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Nanostructured BaTi_{1-x}Sn_xO₃ ferroelectric materials for electrocaloric applications and energy performance

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Abstract

Nanostructured BaTi_{1-x}Sn_xO₃ ($x = 0, 0.05$ & 0.075) were successfully synthesized using the modified Pechini processing method. The phase purity and symmetry were examined by X-ray diffraction and Raman spectroscopy. Tetragonal symmetry was obtained for BaTiO₃ (BT) while orthorhombic symmetry for Sn doped BT. BT exhibits an up-shift of the Curie temperature towards high temperatures ($T_C=139^\circ\text{C}$). In contrast, a down-shift was recorded for Sn doped BT. Then, indirect electrocaloric (EC) adiabatic temperature change ΔT and the energy storage performances were determined based on ferroelectric hysteresis loops. Interestingly, large EC responsivity of $\Delta T/\Delta E = 0.81 \times 10^{-6}$ K.m/V was obtained for the BT accompanied with a moderate stored energy of 23 mJ/cm^3 but with a high energy efficiency of 67%. The incorporation of Sn in BT was found to broaden the EC responsivity and to improve the energy efficiency up to 90%, recorded for the 5% Sn doped BT.

1. Introduction

Lead-based ferroelectric perovskites, such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ system, have attracted great interest owing to their interesting piezoelectric and ferroelectric properties, which makes them good candidates for technological and industrial applications [1–3]. However, due to the latest European directives on environmental and health preservation, the use of lead in electrical and electronic components has been restricted [4]. Consequently, attention has been paid to the development of lead-free materials possessing performances that could compete with lead-based systems [5–7]. Owing to its remarkable dielectric, ferroelectric and piezoelectric properties combined with an excellent chemical and mechanical stability at room temperature [8], barium titanate BaTiO_3 (BT) material is considered a good alternative to lead-based systems for large-scale industrial applications [9–11]. Note that neat BT system presents three main phase transitions. A first paraelectric (cubic, $Pm3m$) to ferroelectric (tetragonal, $P4mm$) phase transition occurring at the Curie temperature, $T_C \sim 403$ K prone to grain size dependence [12]. A second phase transition towards an orthorhombic ($Amm2$) symmetry at 278 K, and a third one at 185 K towards a rhombohedral ($R3m$) symmetry [13]. The highest dielectric permittivity obtained near T_C is very interesting for practical applications such as energy conversion. Indeed, a giant EC effect was found near the sharp phase transition of BT system, demonstrating the high potential of BT-based materials for the development of functional cooling devices [14–16]. However, the sharp phase transition typical of the BT system presents some inherent limitations such as a very weak temperature stability preventing the increase of its dielectric and EC performances, and its high ferroelectric (FE) to paraelectric (PE) transition temperature that needs to be lowered to near ambient to respond to the actual capacitor's needs [17].

To improve the electrocaloric response of the BT, several works were oriented towards grain size engineering, doping, mechanical loading, and the coexistence of positive and negative electrocaloric effects. Indeed, Shan *et al.* recently demonstrated mechanical control of the EC response in BT-based epitaxial thin films [18]. These authors have also demonstrated a strategy to induce the coexistence of both positive and negative EC responses via electric-field-induced FE-FE phase transition in BT-based systems [19]. In addition, the impact of elements doping on EC was also considered on BT system, such as Ca^{2+} , Sr^{2+} , or Ce^{3+} incorporated in the Ba-site, and Mn^{3+} , Zr^{4+} , Sn^{4+} , Hf^{4+} , or Ce^{4+} incorporated in the Ti-site [20–25]. Particularly Sn^{4+} doping on the Ba-site in bulk systems was reported to improve the dielectric, FE, and EC performances

compared to the neat BT [23,26–28]. Moreover, grain size engineering was also reported to have a considerable impact on the EC performances of BT system [29–31].

In this work, we report on the elaboration and characterization of nanostructured $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ceramics and their electrocaloric and energy storage performances. A special attention will be given to the effect of grain size and Sn doping on their structural and physical properties.

2. Experimental methods

Nanocrystalline $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ (BT_xSn) powders ($x = 0 - 7.5\%$) were prepared using the modified Pechini method [32]. The raw materials are titanium (IV) n-butoxide ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ Strem Chemicals 98%), acetic acid (CH_3COOH , Sigma Aldrich, 99,7%), ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, sigma Aldrich, >99%), barium acetate ($\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$, Strem chemicals 99%) and tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Strem Chemicals, 98%). A first solution (A) is prepared by mixing in the following order the n-butoxide titanium, acetic acid and absolute ethanol in molar ratios 1:3:7 respectively. The mixing is then stirred until a clear solution is obtained. Titanium (IV) n-butoxide must not be placed in the presence of water in order to avoid its hydrolysis and the formation of insoluble clusters. A second solution (B) is prepared containing a stoichiometric mixture of tin and barium precursors to which acetic acid and ethanol are added with molar ratios of 1 (Ba/Sn):6:7, respectively. After complete dissolution, the two solutions A and B are vigorously stirred then placed in an oven at 90°C for 45 min to obtain a translucent to slightly cloudy gel. The gel is then calcined in air at 800°C for 6 hours (with heating/cooling ramps rate set at 5°C/min) to obtain nanosized $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ powders. Thermal analysis has been performed using a combined thermogravimetric analysis and differential scanning calorimetry TGA/DSC 3+ STARe System (Mettler Toledo). The scan rate is set to 5 °C/min under an air flow of 40 mL/min. X-Ray diffraction (XRD) patterns were collected using a Rigaku ULTIMA IV diffractometer equipped with Cu anticathode, Soller slits to limit the divergence of X-ray beam and a nickel foil filter attenuates the Cu K_β line. The registered angular range is 20°-80° at 0.1°/min scan resolution using the Bragg-Brentano configuration. Raman spectrometry was performed on Renishaw in Via system using green laser excitation (532 nm) at the power of 1 mW. The dielectric measurements were performed using a Solartron Impedance analyzer SI-12060. Ferroelectric hysteresis loops were collected at different temperatures using a ferroelectric test system (TF Analyzer 2000, aix-ACCT). Powder imaging were carried out using

