}_3)$ Raman mode and the DSC curve of the sintered BTS_{11} ceramic.

202 **3.2. Dielectric analysis**

203

204 Figure 4 illustrates the temperature dependence of the dielectric constant ϵ_r and the dielectric loss $\tan\delta$ at various
 205 frequencies in the BTS_{11} sample from 20 to 80°C. For example, the dielectric constant at 1kHz reaches a maximum
 206 value of $\epsilon_{rmax}=15460$ and a dielectric loss of $\tan\delta=0.055$ at the Curie temperature that happens to be at very
 207 near ambient temperature ($T_c=28^\circ C$) which is far less from the temperature reported in other works of BTS
 208 elaborated by the classic solid-state method [30][31] (Table 2). The high value of ϵ_r may be due to the tricritical
 209 phenomenon occurring at the multi-phase point ($x=11\%$) as well as the elaboration method, the sol-gel
 210 method, which results in homogeneous powder particles and higher density BTS_{11} ceramic (Table 1).

211 The presence of only one anomaly, centered at 28 °C, suggests the existence of the multiphase (R-O-T-C) in the
 212 large temperature range of 20-42°C as predicted by the differential scanning calorimetry and the Raman
 213 spectroscopy.



214

Fig.4 Temperature dependence of dielectric constant and the dielectric loss at various frequencies of the BTS_{11} ceramic sintered at 1350 °C / 7h.

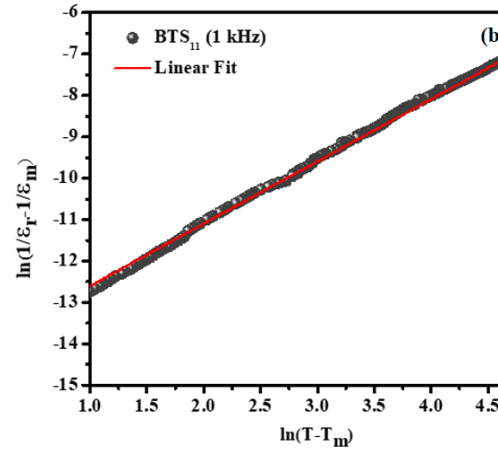
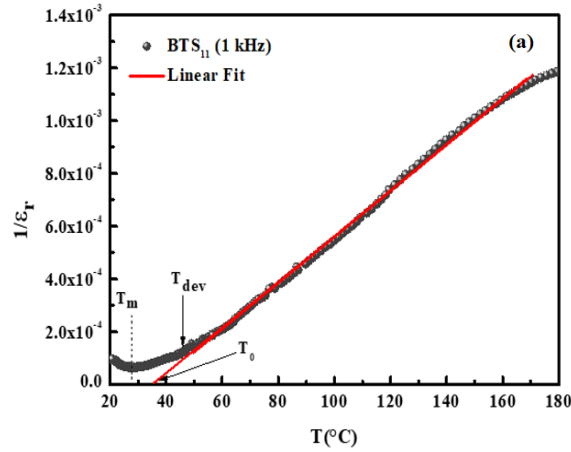
215

216 The critical behavior of our BTS_{11} sample was quantified using the three equations below:

217
$$\frac{1}{\epsilon_r} = \frac{T - T_0}{C} (T > T_0) \text{ (Eq.1)}$$

218
$$\Delta T_m = T_{dev} - T_m \text{ (Eq.2)}$$

219
$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} (1 < \gamma < 2) \text{ (Eq. 3)}$$



ceramic.

220 Where T_0 is the Curie temperature, C is the Curie-Weiss constant, ϵ_m is the maximum dielectric constant and T_m is
 221 the corresponding temperature, and γ is the degree of relaxation.

