ENERGY STORAGE PERFORMANCE OF La-DOPED PZT RELAXOR-FERROELECTRIC THIN FILMS FABRICATED BY SOL-GEL PROCESS

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ABSTRACT

La-doped PZT Relaxor ferroelectric (RFE) thin films have been fabricated on the platinum-buffered silicon substrates by a sol-gel process. The microstructure, grain size, electrical properties, and energy-storage performance of the obtained thin films were investigated in detail. Scanning electron microscopy images revealed that PLZT thin films show the compact and dense structure. Surface morphology and microstructure of PZT and PLZT thin films indicated the surface grain size of PZT is larger than that of PLZT. X-ray diffraction analysis showed that PLZT thin films are strong preferred orientation (100) and have a pure perovskite phase. Room temperature ferroelectric measurements showed that the maximum values of U_{reco} of 6.52 J/cm^3 and energy-storage efficiency of 61.65% are achieved in the PLZT thin film with 8% La-doping at electric fields 1000 kV/cm and 1 kHz frequency. All these results indicated that the relaxor PLZT thin films with 8% La doping possess potential for capacitors with high energy-storage performance.

HIỆU SUẤT TÍCH TRỮ NĂNG LƯỢNG CỦA MÀNG MỎNG SẮT ĐIỆN NHÒE PZT PHA TẠP La CHẾ TẠO BỞI QUY TRÌNH SOL-GEL

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TỪ KHÓA

Vật liệu sắt điện nhòe
Màng mỏng
Sol-gel
Pha tạp
Tích trữ năng lượng

TÓM TẮT

Các màng mỏng sắt điện nhòe PZT pha tạp La (RFE) đã được chế tạo trên đế Pt/Ti/SiO_2 bằng quy trình quay phủ sol-gel. Cấu trúc vi mô, kích thước hạt, tính chất sắt điện và hiệu suất tích trữ năng lượng của các màng mỏng đã được nghiên cứu chi tiết. Hình ảnh quét kính hiển vi lực nguyên tử cho thấy màng mỏng PLZT có cấu trúc nhỏ mịn và dày đặc hơn so với màng PZT. Hình thái bề mặt và vi cấu trúc của các màng mỏng đã thể hiện kích thước các hạt PZT lớn hơn, thô hơn so với các hạt PLZT. Phân tích phổ nhiễu xạ tia X cho thấy màng mỏng PZT và PLZT có định hướng ưu tiên (100) và có pha perovskite tinh khiết. Các phép đo tính chất sắt điện ở nhiệt độ phòng cho phép tính toán trị số năng lượng thu hồi lớn nhất (U_{reco}) là 6,52 J/cm^3, hiệu suất tích trữ và chuyển đổi năng lượng (η) là 61,65% thu được đối với màng mỏng PLZT với 8% pha tạp La, ở điện trường E = 1000 kV/cm và tần số f =1 kHz. Những kết quả này chứng tỏ rằng màng mỏng PLZT với 8% pha tạp La rất có tiềm năng cho các tụ điện tích trữ năng lượng mật độ cao.

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1. Introduction

In recent years, relaxor ferroelectric materials have attracted special attention distinguished by researchers due to their outstanding piezoelectric and energy-storage properties [1] - [3]. Among them, lanthanum-doped lead zirconium titanium (PLZT) materials fabricated in the form of thin films are good candidates for high-density energy storage devices due to their properties dielectric, energy storage performance is superior to that of traditional bulk materials [4] - [6]. In addition, thin films (PLZT) are also widely used in many new generation micro-electromechanical devices includes ultrasonic transducers, sensors, random access memory RAM and actuators with significantly improved performance [7] - [10].

Several reports on PLZT based relaxor ferroelectrics have been reported for energy storage applications [4], [6], [11]. In these reports, PLZT thin films prepared by the sol-gel process. However, in each report, the synthesis process is different. Tong et al [6] reported the PLZT sol synthetic process in which water was used as a solvent. Hao et al [4] also reported the same procedure. Besides, glycerin was added into the solution in the proportion of one mole of glycerin to one mole of lead.

