Giant energy harvesting potential in (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer and (001)-oriented $0.67\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.33PbTiO_3 thin films

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This work emphasis on the competence of (100)-oriented PMN–PT buffer layered ($0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer) and (001)-oriented PMN–PT ($0.67\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.33PbTiO_3) for low grade thermal energy harvesting using Olsen cycle. Our analysis (based on well-reported experiments in literature) reveals that these films show colossal energy harnessing possibility. Both the films are found to have maximum harnessable energy densities (PMN–PT buffer layered: 8 MJ/m^3 ; PMN–PT: 6.5 MJ/m^3) in identical ambient conditions of 30 – 150°C and 0 – 600 kV/cm . This energy harnessing plausibility is found to be nearly five times higher than the previously reported values to date.

Keywords: Giant; energy harvesting; thin films; Olsen cycle.

1. Introduction

Energy crisis and emerging technologies have compelled the researchers to look for sustainable solutions to meet the future energy demands. Despite of enormous attempts it is tough to completely get rid of the losses associated with the energy conversion systems. Among these losses, thermal losses are given top priority in contrast to the conversion devices and equipments being used in the present scenario. The best way to mitigate the energy losses is “recycling”. The thermal by-products from energy conversion devices are topic of great concern for effective utilization of resources. In this context, pyroelectric materials have been extensively explored.^{1–17} These materials generate electrical current on the expense of input thermal energy. This property of these materials can be effectively employed for harnessing energy from ample spectrum of appliances such as internal combustion engines, refrigerator, microwave oven, laptop, television and other domestic apparatus. Literature is flooded with a huge number of novel designs for such kind of energy harvesting applications.^{9,12,14,17–25} In this direction, the

maximum energy density reported using ferroelectric ceramics is 888 J/L/cycle (for 8/65/35 PLZT thick films using Olsen cycle).²⁶ Apart from the innovations in designs, prodigious efforts are being made to have felicitous materials for these applications. One of such studies was manifested by Mischenko *et al.*²⁷ in which they stressed on thin films of $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$. Later, the thin films of many similar configurations were explored and morphotropic phase boundary compositions ($0.30 < x < 0.35$) of $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – $x\text{PbTiO}_3$ (PMN–PT) are found to be among the most promising contender for wide range of electromechanical applications due to their outstanding ferroelectric properties.^{28–30} Therefore, in present work we have considered thin films of two intriguing compositions of this family for low grade thermal energy harvesting using Olsen cycle.

2. Olsen Cycle

Present study addresses the unforeseen potential of novel structurally tailored thin films for giant low grade waste

Fig. 1. Electrical energy harvesting (1-2-3-4) using Olsen cycle operated between different temperatures T_{1-2} and T_{3-4} on isothermal unipolar electric displacement versus electric field (D - E) hysteresis loops for a ferroelectric material.

thermal energy harvesting applications. The concept came into existence in early 1980s and was introduced by Olsen and co-workers.^{10,14,31} They proposed that the pyroelectric effect can be used in a cyclic manner to harness electrical energy. This is due to the ability of these materials to induce change in polarization when subjected to a temperature change. Figure 1 demonstrates a typical shift in the hysteresis loop (from P to Q) for a temperature variation of T_{1-2} to T_{3-4} ($T_{1-2} < T_{3-4}$). Initially, the material is polarized at lower temperature (T_{1-2}) (process 1'-2) and then exposed to waste heat (Q_s) at constant electric field E_H (process 2-3). This causes a decrement in polarization ($P_2 - P_3$) as a result of increase in entropy due to heating. Thereafter, the material is isothermally depolarized (process 3-4) at temperature T_{3-4} and finally cooled isoelectrically (process 4-1) to complete the cycle. This cycle is popular as Olsen cycle and the cyclic integral of the area under curve 1'-2-3-4 gives the overall energy harvesting. Further, in order to have enhanced energy harvesting and to reduce hysteresis losses, it is advised to use unipolar electric field so as to have escalated energy harvesting by an area 1'-1-2. The overall energy harvesting (shaded area in Fig. 1) per cycle is given as:

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

Energy densities reported using Eq. (1) (indirect measurements for Olsen cycle) are documented to have close agreement with that of the direct measurements.^{17,18,26,32-34}

3. Essential Features for Giant Energy Harvesting

We are continuously working in the direction³⁵⁻³⁹ of exploring novel compositions and materials families that suits

best for the Olsen cycle. We figured out that in order to have huge electrical energy conversion from waste thermal energy using Olsen cycle a material should possess:

- (1) A huge difference in spontaneous polarization with respect to the change in temperature ($\partial P_s / \partial T$) should be high. This will lead to significant enhancement of the cycle area and thus energy density.
- (2) Secondly, the piezoelectric coefficient should be as low as possible as it contributes towards piezoelectric noise in the device.
- (3) Moreover, the Curie temperature should be near to operating temperature range for drastic change in polarization and to have advantage of the phase transitions.
- (4) Further, the dielectric loss ($\tan \delta$) contributes towards inherent dissipation of stored electrical energy and hence should be low.
- (5) Consequently, the change in polarization with change in electric field (dP/dE_H) or dielectric constant should be very high to have exponential increase in maximum energy conversion. This signifies higher energy density even at low electric fields.

