

CHAPTER 5

RESULTS AND DISCUSSION - PART 2:

PREPARATION AND CHARACTERIZATION OF PZT/WO₃ THIN FILMS

In this chapter, results of PZT/WO₃ thin film synthesis are analyzed. Various concentrations of WO₃ (0, 0.1, 0.2, 0.3, 0.4, 0.5 and 1 wt%) were added to PZT thin films. Phase, microstructure and electrical properties were investigated to figure out the optimized condition of this composite system for studying of ferroelectric fatigue and being compared to that of pure PZT thin films. Since PZT ferroelectric materials have become popular for electromechanical applications, considerable attention has been focused on preparation of these materials and improvement of their mechanical and electrical properties due to the requirements of long lifetime and large displacements under continuous operation. A design based on nanocomposite concept was proposed by Niihara to improve structural ceramics [131]. This concept has been applied to many ferroelectric ceramic systems [22, 32, 132-135]. It has found that many nanocomposite systems possess high strength, high toughness and unique electrical properties. Previous work on PZT/WO₃ system using a mixed oxide method showed that an addition of a limit amount of WO₃ was enabled to improve electrical and mechanical properties of PZT ceramics [31]. However, similar results have not yet been reported for thin film embodiments. Also, underlying mechanisms of WO₃ effects on structure and electrical properties of PZT still have not been well understood. The purpose of this study is to

fabricate PZT/ WO_3 nanocomposite films by a hybrid chemical solution route and to investigate the effect of WO_3 on microstructure and electrical properties of the composite films.

5.1 Phase of PZT/ WO_3 thin films

Results of X-ray diffraction for PZT/ $x\text{WO}_3$ films where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%, are shown in Fig. 5.1. All films possessed a crystalline perovskite structure with second phases appearing at higher WO_3 added contents.

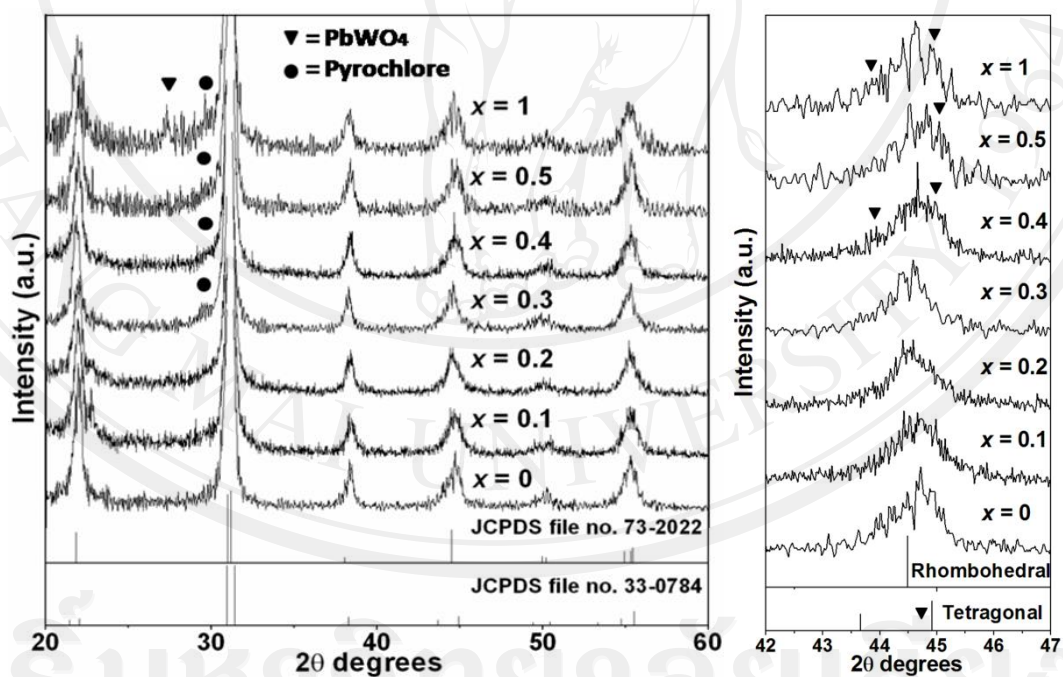


Figure 5.1 XRD patterns of PZT/ $x\text{WO}_3$ films, where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%; pre-heated at 400°C for 30 min and annealed at 600°C for 30 min.

