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**An Analysis of Lead-Free $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.915}-$
 $(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$ Ceramic for Efficient Refrigeration
and Thermal Energy Harvesting**

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Abstract:

This article demonstrates the colossal energy harvesting capability of a lead-free $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.915}(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$ (BULK) ceramic using the Olsen cycle. The maximum harvestable energy density estimated for this system is found to be 1523 J/L (1523 kJ/m³) where the results are presented for extreme ambient conditions of 20-160°C and electric fields of 0.1-4 MV/m. This estimated energy density is 1.7 times higher than the maximum reported to date for the lanthanum-doped lead zirconate titanate (PLZT) (Thick film) system. Moreover, this study introduces a generalized and effective solid state refrigeration cycle in contrast to the ferroelectric Ericson refrigeration cycle. The cycle is based on a temperature induced polarization change on application of a unipolar electric field to ferroelectric ceramics.

1. Introduction

$\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) based materials have recently attracted the attention of researchers¹ due to their remarkable ferroelectric properties. Solid solutions of these ceramics have been extensively studied to improve specific physical properties¹⁻⁴. These include BNT- $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - BiFeO_3 ⁵, BNT- $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - BaTiO_3 ⁶⁻⁸, BNT- $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - SrTiO_3 ⁹, BNT- $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ¹⁰, BNT- $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ^{4, 11}, BNT- BaTiO_3 ³, BNT- KNbO_3 ¹² and BNT- $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ - KNbO_3 ¹³. In addition to these systems, the literature also consists of several attempts to achieve A-site and B-site substitutions^{14, 15}. For example, Zuo et. al.¹⁶ and Li et. al.⁸ have reported tantalum and caesium doped solutions of these ceramics, respectively. In this regard, Lin and Kwok synthesized a new BNT-based lead free composition namely $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.915}(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$ (0.915BNT-0.05BKT-0.02BT-0.015ST) using a conventional solid state route at 1200 °C for 2 h¹⁷. The system has a perovskite structure with rhombohedral symmetry. The piezoelectric constant (d_{33}) for this composition was observed to be 203 pC/N and k_p and k_T values are found to be 31.4% and 46.7% respectively. Interestingly, the material also exhibits two dielectric anomalies at the depolarization temperature (T_d) and T_m (the temperature of maximum dielectric constant). The depolarization temperature is the temperature at which a material undergoes a transition from a ferroelectric state to an anti-ferroelectric state. Similar anomalies have also been reported for other BNT-based ceramics¹⁻¹⁹ and it is well documented that piezoelectricity in BNT-based ceramics almost disappears near T_d ^{9, 12, 14, 20, 21}. However, Tai et. al. determined experimentally that there was no evidence of anti-ferroelectric domains near T_d ²¹. Lin and Kwok explained that this composition may contain both polar and non-polar regions near T_d , which is responsible for deformation of the hysteresis loop in the

vicinity of this temperature¹⁷. A dielectric constant (ϵ_r) of 6000 has been reported for 0.915BNT-0.05BKT-0.02BT-0.015ST at T_m . The promising potential of this BNT based composition for various technological applications makes it interesting for thermal energy harvesting as well as refrigeration investigations, which will be discussed later in this paper.

2. Pyroelectric Energy Harvesting

Pyroelectric materials have been extensively explored for energy harvesting applications²²⁻³⁸. These intriguing materials produce an electrical current when subjected to a change in temperature. This particular feature of these materials can be used to take advantage of low-grade waste heat, which is the thermal by-product of many energy conversion devices such as internal combustion engines, refrigerators, ovens, consumer electronics and other domestic appliances. In this context, numerous studies and novel designs of pyroelectric harvesters are reported in literature^{30, 33, 35, 38-40}. To improve the thermal harvesting capability of ferroelectrics, the concept of energy harvesting by exploiting the ferroelectric hysteresis loop in a cyclic manner (the ‘Olsen’ cycle) was introduced in the early 1980s^{30-35, 41, 42}; this approach provided new opportunities for harnessing waste thermal energy. It has been reported that energy harvesting using the Olsen cycle, by virtue of a change in the induced polarization with a change in temperature and electric field, can be of the order of 10^3 higher than simply using the pyroelectric effect²⁴. This interesting concept led to numerous trials^{30-35, 41, 42} and to the best of author’s knowledge the maximum energy density to date reported in the literature is 888 kJ/m³ (888 J/L/cycle) for 8/65/35 lanthanum-doped lead zirconate titanate (PLZT) operating between temperatures of 25-160°C and fields of 0.2-7.5 MV/m^{30-35, 42, 43}.