Using sol-gel chemistry based on acetic acid, we fabricated PLZT thin films on substrates of platinized silicon (Pt/Si). Details on the solution preparation, deposition, and heat treatment conditions are reported. We have synthesized $Pb_{1-x}La_x(Zr_{0.52}Ti_{0.48})O_3$ precursor for x = 0; 5; 8 and 10% by sol-gel technique. The synthesized gel was subjected to XRD for the phase confirmation. The conditions of preparation were optimized by thermo-gravimetric and differential thermal analysis. For all the samples, the values of U_{reco} and energy-storage performance was investigated as a function of La-doping. The measurements were done at 1000 kV/cm and 1 kHz. For the sample with 8% La doping, we investigated the effect of electric field and frequency on the energy-storage performance.

2. Experimental procedure

The PLZT thin films were prepared through a sol-gel process. Lead acetate trihydrate $[Pb(CH_3COO)_2.3H_2O]$, lantha-num nitrate $[La(NO_3)_3]$, titanium iso-propoxide $Ti[i\text{-}OPr]_4$ and zirconium n-propoxide $Zr[n\text{-}OPr]_4$ were used as the starting materials. In this process, 2-methoxyethanol (MOE) was used as a solvent, while acetic acid was used as the function of a catalyzer. In order to compensate the lead loss during annealing/sintering and to prevent the formation of a pyrochlore phase in the films, 15 mol% excess lead was added into the starting solution. All chemicals to prepare of precursor were supplied by Merck company. Information of chemicals to prepare precursor is shown in following table 1.

Table 1. *Information of chemicals to prepare precursor*

TT	Chemicals	M (g/mol)	T_b (°C)	D (g/ml)	Purity (%)
1	$Pb(CH_3COO)_2.3H_2O$ (Lead acetate)	397.34			99.5
2	$La(NO_3)_3.6H_2O$ (Lanthanum nitrate)	433.02			> 99
3	$Zr(n\text{-}C_3H_7O)_4$ (Zirconium n-propoxide) 70%	327.57	208	1.044	> 98
4	$Ti(i\text{-}C_3H_7O)_4$ (Titanium iso propoxide) 98%	284.25	170	1.04	> 98
5	MOE ($CH_3OCH_2CH_2OH$)	76.09	125	0.965	> 99.5
6	CH_3COOH (Axetic acid) 99.5%	60.05	118	1.05	> 99

Pb acetate and La nitrate were dissolved in methoxyethanol at 90 °C with acetic acid catalyst and then refluxed at 124 °C for 10h. Titanium iso-propoxide and methoxyethanol were refluxed at 124 °C for 5h. Zirconium n-propoxit and methoxyethanol were refluxed at 124 °C for 4h. Then, the complex solution was stirred well at 124 °C for 3h to get a homogeneous solution. The

0.4M PLZT precursor solutions were then deposited Pt/Ti/SiO_2/Si (Pt/Si) substrates by spin-coating at 2000 rpm for 30 seconds and followed by pyrolysis at 400 °C for 10 min (Figure 1). This process was repeated until the desired number of layer was completed. Finally, the multilayered films were then annealed at 650 °C for 60 mins in air.