222 The degree of relaxation γ determines the type of the phase transition, it takes 1 as value when the material is a
 223 normal ferroelectric, and 2 when it is a relaxor, while it takes a value in between ($1 < \gamma < 2$) when there is the presence
 224 of an incomplete-diffused phase or relaxor-type phase transition[30,32]. The fitting results of the third equation
 225 (Eq.3) displayed in figure 5-b were used to quantify the value of the degree of relaxation. The summary of the
 226 dielectric results of our BTS_{11} is displayed in Table2 with a comparison of the dielectric properties at 1 kHz of
 227 other BTS_x ceramics. As we can see in Table 2, our BTS_{11} ceramic exhibits a high dielectric constant and a broad
 228 diffuse peak. In BTS_{11} and $BTS_{10.5}$ ceramics prepared by solid-state and reported S. by Merselmiz et al.[5] and Z.
 229 Luo [33] respectively, a high dielectric constants (17390) at T_m of 41 °C for BTS_{11} and (72000) at T_m of 28 °C for
 230 $BTS_{10.5}$ were reached. Those enhanced dielectric properties are explained by the fast thermodynamic energy
 231 provided by the presence of (C+R+T+O) multiple phase boundaries in the BTS ceramics. However, despite their
 232 high dielectric constant, sharp dielectric peaks were observed. The relaxation degree γ of our ceramic reached
 233 1.428 which shows a rather broad (diffuse) dielectric constant peak compared to 1.34 reported by Merselmiz et al.
 234 [5] in a BTS_{11} elaborated by solid-state. However, M. Cernea et al, M. Kumari et al. and Md. J. Ansaree et al.
 235 reported important γ values of 1.536, 1.44 and 1.5 for a BTS_{13} , BTS_5 and BTS_{10} respectively but the dielectric
 236 constants were relatively low[23],[30],[34]. Hence, the enhanced dielectric properties found in our BTS_{11} ceramic
 237 synthesized by a sol-gel process is mainly due to the quasi quadruple point where all phases coexist.

238

Table3 Comparison of the dielectric properties at 1 kHz of the BTS_x ceramics.

Method	Comp osition (x)	ϵ_m	Tan δ	T_0 (°C)	$C \times 10^5$ (K)	T_m (°C)	T_{dev} (°C)	ΔT_m (°C)	γ	References
Sol-gel	11	15469	0.055	36	1.15	28	45	32	1.428	This work

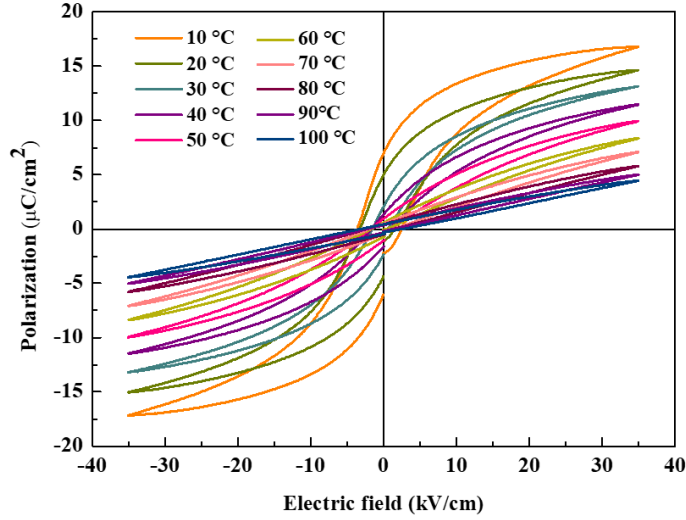
Solid-state	11	17390	0.055	51	1.44	41	80	39	1,34	[5]
Solid-state	10.5	72000	-	-	-	28	-	-	-	[33]
Sol-gel	10	2510	-	-	-	85	-	-	-	[17]
Low temperature aqueous synthesis	13	4800	0.23	-	-	31	-	-	1.536	[23]
Solid-state	5	4182	0.034	-	-	140	-	-	1.44	[30]
Solid-state	10	4610	-	-	-	-	-	-	1.5	[34]
	20	1296	-	-	-	-	-	-	2.01	
Solid-state	5	1230	0.055	81	1.48	77	-	2	1.1	[35]
Solid-state	10	5324	-	-	-	49	-	-	-	[31]

239

240 **3.3. Ferroelectric properties and Energy storage performances:**

241 The electric field dependent polarization performed at different temperatures from 10 to 100 °C under the applied
 242 field of 35kV/cm and a frequency of 100 Hz are shown in figure 6. The maximum value of the polarization
 243 ($P_{\max}=14.72\mu\text{C}/\text{cm}^2$), the remanent polarization ($P_r=2.99\mu\text{C}/\text{cm}^2$), the charge storage density ($Q_c=P_{\max}-P_r$
 244 $=11.73\mu\text{C}/\text{cm}^2$) and the coercive field ($E_c= 1.01 \text{ kV}/\text{cm}$) of the BTS₁₁ ceramic are found near ambient temperature
 245 in the range of 10 to 40 °C. Meanwhile, the P-E hysteresis loop is observed to be slim and gets even slimmer with
 246 the increase of the temperature from 10 to 100 °C due to the ferroelectric-paraelectric phase transition. The
 247 ferroelectric behavior can be noticed in a broad temperature range, even above the Curie temperature ($T_c=28^\circ\text{C}$)
 248 up to 60°C, due to the diffuse phase transition confirmed by the dielectric measurements.