3. Cycles

3.1 Olsen Cycle

Olsen et. al. proposed that any material which exhibits a significant shift in its D - E (hysteresis) loop or induced polarization with respect to a change in temperature and electric field can be employed in a cyclic manner for thermal energy harvesting⁴¹. This phenomenon is not the ‘pure’ pyroelectric effect as it is necessary in the Olsen cycle to induce a polarization using both an electric field and thermal energy. The cycle introduced by Olsen was initially defined for materials in which the polarization decreases with an increase in temperature, since most materials behave in this manner. It is to be noted at this stage that the materials that are most suitable for harvesting using the Olsen cycle are those in which there is a large change in polarization with temperature and electric field. Such features have been reported in the $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.915}-(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$ ceramic¹⁷ and in the composition examined in this paper we consider a more unusual case whereby the material exhibits an increase in polarization with increased temperature. Figure 1 illustrates a peculiar shift in P - E loop of this composition with an increase in temperature from 20 °C to 170 °C, as observed from the detailed characterization study of Lin and Kin¹⁷. Similar shifts have been reported by the same authors for temperatures of 60 °C, 80 °C, 140 °C, 160 °C, 180 °C and 200 °C (which are not shown here)¹⁷. Figure 2 explains the necessary working Olsen cycle for these unusual loop shifts, where loop A and B are sections of the bipolar hysteresis loops for the material at low and high temperature respectively. Area 1-2-3-4’ (Figure 2 (a)) is the effective thermal energy harvesting between the two hysteresis (D - E) loops operated between applied fields of E_H and E_L (where $E_H > E_L$), taken at a high and low temperature (T_L and T_H where $T_H > T_L$). However, this area can be increased by

maintaining a unipolar electric field by cycling between E_H and E_L . This is due to the fact that the hysteresis loop does not form under unipolar electric fields and the polarization can be reversed between P_r (remanent polarization) to P_S (saturation polarization) through the upper branch of the bipolar hysteresis loops in Figure 2a⁴¹. In this scenario, point 4' can be further moved to 4 (Figure 2 (a)) and energy harvesting can be increased by the area 4'-4-3 (shaded area in Figure 2(a)).

The Olsen cycle to be used in this case consists of two isoelectric (1-4 and 3-2) and two isothermal processes (1-2 and 3-4). The 1-2-3-4 cycle is anti-clockwise since the polarization of the material increases with increasing temperature; this is in contrast to the more conventional clockwise direction⁴¹ used when cycling materials whose polarization decreases with increasing temperature. Figure 2 (a) and (b) shows the corresponding electric displacement versus electric field and temperature versus entropy diagrams respectively. The unipolar electric field is raised from a low field (E_L) to a high field (E_H) by doing work (W_P) on the system (Process 1-2). This leads to an increase in polarization from P_1 to P_2 at a constant temperature T_L ; this also decreases the entropy from s_1 to s_2 , as shown in Figure 2(b). It should be noted that due to an increase in the polarization the work of polarization (W_P) leads to some heat (Q_{WP}) being released by the material. Additionally, it can be assumed that there is only a small consumption of electric energy (applied in order to change in polarization) since the materials are good insulators and no current flows through the material. In Process 2-3 heat (Q_S) (generally waste heat from other sources) is supplied to the material (system) iso-electrically to heat the material from T_L to T_H . The polarization of the system then rises from P_2 to P_3 . Again due to a rise in polarization the entropy further decreases to s_3 (Figure 2(b)). Indirectly, the absorption of heat (Q_S) by the

material results in cooling of the surrounding environment. Thereafter, depolarization work (W_{DP}) is done to reduce the applied unipolar electrical field isothermally from E_H to E_L leading to reduction of polarization of the material to P_4 (Process 3-4). This reduction in polarization is responsible for an increase in entropy during this process. Finally, in order to complete the cycle and to bring it to its initial state (T_L, P_L, S_L and E_L) heat (Q_R) is extracted from the system (Process 4-1). This process is known as isoelectric heat rejection. The direction of the T - s diagram is clockwise in Figure 2(b) and is indicative of a cycle for a heat engine.