Apart from abovementioned features, the material should be capable to withstand and sustain hysteresis loops at very large applied electric fields (often noticed in ferroelectric thin films), it will display giant electrical energy harvesting density. However, it is important to note that the net energy in case of thin films will be very small in contrast to the bulk materials as the active material volume is extremely small, which cannot be overruled. Despite of this, there are number of advantages associated with thin film for energy harvesting. First is that as the thickness is very small, a small voltage source is required in comparison to bulk materials for generating appropriate electric field. Secondly, heat transfer rate will be very high because of large surface area which will increase energy harvesting frequency. Therefore, we have chosen recently reported thin films of (100)-oriented PMN-PT buffer layered (0.68PbMg_{1/3}Nb_{2/3}O₃-0.32PbTiO₃ with Pb(Zr_{0.3}Ti_{0.7})O₃/PbO_x buffer layer) and (001)-oriented PMN-PT (0.67PbMg_{1/3}Nb_{2/3}O₃-0.33PbTiO₃)^{40,41} for our consideration in present study as these satisfy most of the alluring conditions for giant energy harvesting.

4. Materials

Feng *et al.*⁴⁰ reported large electrocaloric effect (EC) in (001)-oriented PMN-PT (0.67PbMg_{1/3}Nb_{2/3}O₃-0.33PbTiO₃). They deposited 200 nm PMN-PT thin films on LaNiO₃ (LNO) adhesion layer (200 nm) on a SiO₂ (65 nm)/Si (100) substrate at 250°C using rf magnetron sputtering. LNO has good metallic conductivity and hence was chosen as bottom electrode for PMN-PT thin film. Firstly, LNO was deposited on the SiO₂ substrate and thereafter the PMN-PT thin film was deposited on this multilayered structure under identical

Fig. 2. P - E loops for (001)-oriented $0.67\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.33PbTiO_3 thin films.

conditions using a sintered PMN-PT ceramic target with a substrate temperature of 600°C . Finally grown films were characterized and their dielectric measurements were carried out. Thus obtained P - E loops at 30°C and 150°C are shown in Fig. 2. The films were found to have excellent dielectric properties (dielectric constant = 1585 and $\tan \delta$ as 1.9% at 1 kHz at room temperature). The Curie temperature is noticed to be nearly 152°C for (tetragonal) ferroelectric to (cubic) paraelectric transition. They concluded this study with an EC temperature change of 14.5 K under external applied voltage shift of 12 V ($\Delta E = 600 \text{ kV/cm}$) near morphotropic phase boundary (MPB). Further, the same group extended this study (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.32PbTiO_3 ; with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer.⁴¹ In this study, again 200 nm thin films of PMN-PT were grown on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrate using rf magnetron sputtering. Its dielectric constant and $\tan \delta$ are found to be 1380 and 1.8% at 1 kHz at room temperature, respectively. Another, important consideration is comparative reduction in Curie temperature (146°C) of 6°C . The P - E loops (only 30°C and 150°C) for these films are illustrated in Fig. 3. These films were reported

Fig. 3. P - E loops for (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer thin films.

Fig. 4. Maximum energy densities estimated using Olsen cycle for (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer thin films with T_{1-2} kept fixed at 30°C and E_L at 0 kV/cm .

to have a maximum EC temperature change of 13.4 K for 15 V ($\sim \Delta E = 600 \text{ kV/cm}$).