environmental scanning electron microscopy ESEM Quanta 450 and the ceramic cross section was prepared by liquid nitrogen cleavage technique.

3. Results and discussions

3.1. Thermal analysis

Thermal stability of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 5\%$) oxides and their phase transitions examined by TGA/DSC is depicted in the fig. 1.

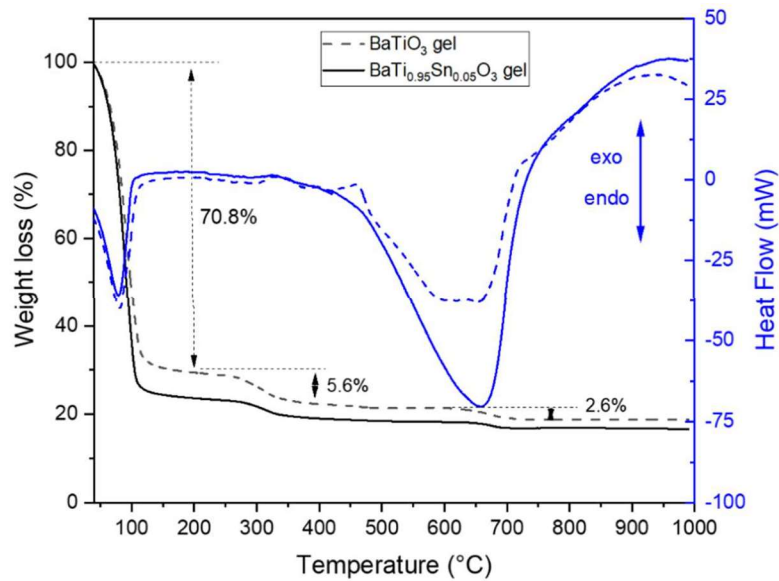


Fig. 1. BaTiO_3 and $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ gels thermal stability and phase transitions recorded in air during TGA/DSC experiment.

As can be seen in fig. 1, the BT weight loss shows three successive transitions: 1) 70.8% weight loss, located at relatively low temperatures (60-110°C), it is attributed to the evaporation of solvents such as water and ethanol present in the wet gel. This evaporation is confirmed by the endothermic heat flow characterized by the peak observed on the DSC signal; 2) 5.6% weight loss, located between 270 to 400°C, which is associated with the exothermic heat flow. This loss is attributed to in one hand, to the decomposition of titanium acetate into TiO_2 and acetic anhydride and to the decomposition of barium acetate into BaCO_3 , in the other hand [33]; 3) 2.6 % weight loss, located at 610-650°C, which is attributed to the formation of BaTiO_3 and the release of CO_2 as byproduct through the reaction between BaCO_3 and TiO_2 [33]. Similarly, the $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ gel weight loss exhibits the same observed thermal decomposition as the BT gel without additional peak that could raise from the decomposition of tin salt. Indeed, the thermal

decomposition of tin (IV) chloride prepared in ethanol medium shows the formation of SnO₂ at a low temperature (< 300°C) [34].

3.2. Structural analysis

The morphology and the grain size of the as-processed BT and Sn doped BTxSn powders were observed in ESEM and given in fig. 2a-c.