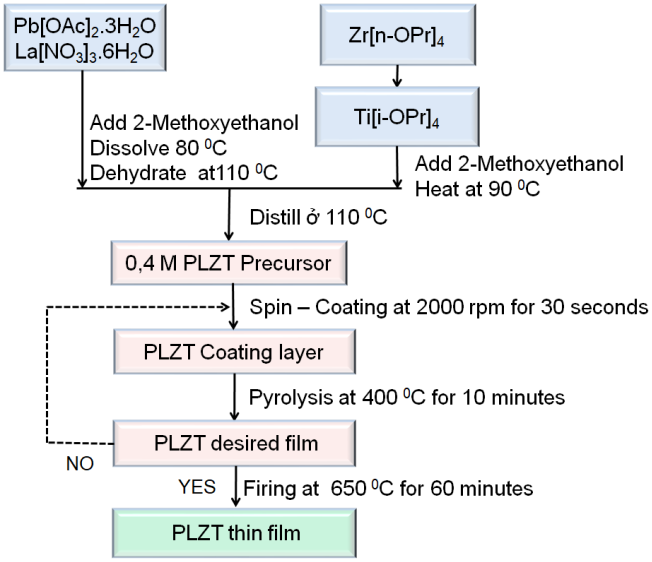

Figure 1. *Flow diagram of PLZT thin films fabricated using the sol-gel spin-coating method*

Crystallographic properties of the thin films were analysed by X-ray θ-2θ scans (XRD) using a PANalytical *X-ray* diffractometer (MalvernPANalytical) with Cu-*Kα*radiation (wavelength: 1.5405 Å). Normal operating power is 1.8 kW (45 kV and 40 mA). Atomic force microscopy (AFM: Bruker Dimension Icon) and cross-sectional high-resolution scanning electron microscopy (HRSEM, Zeiss-1550, Carl Zeiss Microscopy GmbH) were performed to investigate the morphology, microstructure and thickness of the as-grown thin films. For the electrical measurements, the Pt top-electrodes (200×200 μm^2 in size) were deposited and patterned by a lift-off technique. The polarization-electric field (*P-E*) hysteresis loops were measured with the dynamic hysteresis measurement (DHM) option of the ferroelectric module of the aixACCT TF-2000 Analyzer (aixACCT Systems GmbH).

3. Results and discussion

The thermogravimetric analysis (TGA) and differential thermal analysis (DSC) of the PLZT powders were carried out in atmosphere with the heating rate of 20 °C/min and the TGA and DSC for PLZT (10/52/48) is shown in Figure 2. TGA curves exhibit two major losses; the first one located between 180 °C and 290 °C (of about 13%) may be due to the elimination of water content from the prepared sample and the second occurring between 290 °C and 600 °C (of about ~12%) due to the major decomposition reaction of acetic acid and other organic compounds. The DSC curves are in conformity with these observations. There are three exothermic peaks in DSC curve at 231 °C, 320 °C and 507 °C. The first one may be corresponding to the combustion of most of the organic species entrapped in PLZT polymerized gel such as acetic acid and titanium (IV) iso-propoxide. The second with a temperature range of 290-600 °C is due to the decomposition of organic compounds, removed nitrates and the combustion of residual carbon contents [3]. The third broad peak centered at 507 °C indicates the beginning of crystallization of the perovskite phase.

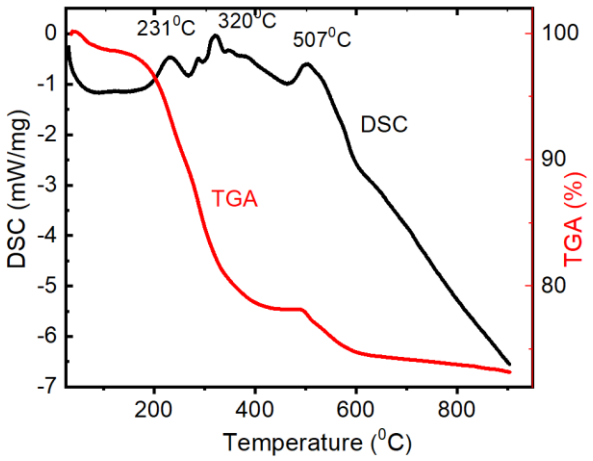

Figure 2. *Thermogravimetric analysis (DSC) and differential thermal analysis (TGA) measurements of as-dried PLZT gel with 8% La-doping*