249



250

251

Fig.6 P-E hysteresis loops of the BTS₁₁ ceramic from 10 °C to 100 °C.

252

The temperature-dependent variation of P_{max} , P_r , Q_c and E_c is shown in figure 7-a. P_{max} and P_r decrease with increasing the temperature due to the ferroelectric-paraelectric phase transition, whilst the coercive field takes a minimum value at 20°C, then stays approximately the same up to 80°C, after which it increases quickly with the increase of the temperature due to the conductive mechanism usually observed at high temperature and low frequencies [8].

257

The energy storage performance of the BTS₁₁ ceramic was further investigated using three equations 4, 5 and 6.

258

The total energy density W_{tot} was calculated by integrating the electric field from 0 to P_{max} , whilst the recovered energy density W_{rec} was determined from the integral of the electric field from P_r to P_{max} . Finally, the lost energy density W_{loss} was the difference between W_{tot} and W_{rec} .

261

$$W_{tot} = \int_0^{P_{max}} EdP \quad (\text{Eq. 4})$$

262

$$W_{rec} = \int_{P_r}^{P_{max}} EdP \quad (\text{Eq. 5})$$

263

$$W_{loss} = W_{tot} - W_{rec} \quad (\text{Eq. 6})$$

264

At ambient temperature, W_{tot} , W_{rec} and W_{loss} are 169.8 mJ/cm³, 110.3 mJ/cm³, and 59.5 mJ/cm³, respectively. The thermal evolution of the energy storage properties is shown in figure 7-b. As we can observe from the figure, W_{tot} decreases with the temperature increase, whereas W_{rec} keeps an approximately constant value of 120 mJ/cm³ in the temperature range of 30 °C-70 °C, and then it starts decreasing gradually with increasing temperature. It is worthy to note that the enhanced thermal stability in the BTS₁₁ ceramic makes our quasi quadruple ferroelectric material a solid candidate for energy storage applications in a large temperature domain from the ambient to 80 °C [12].

271

The efficiency is also estimated using equation 7.

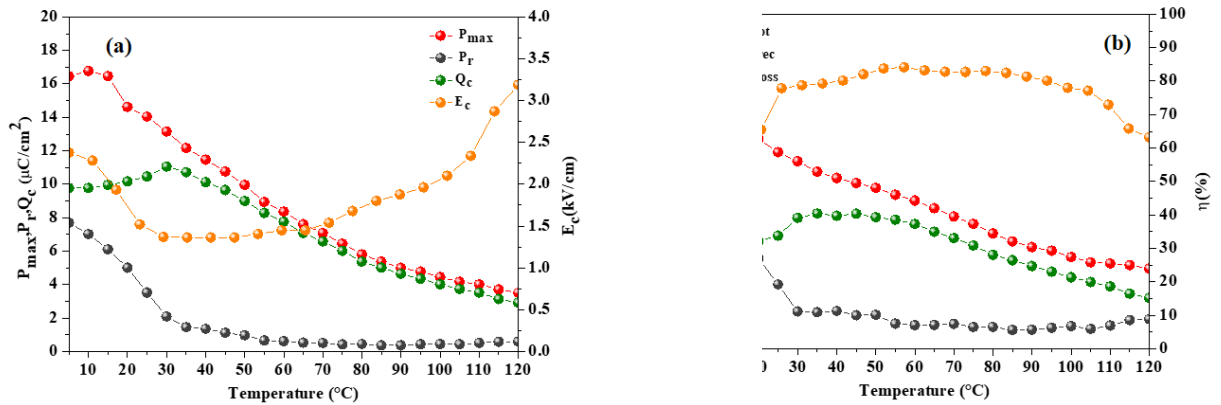
272

$$\eta(\%) = \frac{W_{rec}}{W_{tot}} \times 100 = \frac{W_{rec}}{W_{rec} + W_{loss}} \times 100 \text{ (Eq. 7)}$$

273

The efficiency is a crucial parameter that helps determine the energy storage performance of the sample, as shown in figure 7-a. Initially, η increases quickly with increasing the temperature to 78% at the ambient temperature (25 °C), then it increases very slowly to reach a maximum value of 84% at 60°C, and finally it starts decreasing gradually at 90 °C proving significant thermal stability of the BTS₁₁ ceramic.