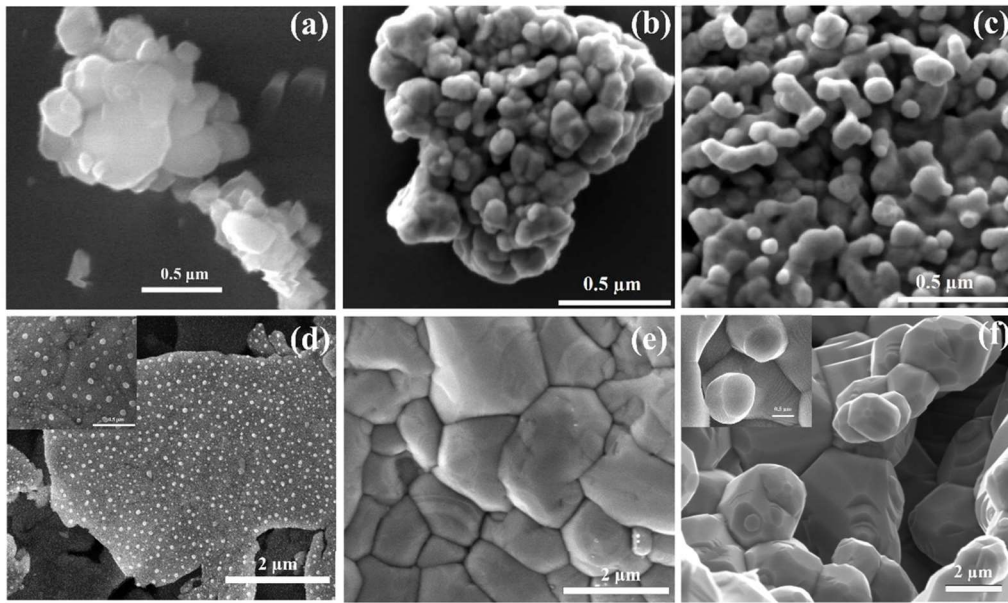


Fig. 2. SEM images of (a) BaTiO₃, (b) BaTi_{0.95}Sn_{0.05}O₃, and (c) BaTi_{0.925}Sn_{0.075}O₃ powders, and (d) BaTiO₃, (e) BaTi_{0.95}Sn_{0.05}O₃, and (f) BaTi_{0.925}Sn_{0.075}O₃ ceramics.

The examination of the as-processed powders (Fig. 2a-c) shows that the nanograins have a relatively spherical shape with 45 nm, 39 nm and 31 nm in diameter for BT, BT5%Sn doped, and BT7.5%Sn doped, respectively. After, casting and sintering, the grain size for the neat BT ceramic is about ~ 70 nm (e.g., fig. 2d) compared to doped compounds (e.g., fig. 2e, f), exhibiting larger grain sizes (1 – 4 μm).

X-ray diffraction patterns were recorded at room temperature for the three compounds as depicted in fig. 3.

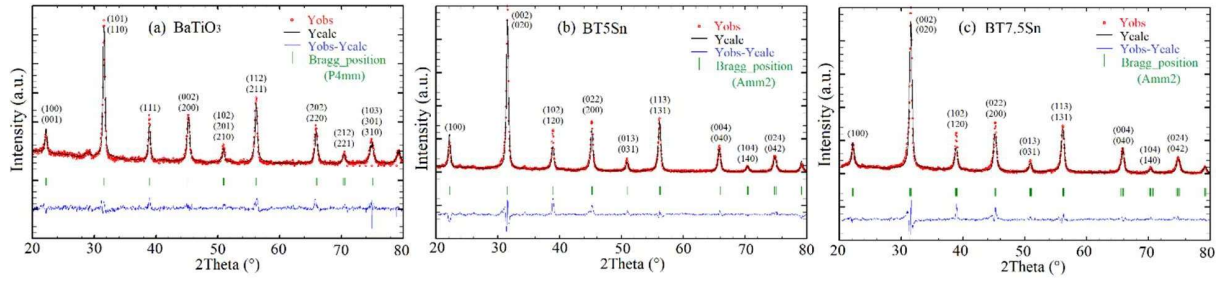


Fig. 3. XRD patterns of the BT_xSn calcined in air at 800°C for 6 hours: a) x=0, b) x=5%, c) x=7.5%.

Structural investigations based on Rietveld calculations using Fullprof software [35] confirmed a tetragonal symmetry for BT nanostructured ceramic and an orthorhombic symmetry phase for both BT5%Sn and BT7.5%Sn. Our calculation approach considers as starting point, the tetragonal phase in *P4mm* (No 99) space group in pattern matching mode. As such, the calculation yielded to a rapid convergence for BT which allows coherent peak identification of the BT X-ray pattern [36]. In contrast, using the same approach for the Sn-doped BT compounds, it did not lead to conclusive results. Hence, different symmetry consideration were tested in accordance to bulk BT_xSn phase diagram reported elsewhere [23,26] where BT doped with 5%Sn and 10%Sn-contents induced tetragonal-to-orthorhombic phase transition. Structural refinement was then conducted in the orthorhombic symmetry with *Amm2* (No 39) as space group that led to satisfactorily results. Visual graphical criteria such as the plots of observed and calculated intensities and their difference instabilities due to the statistics of the recorded X-ray patterns but the reliability factors are conclusive. The plot on the bottom of fig. 3a-c, shows residual intensities due to line profiles, bad scaling parameters and bi-phased structure. Therefore, other assumption using phases mixture were considered but it was clear that the orthorhombic symmetry presents the major contribution.

Moreover, for the six-fold coordination, the Sn⁴⁺ ionic radius is greater than Ti⁴⁺, hence the Sn substitution led to an increase in the lattice parameters according to Vegard's law (Table 1) [37]. Moreover, the well-known Scherrer formula was used to determine their crystallites size from the XRD data (Table 1) [38]. The obtained crystallite size was controlled by the processing temperature. Indeed, the sol-gel synthesis route makes it possible to obtain nanometric crystallites size. These crystallites may coalesce during the calcination carried out at high temperature. Here, we have chosen the lowest temperature 800°C, below which the precursors could not be entirely reacted to lead to the desired phase, favoring the obtained nanometric size. Note that the EC response was found to be directly related to the crystallites size, namely Patel *et al.* [39] have

described the influence of the grains size on the EC properties of BaTiO₃ and M. Kumar *et al.* [40] have reported an improved EC performance in doped BaTiO₃ possessing reduced grain size.