Figure 3 shows the X-ray diffraction patterns of PLZT thin films with different La-doped contents. It indicates that the thin films have both completely crystallized to the pure perovskite phase and no pyrochlore phase is detected. Moreover, all the films have mixed (100), (110) and (111) crystallographic orientations which also obtained in the sol-gel PLZT thin films deposited on Pt/Si in literature [6]. The orientation of the PLZT film shows similarity structural with the PZT film fabricated on the same substrate [12]. In Figure 3b, the diffraction PLZT (200) peaks shift towards higher 2-θ values, and therefore, the out-of-plane (OP) lattice parameters derived from the corresponding peaks decrease with increasing La concentration.

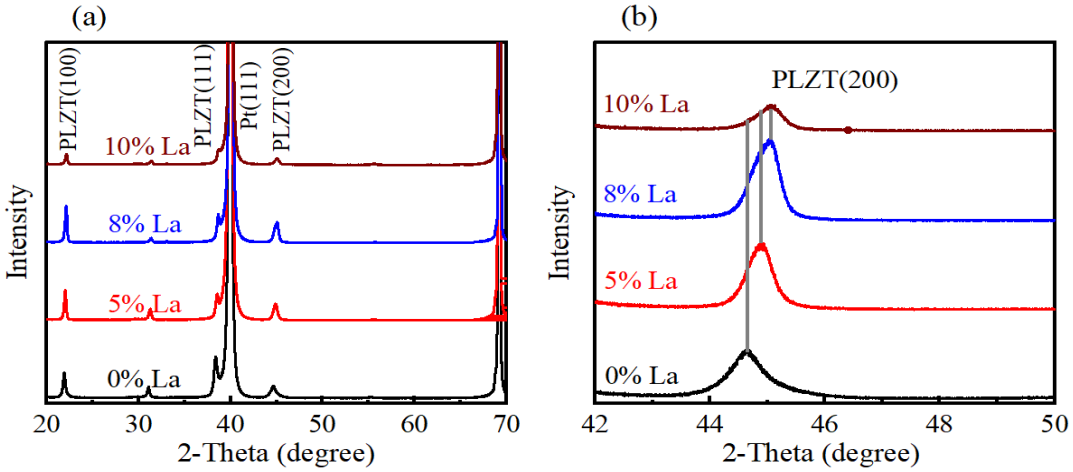

Figure 3. *(a) XRD patterns of PLZT thin films as a function of La-doping; (b) zoom of PLZT(200) peaks for identifying the shift*

Surface morphology and microstructure of PZT and PLZT thin films, analyzed using atomic force microscopy (AFM) and cross-sectional scanning electric microscopy (SEM), are shown in Figure 4. It indicates that the films have a homogeneous and fine grain structure without any cracks. Root-mean-square roughness values were calculated from the AFM measurements and are about 4.7 and 4.2 nm, respectively, for the sol-gel PZT and PLZT with 8% La-doping thin films. This result is consistent with the research work [13].

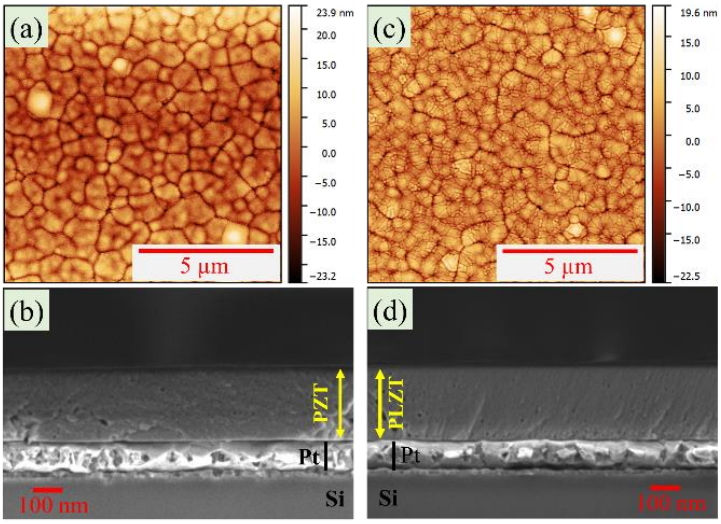

Figure 4. *AFM and cross-sectional SEM images of (a,b) PZT and (c,d) PLZT with 8% La-doping thin films*