X-ray peaks in the range of $2\theta \approx 42-47^\circ$ corresponded to (200) of rhombohedral (R) phase (JCPDS no. 73-2022). The inclusion of WO_3 appeared likely to affect the phase of PZT films by introducing a broad peak which are probably to be a mixing phase of rhombohedral and tetragonal when WO_3 concentration was manipulated in the range of 0.4 - 1 wt% (Fig. 5.1), although the mixing phase was unclear because of the small intensity given by the small angle technique with thin films. However, this could also be confused by the broadening peak due to nano-size grains in films. The variations of PZT phase are attributed to microscopic, compositional fluctuations [136]. However, a broad hump peak at $2\theta \approx 29^\circ$ pertaining to a pyrochlore phase appeared to increase with increasing WO_3 concentration. A possible mechanism for this is the reaction between PbO and WO_3 confirmed by the presence of monoclinic PbWO_4 , as shown in equation 5.1. Because of Pb in this system was consumed to produce PbWO_4 phase. Therefore, Pb became insufficient to control Pb valence state in PZT system when PbWO_4 phase are increased. Nevertheless, this phase was not observed in PZT/ $x\text{WO}_3$ films where $x = 0-0.5$ wt% because the amount of this phase was deficient to be detected by XRD technique.



5.2 Microstructure of PZT/ WO_3 thin films

The microstructures of PZT/ WO_3 thin films were shown in Fig. 5.2. The optical microscope (OM) micrograph showed a dense, crack-free PZT/ $x\text{WO}_3$ thin film, where $x = 0 - 0.3$ wt% (Fig. 5.2(a-d)).