Table 1: Space group, lattice parameters, average crystallite size, and Rietveld refinement parameters of BTxSn.

%Sn	Space group	a (Å)	b (Å)	c (Å)	V (Å ³)	D (nm)	R _F	R _B
0	<i>P4mm</i>	3.99	3.99	4.01	64.18	43	5.55	7.45
5	<i>Amm2</i>	4.01	5.67	5.67	129.10	38	5.03	7.85
7.5	<i>Amm2</i>	4	5.66	5.70	129.25	33	8.3	5.8

By deconvolving the instrumental part across the Full Width at Half Maximum (FWHM), a slight decrease in crystallite size when x increases, is obtained. This trend agrees with the SEM observations. Atomic positions, isotropic thermal agitation parameters and occupancy of BTxSn ceramics are depicted in Table 2.

Table 2: Refined lattice parameters of BT (tetragonal *P4mm*), BT5%Sn (orthorhombic *Amm2*), and BT7.5%Sn (orthorhombic *Amm2*).

BaTiO₃						
Atom	Site	x	y	z	B(Å)	Occupancy
Ba	1a	0	0	0.10552	-0.099	1
Ti	1b	0.5	0.5	0.54338	-3.741	1
O ₁	1b	0.5	0.5	0.04157	-2.384	1
O ₂	2c	0.5	0	0.69073	-3.398	2
BT5Sn						
Ba	2a	0	0	-0.02445	-3.092	1
Ti/Sn	2b	0.5	0	-0.48254	3.795	0.95/0.05
O ₁	2a	0	0	0.31689	2.510	1
O ₂	4e	0	0.36845	0.21026	-3.364	2
BT7.5Sn						
Ba	2a	0	0	-0.02898	2.189	1
Ti/Sn	2b	0.5	0	0.46696	1.519	0.925/0.075
O ₁	2b	0.5	0	0.27605	3.194	1
O ₂	4d	0.5	0.26238	0.23701	-2.827	2

The obtained values show an average increase of lattice parameters due to the substitution of Ti (smaller ionic radius) by Sn larger ionic radius at the perovskite B-site. Furthermore, the thermal agitation parameters are abnormal. This is in favor to an additional symmetry contribution.

3.3. Raman spectroscopy

The room-temperature Raman spectra of the BT_xSn ($x = 0, 5\%, 7.5\%$) ceramics synthesized using the sol-gel route are shown in fig. 4. Note that the spectra are Bose-Einstein corrected. Regarding the pure BaTiO₃ ceramic, Raman spectrum shows a highly damped soft mode, an interference dip at around 180 cm⁻¹, a broad band at ~270 cm⁻¹ assigned to the A₁ (TO) mode, a sharp mode at ~307 cm⁻¹ attributed to the B₁ + E (TO, LO) modes (“silent” mode), an intense band at ~518 cm⁻¹ attributed to the A₁ (TO) mode, and a high frequency mode at ~720 cm⁻¹ assigned to the A₁ (LO) + E (LO) phonon modes (where the notation TO and LO denotes the transverse and longitudinal optical modes, respectively). Noting that the high wavenumber mode is reported to be related to the existence of oxygen vacancies [41,42]. It should also be mentioned that the presence of the interference dip and the sharp “silent” mode, are only observed in long-range FE phase [43]. The observed Raman modes are in good agreement with previous works reporting on the tetragonal (*P4mm*) structure of BT with a corresponding point group of symmetry C_{4v}^1 [44–48]. Interestingly, the introduction of Sn element in BaTiO₃ matrix resulted in several changes on the Raman spectra. First, an underdamped soft mode can be observed for the Sn doped samples (obvious in the case of BT5%Sn) compared to the highly damped one of BT system. In addition, the A₁ (TO) ~270 cm⁻¹ mode is observed to soften to ~250 cm⁻¹ for the doped BT_xSn compositions. The presence of the underdamped soft mode in addition to the frequency downshift of the A₁ (TO) mode are the signature of the orthorhombic (*Amm2*) symmetry [49], in good agreement with our structural findings. Moreover, a new interference dip is observed on the doped ceramics at ~130 cm⁻¹, which is probably due to the response of two different local octahedral environments owing to the involvement of cations with different ionic radii (Ti⁴⁺ and Sn⁴⁺) in BT_xSn system [12]. Besides, the presence of the “silent” mode in the doped samples indicates that the Sn-doping content preserves the long-range order of the FE BT system, especially in the case of the BT5%Sn system [50]. Moreover, we can observe an obvious broadening of all Raman modes as the doping content increases, resulting from the disorder induced by Sn introduction. Regarding the BT7.5%Sn sample, an evident broadening of the A₁ (TO) mode, in addition to the intensity decline of the “silent” mode and the reduction of the interference dip (180 cm⁻¹) express a reduction of the long-range FE ordering, as observed in BaTi_{1-x}Zr_xO₃ system [51].