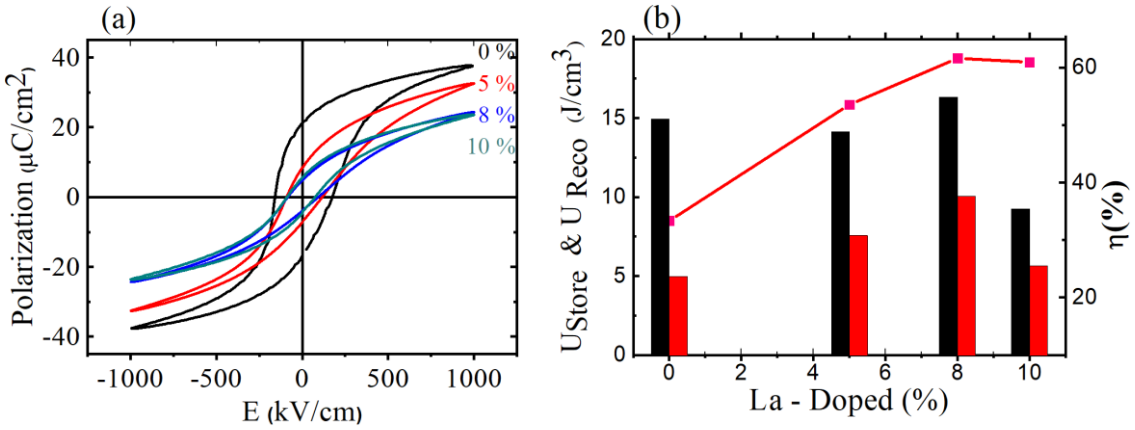

Figure 5. *(a) Polarization hysteresis (P-E) loops and (b) energy storage performance of PLZT thin films as a function of La-doping. The measurements were done at 1000 kV/cm and 1 kHz.*

Room temperature (*P-E)* loops of the PLZT with different La-doped contents are shown in Figure 5(a), which were measured at 1000 kV/cm and 1 kHz frequency. With the increase in the La-doping content, the maximum polarization (P_{max}) at maximum electric field (E_{max}) first increases with La content (till 8% doping) and then decreases for higher doping concentration. Meanwhile, the positive remanent polarization (P_r) at E=0 decreases slightly with the addition of La content. The recoverable energy storage density can be estimated from the (*P-E)* loops and calculated with the equation:

$$U_{reco} = \int_{P_r}^{P_{max}} EdP \quad (1)$$

According to the doping content dependence of polarization and Eq. (1), the maximum values of Ureco (6.52 J/cm3) and energy-storage efficiency (η = 61.65%, $\eta = 100\% \times U_{reco}/U_{store}$; where $U_{store} = \int_{-P_r}^{P_{max}} EdP$ is the energy stored per unit volume, in which $-P_r$ is the negative remanent polarization) are achieved in the PLZT thin film with 8% La-doping at 1000 kV/cm and 1 kHz frequency, as shown in Figure 5(b). These results indicate that the La-doping can help to improve the energy storage performance, especially for the energy efficiency in the PZT thin films for high-power capacitor applications.