277



278

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280

Fig. 7. Temperature dependence of (a) P_{max} , P_r , Q_c and E_c and (b) W_{rec} , W_{loss} and η of the BTS₁₁ ceramic.

281

Table 3 sums up some energy storage properties of other barium titanate based ceramics. The results concerning the BTS, BST and BCZT ceramics reported in previous works (Table 3) are conducted under a high electric field and/or at high temperature, which is not a requirement for energy storage devices, the main goal is to obtain a slim hysteresis loop preferably at very near ambient temperature which is the case of our material, which makes it a good candidate for energy storage applications[12],[36],[5],[20].

286

287

Table 4 Comparison of the energy storage properties of our BTS₁₁ ceramic with other barium titanate based ceramics.

Ceramic	Method	W_{tot} (mJ/cm ³)	W_{rec} (mJ/cm ³)	η (%)	E (kV/cm)	T (°C)	References
BaTi _{0.89} Sn _{0.11} O ₃	Sol gel	151	117	78	35	30	This work
BaTi _{0.89} Sn _{0.11} O ₃	Sol gel	104.9	71.3	67.9	25	28	This work
BaTi _{0.895} Sn _{0.105} O ₃	Solid state	31	-	-	10	37	[12]
BaTi _{0.89} Sn _{0.11} O ₃	Solid state	92.7	84.4	91.04	25	60	[5]

$\text{Ba}_{0.95}\text{Ca}_{0.05}\text{Ti}_{0.89}\text{Sn}_{0.11}\text{O}_3$	Sol-gel	208.83	107.25	51.36	31	30	[37]
$\text{Ba}_{0.4}\text{Sr}_{0.6}\text{TiO}_3$	oxalate co- precipitation	530	-	96.4	136	-	[38]
$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.10}\text{Ti}_{0.90}\text{O}_3$	Solvothermal	-	14	80	6.5	120	[20]

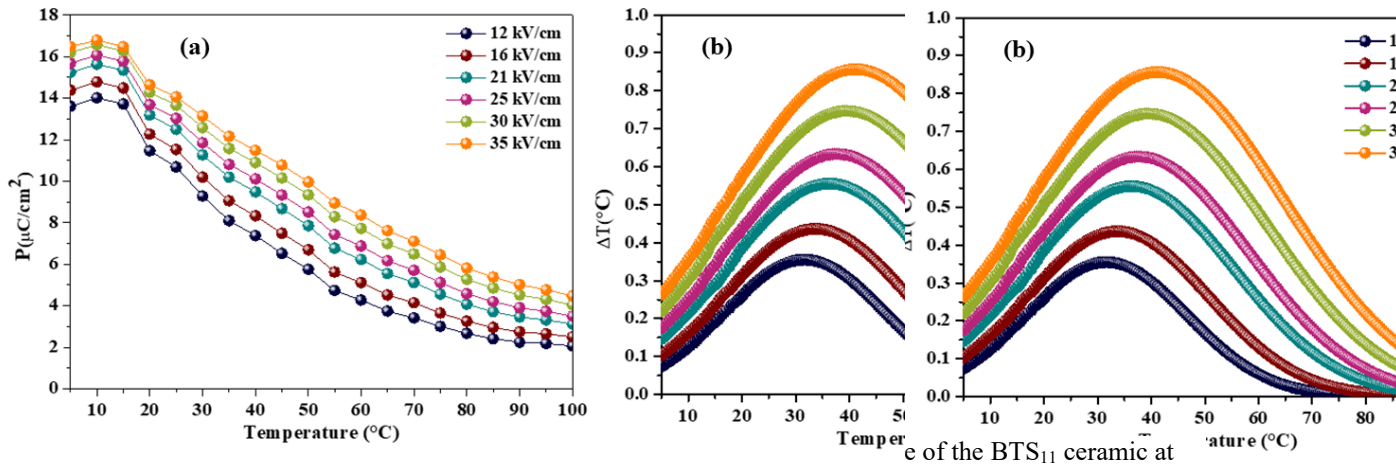
288

289 3.4. Indirect electrocaloric measurements

290 The electrocaloric measurements in the BTS_{11} sample were done indirectly using the maxwell equation (Eq. 8),
 291 which exploits the hysteresis loops' thermal evolution.