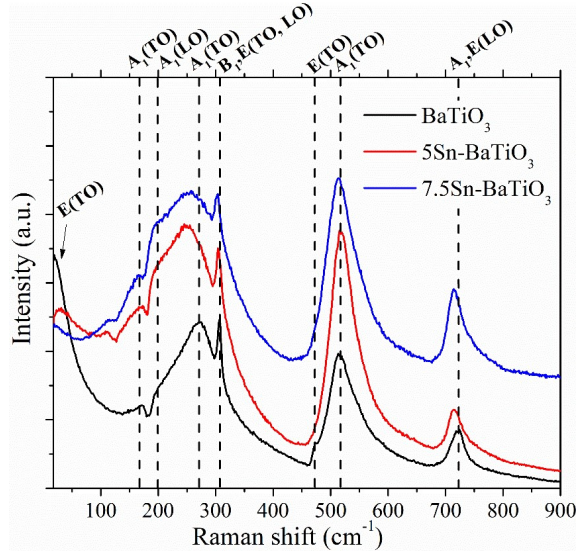


Fig. 4. Raman spectra of Sn^{4+} doped BaTiO_3 system. The modes assignments are shown in the tetragonal phase of bulk BT.

3.4. Dielectric properties

To determine the phase transition temperatures, dielectric properties measurements were carried on the samples. Fig. 5a-c presents the frequency and temperature dependence of the dielectric constant (ϵ_r) for the neat and Sn doped BT nanostructured systems.

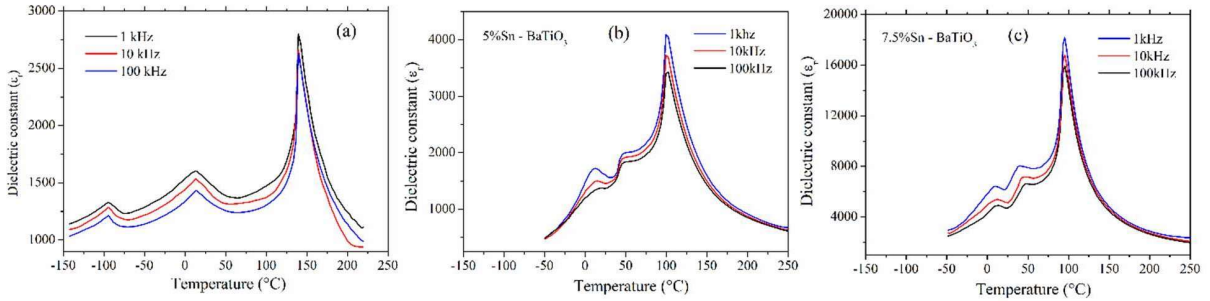


Fig. 5: Temperature and frequency dependence of the dielectric constant: a) BaTiO_3 , b) $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$, and c) $\text{BaTi}_{0.925}\text{Sn}_{0.075}\text{O}_3$.

One can observe in Fig. 5a, the presence of the three known phase transition temperatures (T_{R-O} , T_{O-T} , and T_{T-C}) in neat nanostructured BT as reported elsewhere [52]. However, here a slight shift toward high temperatures for T_{T-C} is also observed. This could be attributed to the presence of polar nanoregions (PNRs) in nanostructured BT [53]. This induces the phase transformation towards the global symmetry at relatively higher temperature ($\sim 139^\circ\text{C}$) compared to bulk BT possessing larger FE domains. Besides, ϵ_r was found to be smaller to reported values for bulk BT system as reported elsewhere [54]. These authors showed significant decrease in the dielectric

permittivity values from $\epsilon_r \sim 8000$ to $\epsilon_r \sim 1000$, as grain size decreases from 500 nm to 50 nm, respectively [54]. Furthermore, the phase transition temperatures T_{R-O} and T_{O-T} remain very close to observed ones in bulk BT. This means that the dynamic of phase transformations mainly concerns FE-to-PE transition.

As can be seen, the introduction of Sn^{4+} affects the three phase transition temperatures. As shown in fig. 5b, c) a down shift of the T_{T-C} transition temperature is observed when increasing of Sn-content. Whereas a reverse trend is observed for the T_{R-O} and T_{O-T} phase transition temperatures where a significant upshift is occurring with the increasing Sn-content as reported elsewhere [1,28].

Recall that in the R-phase of BT, the polarization aligns parallel to the (111) axis, whereas it is parallel to the (011) axis in the O-phase, (001) axis in the T-phase, and vanishes in the C-phase [55]. The Sn incorporation in the BT matrix, impedes the Ti-polar displacement leading to a disturbance of the long-range Coulomb potential. Laulhé *et al.* [56], by using first principles supercell calculation on $\text{BaTi}_{0.75}\text{Zr}_{0.26}\text{O}_3$ (a homovalent substitution as in our case), reported that the type of a Ti-displacement is determined by the Ti/Zr distribution in the adjacent local strain effects, which is governed by the size difference between Ti and Zr atoms. Furthermore, Keeble *et al.* [57] on studying BCZT system, reported that the reduction of the number of Ti^{4+} (111)_{pc} displacements is originated from a competition between A-site and B-site polar instabilities.