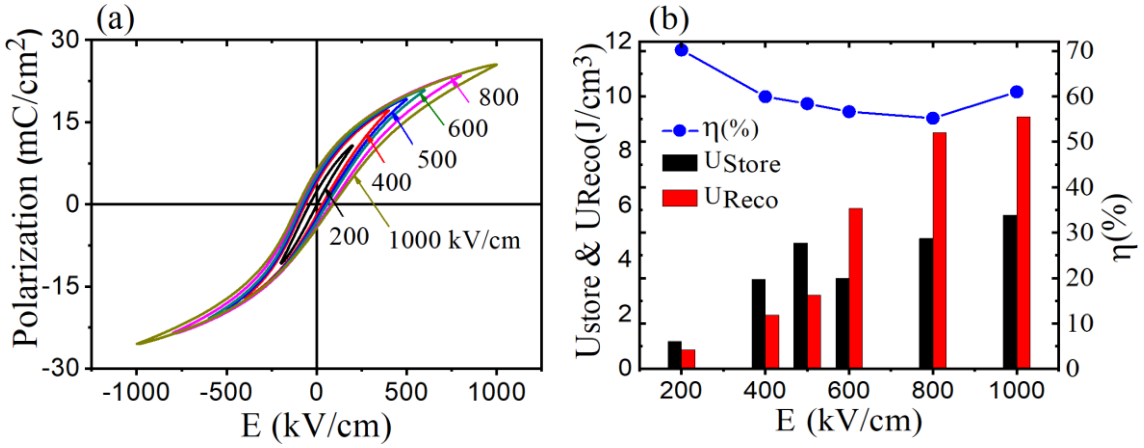

Figure 6. *(a) Polarization hysteresis (P-E) loops and (b) energy storage performance, of PLZT thin films with 8% La-doping and as a function of applied electric field (measured at 1 kHz).*

In order to investigate the effect of measured conditions on the energy storage properties, the (*P-E)* loops of PLZT thin films with 8% La-doping were performed under different applied electric fields and also frequencies. Figure 6(a) shows the (*P-E)* loops of the PLZT thin films with 8% La-doping at selected applied electric fields. It can be seen that the (P_{max}) increases gradually and the (P_r) increases slightly with an increase of the applied electric field and reach about 24.98 and 6.26 μC/cm^2 at E = 1000 kV/cm, respectively.

Figure 6(b) illustrates the electric field dependence of energy-storage density (U_{store} and U_{reco}) and energy-storage efficiency (η) of the PLZT thin films with 8% La-doping, which were measured from 100 kV/cm to its electric breakdown field (E_{BD}) of 1200 kV/cm at 1 kHz and room temperature (see Figure 7). According to Eq. (1), the devices with low (P_r), high (P_{max}) and large (E_{BD}) are more favorable for energy storage. Clearly, the (U_{store}) and (U_{reco}) values gradually increase as the applied electric field is increased. The (U_{store}) and (U_{reco}) values at its (E_{BD}) of 1200 kV/cm are 20.9 and 11.9 J/cm^3, respectively. The (U_{reco}) value obtained in this study can be compared with the other sol-gel PLZT thin films in the previous reports [6], [14].

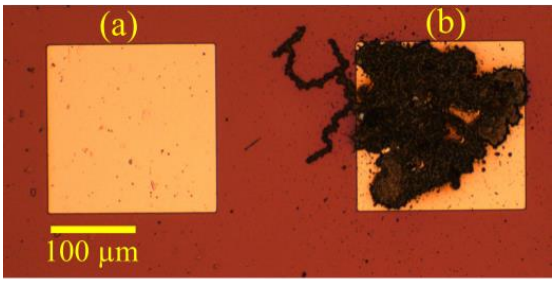

Figure 7. *Optical images of PLZT thin-film capacitors with 8% La-doping (a) before and (b) after broken (under an applied electric field larger than E_{BD} value (1200 kV/cm))*

The switching behavior of ferroelectric materials is a process of domain nucleation, domain growth and domain wall motion [15]. The switching time for domains in the ferroelectric films is usually in the range of a few hundred nano-seconds, which means that a frequency below 1 MHz provides enough time (τ = 1/f, where τ is the domain switching time and f is the measured frequency) for full switching of the ferroelectric domains. In order to investigate how the polarization properties depend on frequency of PLZT thin films, (P-E) loops were measured in the range of 25-1000 Hz and at an applied electric field of 1000 kV/cm.