292

$$\Delta T = - \int_{E_2}^{E_1} \frac{T}{\rho C_p} \left(\frac{\partial P}{\partial T} \right) E dT \quad (\text{Eq. 8})$$



different applied electric fields.

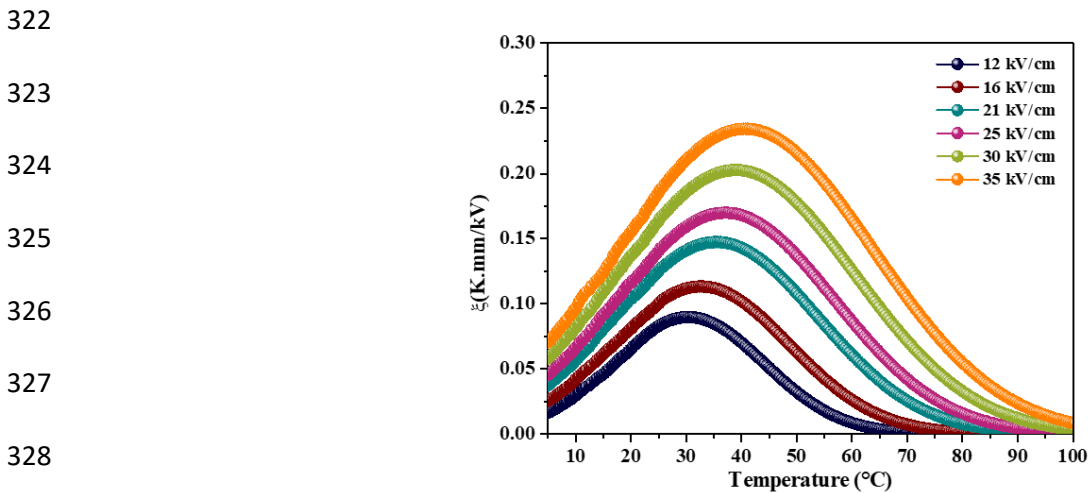
293 The evolution of the polarization P as a function of the temperature is shown in figure 8-a. P reaches a maximum
 294 value at 10 $^{\circ}\text{C}$ then decreases with a further increase in temperature due to the transition from the ferroelectric
 295 phase to the paraelectric phase, as previously mentioned. Figure 8-b depicts the thermal evolution of the adiabatic
 296 temperature of the BTS_{11} sample. The one thermally stable curve observed also confirms the existence of the
 297 multiphase as predicted by the DSC and Raman and confirmed by the dielectric measurements and shows the
 298 thermally stable electrocaloric performance in BTS_{11} . The maximum value of ΔT_{max} under 12 kV/cm is reached
 299 at 30 $^{\circ}\text{C}$, whereas under 35 kV/cm, ΔT_{max} is attained at 41 $^{\circ}\text{C}$, which is commonly observed in ferroelectric
 300 materials[39].

301 The enhanced ΔT values of 0.86 and 0.64 K are obtained at 41 and 37 $^{\circ}\text{C}$ under 35 and 25 kV/cm respectively. As
 302 commonly reported in the literature, interesting electrocaloric response is usually observed at the quasi quadruple
 303 point where the total number of polar states is significant (12 polar states in an O phase, 8 polar states in a R phase,