Indeed, we surmise that the involvement of two different octahedral environments in the system (Ti-O and Sn-O), disturb the off-centering displacement of Ti ions in BTxSn system leading to the observed shifts of the phase transition temperatures.

Besides, from figure 5, we can observe a broadening of the sharp T_C transition temperature in the presence of Sn^{4+} ions, revealing the evolving disorder in the BTxSn system. These results are in good agreement with our vibrational investigations, showing a reduction of the long-range FE ordering along with an increasing disorder in the system while increasing the Sn content.

In addition, the maximal value of the dielectric permittivity at T_C is observed to dramatically increase up to ~ 18000 for BT7.5%Sn system. Hence, we surmise that the presence of Sn is responsible for the increased dielectric constant owing to the induced PNRs in the BTxSn system, as reported by Shi *et al.* using high-resolution transmission electron microscopy [27]. Furthermore, high dielectric constants are commonly reported for relaxor ferroelectrics to be associated to the presence of PNRs [58]. Besides, the increased grain size in the case of the doped

materials (2-3 μm for BTxSn instead of 70 nm for BT) could also be responsible for this enhancement.

3.5. Ferroelectric properties and stored energy

To examine the ferroelectric properties of processed samples, P-E loops were recorded as a function of temperature. Fig. 6 depicts the hysteresis loops of the three samples captured around their Curie temperatures.

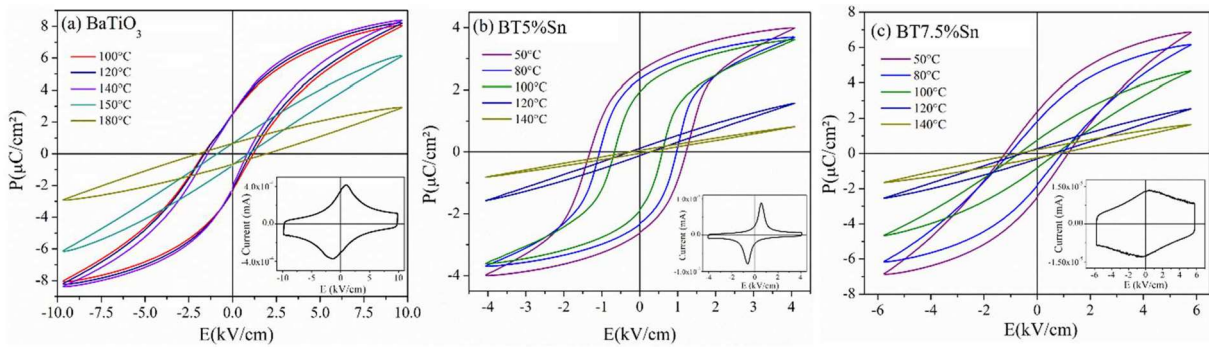


Fig. 6. Temperature dependence of the ferroelectric hysteresis loops: BaTiO₃, b) BaTi_{0.95}Sn_{0.05}O₃, and c) BaTi_{0.925}Sn_{0.075}O₃. The insets show their corresponding polarization current curves at 100°C.

The neat BT compound (e.g., fig. 6a), exhibits narrow hysteresis loops with a corresponding maximum polarization of $P_{\text{max}} = 8\mu\text{C}/\text{cm}^2$, low remanent polarization $P_r = 2\mu\text{C}/\text{cm}^2$ and low coercive field $E_c = 1\text{kV}/\text{cm}$, in the FE phase. These narrow hysteresis loops compared to the saturated loops usually obtained in the bulk system are mainly due to the grain size effects as commonly admitted [59]. In contrast, the P-E loops appear to have square-like shape signature of saturated P-E hysteresis loops for the BT5%Sn (e.g., fig. 6b) indicating a reinforced FE activity at this Sn concentration visible by the sharp current peak obtained (e.g., inset of fig. 6b). This agrees with reported study carried out on BTxSn compounds having higher grain size (50 – 70 μm) [26], which seems to remain valid for our BTxSn doped compound. However, a different trend is observed for BT doped with 7.5%Sn content (e.g., fig. 6c), although the P-E loops are wider than the ones obtained for neat BT, they remain narrow in comparison with the BT5%Sn. This is coherent with the broader integrated current peaks observed for BT7.5%Sn, which is the signature of the presence of disorder or to several polarized nano-regions.

Moreover, the significant decrease of the coercive field from 1.4 kV/cm for neat BT to 0.6 kV/cm for BT5%Sn, reveals an easier polarization switching of the FE domains.

To examine the grain size effects on the energy storage performances of the nanostructured BTxSn, we have computed the recoverable energy density (W_{rec}) and energy efficiency (η) as described elsewhere [60]. The obtained results are reported in fig. 7.