The overall electrical energy that can be harvested using this cycle can be calculated as the area enclosed by the complete cycle (1-2-3-4 of D - E curve) and is expressed as^{34, 43}

$$N_D = \oint E.dD \quad (1)$$

3.2 Reversed Olsen/Proposed Ferroelectric Refrigeration Cycle

It is to be noted that if the direction of the above explained cycle can be reversed then the material will exhibit a refrigeration effect. Though similar attempts exist in literature^{44, 45}, the cycle proposed by us is generalized for all ferroelectric materials as it is based on a temperature induced change in the unipolar P - E loop. It also provides a broad idea of the ideal working range and is more effective as hysteresis losses are reduced. In order to have better understanding of refrigeration cycle the P - E and T - s diagrams for this regime are shown in Figure 3 (a) and 3 (b) respectively. The T - s diagram with an anticlockwise direction indicates a refrigeration cycle. Here, the initial Process 1-2 of heating from T_L to T_H at E_L corresponds to the compressor work of a “Vapor Compression Cycle”. This can be termed as the work of heating (W_H) in the case of solid state refrigeration. During Process 1-2 the heat (Q_S) from a waste source is supplied to the

material (system). In Process 2-3 work of polarization (W_P) is done on the material to raise the applied field to E_H from E_L , which is equivalent to the heat (Q_{WP}) rejected in a condenser in a “Vapor Compression Cycle” as the entropy of the system is reduced from s_1 to s_2 (Figure 3 (b)) due to the electrocaloric effect. Thereafter, as the material is cooled from T_H to T_L in Process 3-4 the heat (Q_R) of the system is rejected to the surroundings using some mechanical arrangement, such as using heat exchanger fins. Finally, reduction of the applied field from E_H to E_L in Process 4-1 is responsible for the refrigeration effect (heat absorption (Q_{Ab})) corresponding to work of depolarization (W_{DP}) in the evaporator. The area under the curve can be termed as overall work done (W_D) to run the cycle. This cycle can also work for a more usual shift of the unipolar ferroelectric loop in which there is a decrease in polarization with increasing temperature.

In order, to have a comparison criterion for “Electrocaloric refrigeration”, Emmanuel et.al.⁴⁶ introduced the Electrocaloric (EC) efficiency (η), which is given as :

$$\eta = \frac{|Q|}{|W|} \quad (2)$$

Where Q (isothermal heat) and W (electrical work) can be calculated as follows

$$|Q| = \left| \int_{E_L}^{E_H} T \left(\frac{\partial D}{\partial T} \right)_E dE \right| \quad (3)$$

$$|W| = \left| \int_{D_1}^{D_2} E dD \right| \quad (4)$$

In the similar way for the novel refrigeration cycle proposed here, the efficiency can be defined as

$$COP_{\text{Refrigerator}} = \frac{\text{Net Isothermal Heat}}{\text{Overall Work Done}} = \left| \frac{Q_{wp} - Q_{Ab}}{W_D} \right| \quad (5)$$

The net isothermal heat in the present scenario is the difference of the heat absorbed

$$\left(|Q_{Ab}| = \left| \int_{E_L}^{E_H} T_L \left(\frac{\partial D}{\partial T} \right) dE \right| \right) \text{ by the material (system) and the heat released}$$

$$\left(|Q_{wp}| = \left| \int_{E_L}^{E_H} T_H \left(\frac{\partial D}{\partial T} \right) dE \right| \right) \text{ by the material to the surroundings.}$$