5. Results and Discussion

In order to have better energy conversion efficiencies various research groups have made several intriguing attempts and furnished distinct energy densities for different materials (8/65/35 PLZT (888 J/L/cycle),²⁶ PZST (100–130 J/L/cycle),^{11,13,14} 73/27 P(VDF-TrFE) (30 J/L/cycle),³¹ 60-40 P(VDF-TrFE) (52–130 J/L/cycle),^{2,34} PZN-5.5PT (52–130 J/L/cycle),⁴ PZN-5.5PT (52–130 J/L/cycle),¹⁷ PMN-PT (100–186 J/L/cycle)^{3,23}). Recently, we divulged the biggest breakthrough in this area and reported an energy density of 1523 J/L (1523 kJ/m^3) for lead-free $(\text{Bi}_{0.5}\text{K}_{0.5})_{0.05}\text{Ba}_{0.02}\text{Sr}_{0.015}\text{TiO}_3$ (0.915BNT - 0.05BKT - 0.02BT - 0.015ST) ceramics.³⁵ However, in the present study we are focused on PMN-PT and PMN-PT buffer layer thin films. We measured the energy densities for both PMN-PT buffer layer and PMN-PT thin films using the ferroelectric hysteresis loops reported by Feng *et al.*⁴⁰ Figure 4 furnishes the estimated energy densities for (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer thin films. Here, we have kept T_{1-2} fixed at 30°C (room temperature) to have better understanding of the energy densities with temperature ranges in contrast to the possible applications for consumer electronics. The lower value of applied electric field (E_L) is kept constant at 0 kV/cm and energy densities are plotted as a function of varying higher applied electric field. The maximum energy density is found to be nearly 8 MJ/m^3 (8 kJ/L), which is exceptionally higher (by a factor of 5) than any existing value. This is for the ambient conditions of 30 – 150°C and 0 – 600 kV/cm (15 V). Primarily, it is due to the coexistence

of a huge difference is saturation polarization ($60 \mu\text{C}/\text{cm}^2$: 30°C ; $30 \mu\text{C}/\text{cm}^2$: 150°C) and pyroelectric coefficient with change in temperature. At the same time, these films demonstrate a capability to withstand very high applied electric field that contributes towards substantial enhancement in the cycle area and thus energy density. Another important consideration is sudden jump in the energy density from temperature ranges of 30 – 120°C to 30 – 150°C . This clearly indicates that a sharp elevation in energy densities can be achieved in the vicinity of the Curie temperature and MPB.

Secondly, we compared the energy densities of PMN–PT buffer layered thin films to that of PMN–PT thin films as these are observed to have better EC effect and ferroelectric properties. Similarly, measurements are carried out for the PMN–PT thin films and the energy densities of both films are plotted as a function of increment in the range of the thermal exposure as shown in Fig. 5. Figure 6 provides the comparative details of this work to that of previously reported studies. The lower temperature and applied electric field are kept constant at 30°C and 0 – $600 \text{ kV}/\text{cm}$. The maximum energy density in this case is found to be $6.5 \text{ kJ}/\text{L}$ (30 – 150°C and 0 – $600 \text{ kV}/\text{cm}$). Despite of better ferroelectric properties in PMN–PT thin films the energy densities are found higher in PMN–PT with buffer layer for all temperature ranges under consideration. Careful examination of the P – E loops and difference in remnant and saturation polarization in both the cases helps to explain this unexpected trend. The saturation polarization in both the cases is nearly same but there is a small difference (30°C : $22 \mu\text{C}/\text{cm}^2$, 150°C : $2 \mu\text{C}/\text{cm}^2$ — PMN–PT; 30°C : $19 \mu\text{C}/\text{cm}^2$, 150°C : $0 \mu\text{C}/\text{cm}^2$ — PMN–PT buffer layer^{40,42}). in remnant polarizations which is responsible for this shift. Moreover, relatively lower Curie temperature of the PMN–PT buffer layer thin film also causes a

Fig. 5. Comparative energy densities estimated using Olsen cycle for (001)-oriented $0.67\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.33PbTiO_3 and (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer thin films with T_{1-2} kept fixed at 30°C , $E_L = 0 \text{ kV}/\text{cm}$ and $E_H = 600 \text{ kV}/\text{cm}$.

Fig. 6. Maximum energy densities reported using Olsen cycle in various compositions (a,²⁶ b,³⁷ c³⁵ d and e: Present work).

difference in the loop (note the difference in loops with change in temperature in Figs. 2 and 3). Interestingly, we revealed that PMN–PT thin films with buffer layer are better performer for Olsen cycle while for EC refrigeration PMN–PT thin films serves more efficiently. Finally, we conclude that both the thin films under consideration are the potential candidates for thermal energy harvesting using Olsen cycle. Here, it is important to note that the present study only tells about the maximum energy that can be harvested but the real-time scenario may largely vary as it is subjected to the limitations of the electrical design. Moreover, leakage current and dielectric losses can also influence the performance of the device working on Olsen cycle.

6. Conclusions

To recapitulate it all, our investigations shed light on the facts that (001)-oriented $0.67\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.33PbTiO_3 and (100)-oriented $0.68\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – 0.32PbTiO_3 with $\text{Pb}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3/\text{PbO}_x$ buffer layer thin films are exceptionally best contenders for energy conversion applications using Olsen cycle. These are not only a suitable candidate to be operated with Olsen cycle but are also capable of making a paradigm shift in the field of consumer electronics. The predicted energy densities are quite large in comparison to previously documented values for any ferroelectric material. Therefore, the present work will unfurl new dimensions for waste energy harvesting technologies.

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