Figure 8 (a) shows the measured frequency dependence of the (*P-E*) loops of PLZT thin films with 8% La-doping. As the PLZT thin films are the polycrystalline with different domain orientations (multi-domain structure), decreasing measured frequency leads to an increase of time for domain switching process, and then the remanent polarization (P_r) and coercive field (E_c) values. Together with the (*P-E*) loops, the (U_{store}) is slightly decreased whereas the (U_{reco}) is increased with the frequency in the range of 25-250 Hz, and both (U_{store}) and (U_{reco}) values are almost constant with the higher frequencies (Figure 8 (b)). Based on the measured frequency dependent (U_{store}) and (U_{reco}) values, the (η) value is significantly enhanced in the range of 25-250 Hz and much stable at the higher measured frequencies. It is thus revealed that the PLZT thin films exhibit high frequency stability in the energy storage performance.

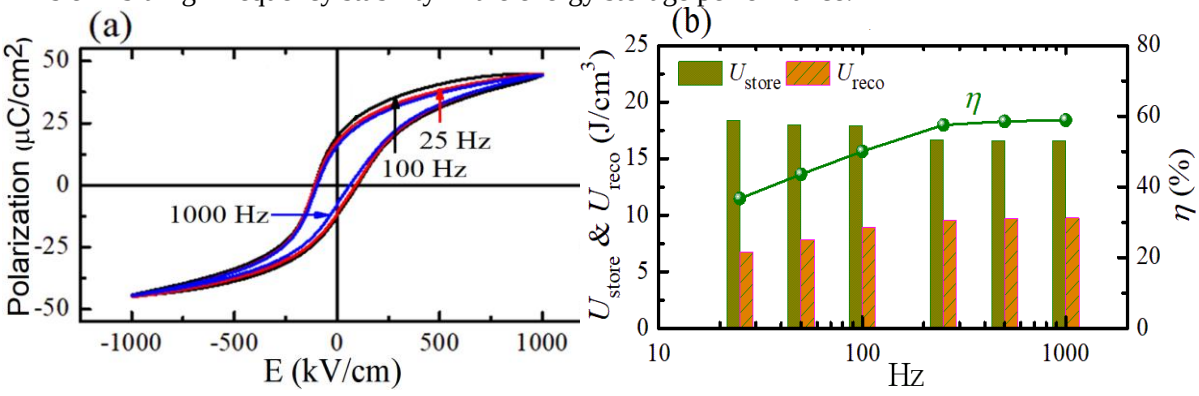

Figure 8. *(a) Polarization hysteresis (P-E) loops and (b) energy storage performance of PLZT thin films with 8% La-doping measured at 1000 kV/cm and various frequencies*

4. Conclusion

In conclusion, PLZT relaxor FE thin film with a strong preferred orientation (100) were fabricated on Pt(111)/Pt/Ti/SiO_2/Si substrates by the sol-gel process. We investigated the effect of measured conditions on the energy storage properties. The (*P-E*) loops of PLZT thin films with 8% La-doping were performed under different applied electric fields and frequencies. We found that the (P_{max}) increases gradually and the (P_r) increases slightly with an increase of the applied electric field and reach about 24.98 and 6.26 μC/cm^2 at E = 1000 kV/cm, respectively. The PLZT thin films exhibit high frequency stability in the energy storage performance. The film had a breakdown field of 1200 kV/cm. A positive linear relationship between the deriving field and energy-storage density was obtained, which resulted in a large recoverable energy-storage density of 11.9 J/cm^3 at its critical breakdown field. These results indicated that the lead base relaxor FE thin films had the promising for application advanced capacitors with high energy-storage density.

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