4. Results and Discussion

Finally, we perform thermal energy harvesting calculations for this composition for a fixed value of lower temperature ($T_L \sim 20^\circ\text{C}$) since the hysteresis loop becomes almost paraelectric at this temperature¹⁷. The resulting energy densities are shown in Figure 4 as a function of an increase in maximum values of applied electric fields (E_H) for the temperature ranges of 20-60°C, 20-80°C, 20-140°C, 20-160°C, 20-170°C, 20-180°C, and 20-200°C. Thermal energy harvesting using the Olsen cycle is for operation under unipolar electric fields thus the lower value of electric field (E_L) is maintained constant at 0.1 MV/m for all cycles under consideration. The maximum energy density for the system under study is estimated to be 1523 kJ/m³ (1523 J/L) in the temperature range of 20-160°C (0.1-4 MV/m). This value is substantially higher than many reported lead-based ferroelectrics such as 8/65/35 PLZT (888 J/L/cycle)⁴³, PZST (100-130 J/L/cycle)^{32, 34, 35}, 73/27 P(VDF-TrFE) (30 J/L/cycle)⁴², 60-40 P(VDF-TrFE) (52-130

J/L/cycle)^{23, 47}, PZN-5.5PT (52-130 J/L/cycle)²⁵, PZN-5.5PT (52-130 J/L/cycle)³⁸, PMN-PT (100-186 J/L/cycle)^{24, 48}. The trend in the energy density plots reveal that the energy density for the temperature range of 20-80°C is much higher in comparison to 20-60°C. This is due to the gradual intensification of the pyroelectric coefficient with an enhancement in temperature from 60°C ($p=20\mu\text{C}/\text{cm}^2$) to 80°C ($p=35\mu\text{C}/\text{cm}^2$)¹⁷. Intriguingly, the variations in the energy density for 20-140°C, 20-160°C and 20-170°C are nearly equal throughout with the increase in E_H . This suggests that 20-140°C is the most appropriate working range for a thermal energy harvesting device made of 0.915BNT-0.05BKT-0.02BT-0.015ST since for a smaller temperature change it is possible to harvest the same amount of energy. Thereafter, in the temperature limits of 20-180°C the energy density falls and this trend continues further for the temperature domain of 20-200°C. This is due to ferroelectric to anti-ferroelectric like transition in this composition. The depolarization temperature (T_d) for this composition is reported to be 184°C and it has been reported that the piezoelectricity of BNT-based ceramics almost vanishes above T_d ^{4, 9, 12, 14}. Careful examination of the pyroelectric coefficient with temperature provides an understanding of the decrease in energy density since it decreases exponentially after 170°C ($23\mu\text{C}/\text{cm}^2$) to approximately $7\mu\text{C}/\text{cm}^2$ at 180°C and the value keeps on falling until 200°C¹⁷. This suggests that the energy harvesting devices built using BNT-based compositions should not be used beyond the depolarization temperature. Moreover, the governing conditions of lead-based ferroelectrics indicate that most of these provide a high energy density under the application of large applied electric fields, e.g. P(VDF-TrFE: 4-60 MV/m^{23, 31, 42, 47, 49, 50}; PLZT (0.2-7.5 MV/m)⁴³. This clearly indicates that the lead-free composition under study is a thermal energy harvesting material of interest based on the maximum energy harvesting and the low applied electric fields

within similar temperature ranges. Moreover, 0.915BNT-0.05BKT-0.02BT-0.015ST composition possesses the highest estimated energy harvesting potential (1523 kJ/m^3) reported to date. Secondly, we estimate the efficiency of refrigeration ($COP_{\text{Refrigerator}}$) for all temperature ranges under various possible combinations of applied electric field. The maximum efficiency ($COP_{\text{Refrigerator}}$) (using eq 5) is found to be 2.016 within the temperature range of 80-160 °C for an applied field of 0.1-0.5 MV/m. Although this value is calculated for the bulk material, it is high in comparison to reported efficiency ($COP_{\text{Refrigerator}} \sim 1.2$) of doped multilayered thin films of BaTiO_3 ⁴⁶. It is important to note that the aforementioned efficiency does not provide refrigeration efficiency or COP (coefficient of performance) of the cycle. Here, our aim is merely to provide a figure of merit for the selection and comparison of materials working on these cycles from application view point.

Conclusions

The present study demonstrated the potential for colossal thermal energy harvesting using lead-free materials with a peculiar polarization shift with an increase in temperature for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.915}-(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$. This material has an estimated maximum energy density of 1523 J/L (1523 kJ/m^3) in the temperature domain of 20-160°C at an applied electric field 0.1-4 MV/m. Interestingly, the energy density for 20-140°C, 20-160°C and 20-170°C are found to be nearly equal in the same electric field range. Thus we conclude that this material should be explored in the temperature span of 20-140°C to have maximum thermal energy harvesting. In addition, we have introduced a potentially efficient solid state refrigeration cycle based on the Olsen cycle using the temperature induced polarization in ferroelectric ceramics.