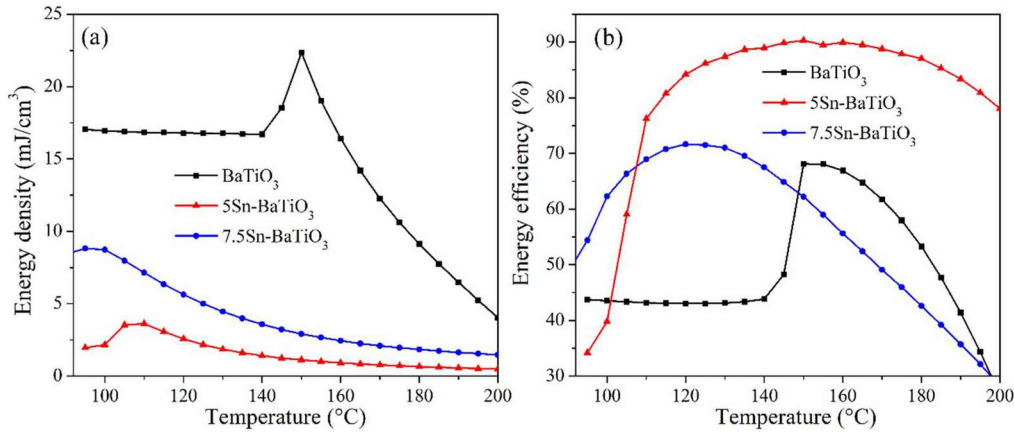


Fig. 7. a) Energy storage density and b) energy efficiency of $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$.

Regarding the neat BT system, high yield stability was observed in the temperature range 95-140°C with $W_{\text{rec}} = 17.4 \text{ mJ/cm}^3$ and $\eta = 43\%$ and a maximum of 23 mJ/cm^3 with a high energy efficiency of 67%. Remind that in neat BT, significant energy storage performances are not expected due to the quasi-square hysteresis loop observed in the bulk system and relatively low surface of stored energy in P-E loops. In the PE region, a drastic decrease of the recoverable energy is observed in the BT5%Sn and BT7.5%Sn compared to the neat BT. However higher energy efficiency $\sim 90\%$ was obtained for BT5%Sn, in a large range of temperatures. Thus, Sn^{4+} ions appear to be an adjusting parameter to control the energy storage performances in BTxSn system. Therefore, the BT5%Sn has a great potential to be considered as low energy consumption in nano-cooling devices.

3.6. Electrocaloric effect investigations

It is worth noting that various experimental techniques were developed to directly measure and extract the EC effect such as differential scanning calorimetry [61], the modified high-resolution calorimetry [62], the fast infrared photometry [63], and the scanning thermal microscopy [64]. Besides, since the EC effect is a thermodynamic phenomenon, it can be indirectly evaluated using Maxwell equations as reported elsewhere [61]. Using the indirect approach, in this work, P-E hysteresis loops data were used to extract the EC adiabatic temperature change in BTxSn as a function of temperature. This indirect determination of EC effect, based on Maxwell equations, is

described elsewhere [61]. Note that the cyclic application of an electric field on a FE material leads to an entropy change, which is at the origin of temperature variations in the system giving rise to the EC effect, where the adiabatic temperature change is estimated using the following equation:

$$\Delta T = - \frac{1}{\rho C_p} \int_{E_1}^{E_2} T \left(\frac{6P}{6T} \right) dE \quad 1$$

where $E_{1,2}$ stands for the initial and final applied electric fields, P represents the polarization. ρ and C_p correspond to the density of the neat BT, BT5%Sn and BT7.5%Sn respectively, 6.034, 6.090, 6.129 g/cm³ and to thermal heat capacity 550, 450, 430 J/K Kg. Fig. 8 gives the temperature dependent of EC temperature change of BTxSn samples with respect to the applied electric fields.

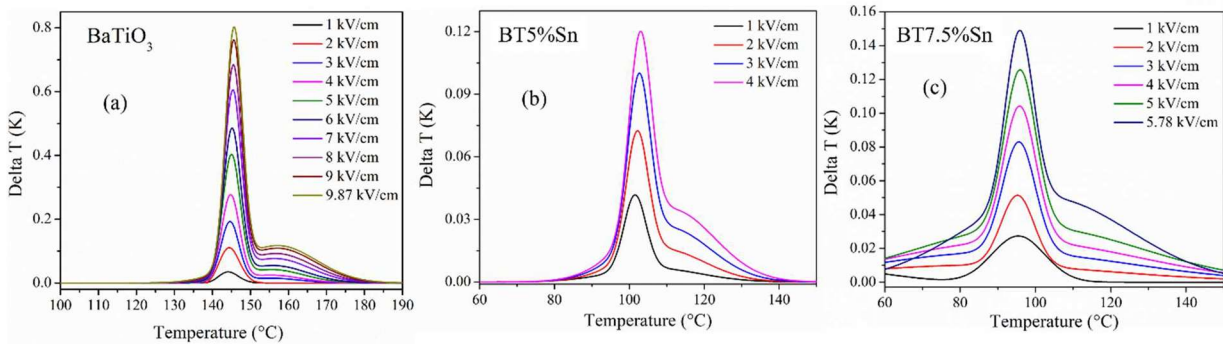


Fig. 8. Temperature and electric field dependence of the adiabatic temperature change (ΔT) of a) BaTiO_3 , b) $\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$, and c) $\text{BaTi}_{0.925}\text{Sn}_{0.075}\text{O}_3$ systems.