304 and 6 polar states in a T phase), given that the entropy of an electrocaloric material depends on the total number
 305 of the polar states [39]. Thus, in the quasi quadruple BTS reported in our work and also in the results reported by
 306 Z. Luo et al. [33], high adiabatic temperature is noticed under low electric field at low temperature. When the tin
 307 content is slightly below the quasi quadruple point ($x < 10.5$), higher temperature is required to reach a high ΔT_{\max} .
 308 For instance, in BTS_8 and BTS_{10} systems reported by W. Kayaphan et al. and S. Qiet al., a ΔT_{\max} of 0.52 and
 309 0.48 K were reached under an applied field of 20 and 15 kV/cm at 58 and 64 °C respectively [40],[41]. Furthermore,
 310 H. Zaitouni et al. yielded an adiabatic temperature of 0.14 K in a BST system but at 108 °C [42], which is quiet
 311 comparable with what has been reported by H. Mezzourh et al. in the BCZT system [43]. Meanwhile, in
 312 $\text{Ba}_{0.95}\text{Sr}_{0.05}(\text{Ti}_{0.95}\text{Zr}_{0.05})_{0.75}\text{Sn}_{0.25}\text{O}_3$, ΔT reaches only 0.1 K under 10 kV/cm at 90 °C [44], and in
 313 $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Hf}_{0.10}\text{O}_3$, the adiabatic temperature attains 0.74 K under 35 kV/cm but at high temperature (123 °C)
 314 [45]. Therefore, the BTS_{11} is a promising ambient temperature electrocaloric material compared with other lead
 315 free system.

316 Furthermore, the electrocaloric responsivity ζ calculated by equation 9 (Figure 9) is used for further analysis of
 317 the electrocaloric behavior of the BTS_{11} ceramic. The maximum value of ζ (0.24 K.mm/kV) is obtained at near
 318 ambient temperature, and its evolution as a function of the temperature in a broad temperature range is similar to
 319 the adiabatic temperature evolution. These results make our BTS_{11} material a potential candidate for practical near-
 320 ambient temperature frigorific applications.

321
$$\zeta = \Delta T / \Delta E \text{ (Eq. 9)}$$



329 **Fig.9** Temperature dependence ζ at different applied electric fields.

330 Table 4 summarizes the electrocaloric properties in our sample in comparison with similar and other lead-free
 331 materials at different applied electric field values.

332

333
334

Table5 Comparison of the electrocaloric properties of our BTS₁₁ sample with other barium titanate based ceramics.

Ceramics	Method	T(°C)	ΔT_{\max} (K)	ΔE (kV/ cm)	ξ (K mm kV ⁻¹)	References
BaTi _{0.89} Sn _{0.11} O ₃	Sol-gel	41	0.86	35	0.24	This work
BaTi _{0.89} Sn _{0.11} O ₃	Sol-gel	37	0.64	25	0.17	This work
BaTi _{0.895} Sn _{0.105} O ₃	Solid state	28	0.61	20	0.31	[33]
BaTi _{0.92} Sn _{0.08} O ₃	Solid state	58	0.52	20	0.26	[40]
BaTi _{0.9} Sn _{0.1} O ₃	Solid state	64	0.48	15	0.32	[41]
Ba _{0.9} Sr _{0.1} TiO ₃	Semi wet	108	0.14	7	0.2	[42]
Ba _{0.95} Ca _{0.05} Ti _{0.89} Sn _{0.11} O ₃	Sol-gel	62	0.807	30	0.268	[37]
Ba _{0.85} Ca _{0.15} Zr _{0.10} Ti _{0.90} O ₃	Sol-gel	100	0.15	6	0.25	[43]
0.7BaZr _{0.2} Ti _{0.8} O ₃ – 0.3Ba _{0.7} Ca _{0.3} TiO ₃	Solid state	55	0.3	20	0.15	[46]
Ba _{0.95} Sr _{0.05} (Ti _{0.95} Zr _{0.05}) _{0.75} Sn _{0.25} O ₃	Solid state	101	0.095	10	0.095	[44]
Ba _{0.85} Ca _{0.15} Ti _{0.90} Hf _{0.10} O ₃	Solid state	123	0.74	35	-	[45]

335

336 4. Conclusion

337 To summarize, we have investigated the structural, dielectric, ferroelectric, and energy storage and electrocaloric
 338 properties at very near ambient temperature in the eco-friendly BTS₁₁ ceramic synthesized by the sol-gel method.
 339 As a result, a high dielectric constant of 15460, high recovered energy of 122 mJ/cm³ with 79% efficiency and a
 340 significant electrocaloric effect ($\Delta T=0.86$ K, $\xi=0.24$ K.mm/kV under 35 kV/cm)are obtained near ambient
 341 temperature with remarkable thermal stability due to the overlap of the three phases transition. Hence, the BTS₁₁
 342 ceramic can be considered an excellent candidate for energy storage and frigorific applications near ambient
 343 temperature.

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