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References

1. Y. Hiruma, H. Nagata and T. Takenaka, Journal of applied physics **105** (8), 084112-084112-084118 (2009).
2. B. Jaffe, *Piezoelectric ceramics*. (Academic press, 1971).
3. T. Takenaka, K.-I. Maruyama and K. Sakata, Japanese journal of applied physics **30** (9B), 2236-2239 (1991).
4. K. Yoshii, Y. Hiruma, H. Nagata and T. Takenaka, Japanese journal of applied physics **45**, 4493 (2006).
5. C. Zhou, X. Liu, W. Li and C. Yuan, Materials Chemistry and Physics **114** (2-3), 832-836 (2009).
6. X. Wang, X. Tang and H. Chan, Applied physics letters **85** (1), 91-93 (2004).
7. S. Zhang, T. R. Shrout, H. Nagata, Y. Hiruma and T. Takenaka, IEEE transactions on ultrasonics, ferroelectrics, and frequency control **54** (5), 910-917 (2007).
8. Y. Li, W. Chen, Q. Xu, J. Zhou, Y. Wang and H. Sun, Ceramics international **33** (1), 95-99 (2007).
9. Y. Hiruma, Y. Imai, Y. Watanabe, H. Nagata and T. Takenaka, Applied physics letters **92** (26), 262904-262904-262903 (2008).
10. A. B. Kouna, S.-T. Zhang, W. Jo, T. Granzow and J. Rodel, Applied physics letters **92** (22), 222902-222902-222903 (2008).
11. S. Zhao, G. Li, A. Ding, T. Wang and Q. Yin, Journal of Physics D: Applied Physics **39** (10), 2277 (2006).
12. G. Fan, W. Lu, X. Wang and F. Liang, Journal of Physics D: Applied Physics **41** (3), 035403 (2008).
13. G. Fan, W. Lu, X. Wang and F. Liang, Applied physics letters **91** (20), 202908-202908-202903 (2007).