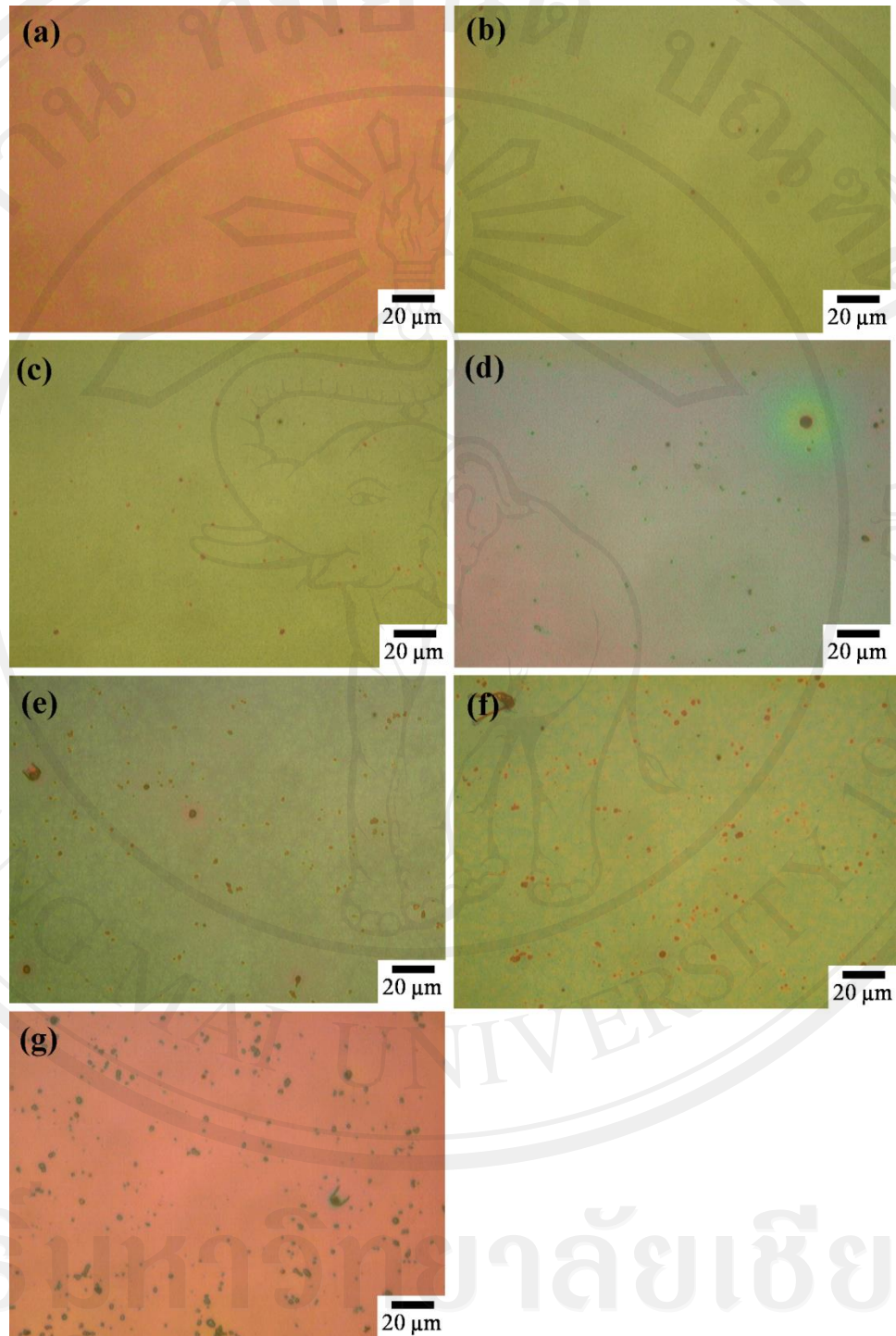


Figure 5.2 OM micrographs of PZT/ x WO₃ films, where x = (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1 wt%.

However, a few small cracks appeared at the higher concentration (≥ 0.4 wt%) of WO_3 nanoparticles in PZT films as shown in Fig. 5.2(e-g)). The dark spots in the film showed a cluster of WO_3 , and it seemed to increase with increasing WO_3 concentrations (Fig. 5.2). The cracks were spread out from large WO_3 particles which possibly are a cluster of WO_3 nanoparticles.

Figure 5.3 shows microstructural evolution of $\text{PZT}/x\text{WO}_3$ films. SEM micrographs indicated dense, crack-free, and equiaxed grains for all films. The film surface showed a hillock-like structure of a nanometer size grains aggregated on the surfaces of the film [137] as schematically explained in Fig. 5.4. When the surfaces of the films were observed from above, it showed the hillock-like structure (Fig. 5.3). The film's cross sections in Fig. 5.5 reveal an aggregation of nanometer-sized grains, which suggested that the aggregated grains formed the hillock-like structure on the surface. The surface ripples arose because the film was under compressive stress; strain-induced surface ripples on the films while the heat-treatment process as shown in Fig. 5.4 [138]. No change was observed in the surface morphology of all films except the differences in the size of hillock. This could be due to the difference in the environment in which the films were prepared such as temperature and humidity which are difficult to control. However, the physical properties, such as grain size and density, could not be revealed from the surface due to the different morphology between on and underneath the surface of the film. The cross sections of $\text{PZT}/x\text{WO}_3$ films, where $x =$ (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1 wt% are shown in Fig. 5.5.