These EC temperature change curves show the FE-to-PE phase transitions in the BTxSn samples where maximal ΔT is obtained at T_C . It is worth to note the presence of an evident enlargement of the EC peak at T_C with increasing Sn-content, which corroborates with the existence of polarized nano-regions in doped BT induced by the incorporation of Sn. Furthermore, a slight peak shoulder seems to appear at specific applied electric fields, and it is more pronounced at high electric fields at around 160°C, 120°C, and 110°C for neat BT, BT 5%Sn, and BT 7.5%Sn, respectively.

This peak might be attributed to the hard switching dynamics of the PNRs, which are assumed to be hard to undergo changes of their orientations at T_C and needed higher temperatures and applied electric fields to achieve the switching. The increasing of Sn-content induced the shift of the shoulder position towards the main EC peak, which could lead to the merge of both peaks at

higher Sn-content. This will result in one broad EC peak presenting high temperature stability suitable for cooling devices.

Table 3 summarizes the obtained EC performances of the BTxSn samples at T_C , compared to some other BT-based systems [26,65–67].

Table 3. Electrocaloric performances obtained in this work compared to other literature data of BT-based systems.

Composition	ΔT (K) at T_C	ΔE (kV/cm)	$\Delta T / \Delta E$ $\times 10^{-6}$ (K.m/V)	Grain size (μm)	Synthesis method
BaTiO_3 ^{This work}	0.80	9.87	0.81	~ 0.07	Modified Pechini
$\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ ^{This work}	0.12	4.07	0.29	~ 2	Modified Pechini
$\text{BaTi}_{0.925}\text{Sn}_{0.075}\text{O}_3$ ^{This work}	0.15	5.78	0.26	~ 3	Modified Pechini
BaTiO_3 [26]	0.01	9.98	0.1	~0.5	Solid-state reaction
$\text{BaTi}_{0.95}\text{Sn}_{0.05}\text{O}_3$ [26]	0.079	3.62	0.21	~50	Solid-state reaction
$\text{BaTi}_{0.9}\text{Sn}_{0.1}\text{O}_3$ [26]	0.05	10.13	0.049	~25	Solid-state reaction
$\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$ [65]	0.12	7.95	0.15	~8	Solid-state reaction
$\text{Ba}_{0.975}\text{La}_{0.017}(\text{Zr}_{0.05}\text{Ti}_{0.90})\text{Sn}_{0.05}\text{O}_3$ [66]	0.243	12	0.20	~0.4	Solid-state reaction
$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.1}\text{O}_3$ [67]	0.109	6.65	0.16	-	Solvothermal

As can be observed, a high value of the adiabatic temperature change is obtained for the nanostructured neat BT system, namely $\Delta T = 0.8$ K at 9.87 kV/cm, with a significant corresponding responsivity of $\Delta T/\Delta E = 0.81 \times 10^{-6}$ K m/V. In comparison to bulk BT elaborated via solid-state method, a clear weak responsivity of 0.1×10^{-6} K m/V was reported [26]. Thus, the EC effect appears to be maximized in nanostructured neat BT used in this study, which was processed via modified Pechini method; especially higher responsivity is obtained to be compared to the one of BT system with micrometric grain size. These results are comparable to the work reported by Moya *et al.* [68] where an important EC responsivity of $\Delta T/\Delta E = 0.75 \times 10^{-6}$ K m/V, was obtained in commercial single-crystal BaTiO_3 sample. In contrast, low EC responses were reported for commercial multilayer ceramic capacitors (MLCC) based on BT system (Y5V capacitor type) of $\Delta T/\Delta E < 0.06 \times 10^{-6}$ K m/V [64,69].

Moreover, in this work, the Sn doped BT ceramics prepared using the modified Pechini method present an improved EC responsivity compared to similar compositions synthesized using the conventional solid-state method (see Table 3). In particular, BT5%Sn, and BT7.5%Sn samples exhibited an important EC responsivity, respectively of 0.29×10^{-6} , and 0.26×10^{-6} K m/V at T_C .

4. Conclusions

Nanostructured lead-free $\text{BaTi}_{1-x}\text{Sn}_x\text{O}_3$ ($x = 0, 0.05$ and 0.075) were successfully elaborated using modified Pechini method. For neat BaTiO_3 , phase symmetry is confirmed to match with tetragonal symmetry ($P4mm$, No 99) while orthorhombic symmetry phase ($A2mm$, No 38) was confirmed for doped BaTiO_3 with 5%Sn and 7.5%Sn contents. Dielectric properties investigations confirmed phase transition temperatures in this system and the enhancement of the dielectric permittivity with increasing Sn-content. The Curie temperature up shifted towards higher temperatures was observed in neat BT $T_C = 139^\circ\text{C}$, compared to 120°C reported for BT bulk material. Therefore, the incorporation of a small amount of Sn in the BT host lattice was found to lower T_C . Electrocaloric effects and energy storage properties were examined for the investigated samples. Remarkably, a high electrocaloric responsivity was obtained for the nanostructured neat BT, which greatly exceeds the reported values for the equivalent bulk materials that deserves vivid interest for developing new refrigeration devices based on nanostructured BT compound.

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