14. Y.-Q. Yao, T.-Y. Tseng, C.-C. Chou and H. H. Chen, *Journal of applied physics* **102** (9), 094102-094102-094105 (2007).
15. C. Zhou and X. Liu, *Materials Chemistry and Physics* **108** (2), 413-416 (2008).
16. R. Zuo, C. Ye, X. Fang and J. Li, *Journal of the European Ceramic Society* **28** (4), 871 (2008).
17. D. Lin and K. W. Kwok, *Journal of the American Ceramic Society* **93** (3), 806-813 (2010).
18. Y. Li, W. Chen, Q. Xu, J. Zhou, X. Gu and S. Fang, *Materials Chemistry and Physics* **94** (2-3), 328-332 (2005).
19. H. Yu and Z.-G. Ye, *Applied physics letters* **93**, 112902 (2008).
20. J. Suchanicz, J. Kusz, H. Böhm, H. Duda, J. Mercurio and K. Konieczny, *Journal of the European Ceramic Society* **23** (10), 1559-1564 (2003).
21. C. W. Tai, S. H. Choy and H. L. Chan, *Journal of the American Ceramic Society* **91** (10), 3335-3341 (2008).
22. D. Guyomar, S. Pruvost and G. Sebald, *Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on* **55** (2), 279-285 (2008).
23. M. Ikura, *Ferroelectrics* **267** (1), 403-408 (2002).
24. R. Kandilian, A. Navid and L. Pilon, *Smart Materials and Structures* **20** (5), 055020 (2011).
25. A. Khodayari, S. Pruvost, G. Sebald, D. Guyomar and S. Mohammadi, *Ultrasonics, Ferroelectrics and Frequency Control, IEEE Transactions on* **56** (4), 693-699 (2009).
26. L. Kouchachvili and M. Ikura, *International Journal of Energy Research* **32** (4), 328-335 (2008).
27. L. Kouchachvili and M. Ikura, (Google Patents, 2008).
28. A. Navid, C. S. Lynch and L. Pilon, *Smart Materials and Structures* **19** (5), 055006 (2010).
29. A. Navid, D. Vanderpool, A. Bah and L. Pilon, *International journal of heat and mass transfer* **53** (19), 4060-4070 (2010).
30. R. Olsen and D. Brown, *Ferroelectrics* **40** (1), 17-27 (1982).
31. R. Olsen and D. Bruno, presented at the IECEC'86; Proceedings of the Twenty-first Intersociety Energy Conversion Engineering Conference, 1986 (unpublished).
32. R. Olsen, D. Bruno, J. Briscoe and J. Dullea, *Ferroelectrics* **59** (1), 205-219 (1984).
33. R. B. Olsen, *Journal of Energy* **6** (2), 91-95 (1982).
34. R. B. Olsen, J. M. Briscoe, D. A. Bruno and W. F. Butler, *Ferroelectrics* **38** (1), 975-978 (1981).
35. R. B. Olsen, D. A. Bruno and J. M. Briscoe, *Journal of applied physics* **58** (12), 4709-4716 (1985).
36. G. Sebald, L. Seveyrat, D. Guyomar, L. Lebrun, B. Guiffard and S. Pruvost, *Journal of applied physics* **100** (12), 124112-124112-124116 (2006).
37. H. Zhu, S. Pruvost, D. Guyomar and A. Khodayari, *Journal of applied physics* **106**, 124102 (2009).
38. I. M. McKinley, R. Kandilian and L. Pilon, *Smart Materials and Structures* **21** (3), 035015 (2012).
39. F. Y. Lee, A. Navid and L. Pilon, *Applied thermal engineering* **37**, 30-37 (2012).
40. A. Cuadras, M. Gasulla and V. Ferrari, *Sensors and Actuators A: Physical* **158** (1), 132-139 (2010).
41. R. B. Olsen and D. Evans, *Journal of applied physics* **54** (10), 5941-5944 (1983).
42. R. B. Olsen, D. A. Bruno, J. M. Briscoe and E. W. Jacobs, *Journal of applied physics* **57** (11), 5036-5042 (1985).
43. F. Y. Lee, S. Goljahi, I. M. McKinley, C. S. Lynch and L. Pilon, *Smart Materials and Structures* **21** (2), 025021 (2012).
44. J. He, J. Chen, Y. Zhou and J. T. Wang, *Energy Conversion and Management* **43** (17), 2319-2327 (2002).
45. J. He, J. Chen, J. T. Wang and B. Hua, *International Journal of Thermal Sciences* **42** (2), 169-175 (2003).

46. E. Defay, S. Crossley, S. Kar - Narayan, X. Moya and N. D. Mathur, *Advanced Materials* (2013).
47. H. Nguyen, A. Navid and L. Pilon, *Applied thermal engineering* **30** (14), 2127-2137 (2010).
48. G. Sebald, S. Pruvost and D. Guyomar, *Smart Materials and Structures* **17** (1), 015012 (2008).
49. A. Navid and L. Pilon, *Smart Materials and Structures* **20** (2), 025012 (2011).
50. H. Zhu, S. Pruvost, P. Cottinet and D. Guyomar, *Applied physics letters* **98** (22), 222901-222903 (2011).

Figures Captions:

Figure 1: Ferroelectric (D - E) hysteresis loops for 0.915BNT-0.05BKT-0.02BT-0.015ST samples at two different temperatures¹⁷. Note the increase in polarization with an increase of temperature.

Figure 2: (a) Isothermal unipolar electric displacement versus electric field (D - E) hysteresis loops (b) temperature versus entropy (T - S) curves for electrical energy harvesting (1-2-3-4) using Olsen cycle operated between different temperatures T_L and T_H

Figure 3: (a) Isothermal unipolar electric displacement versus electric field (D - E) hysteresis loops (b) temperature versus entropy (T - S) curves for a ferroelectric refrigeration cycle (1-2-3-4) operated between different temperatures T_L and T_H

Figure 4: Estimated energy density for 0.915BNT-0.05BKT-0.02BT-0.015ST as a function of high electric field (E_H). The cold temperature (T_L) source and low electric field (E_L) are kept at 20 °C and 0.1 MV/m respectively.