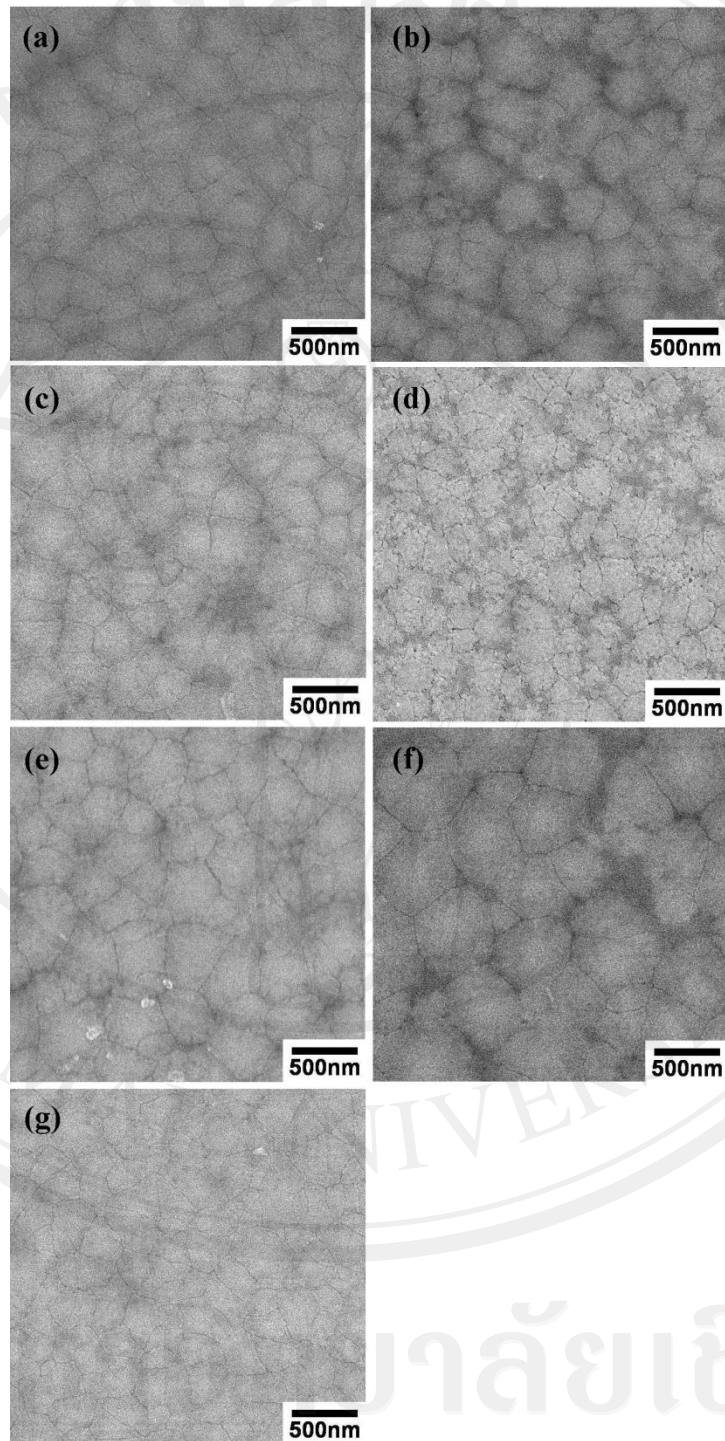


Figure 5.3 SEM micrographs of PZT/ x WO₃ films' surfaces, where x = (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1 wt%, (Magnification = $\times 30,000$).

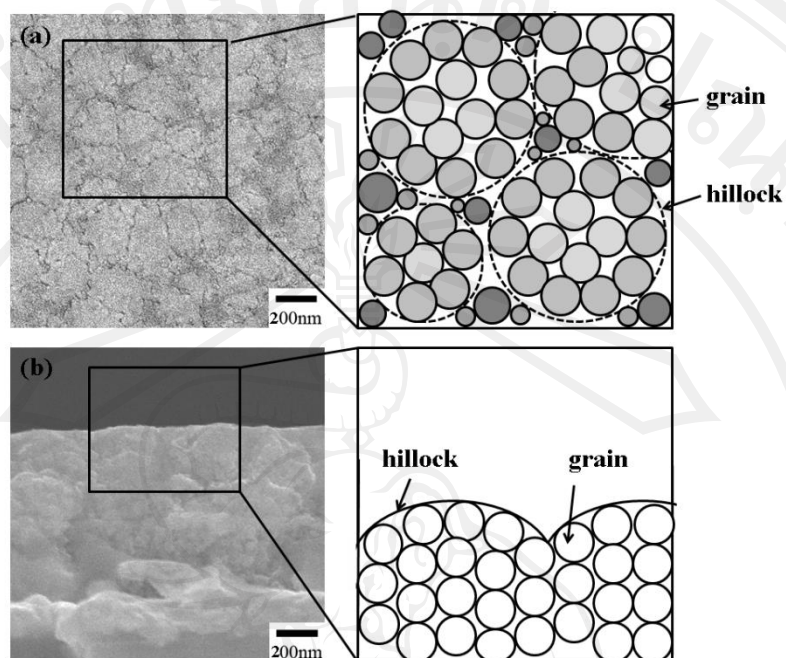


Figure 5.4 SEM micrographs of PZT/WO₃ film and accompanying schematic depiction of the hillock-like structure; (a) is a surface (darker colors show lower level of grain) and (b) is a cross sections.

It was found that the first layer of all films is about 350 nm thick, and the thickness of two layers films are about 700 nm as shown in Fig. 5.5. The layers PZT film and PZT/WO₃ nanocomposite films were not different in thickness and the thickness of composite films could not be increased. All of films' cross sections show densely microstructure. Grain size of the PZT/WO₃ nanocomposite films was measured from SEM cross sections as listed in Table 5.1. It was found that the grain size was slightly reduced with increasing WO₃ concentration.

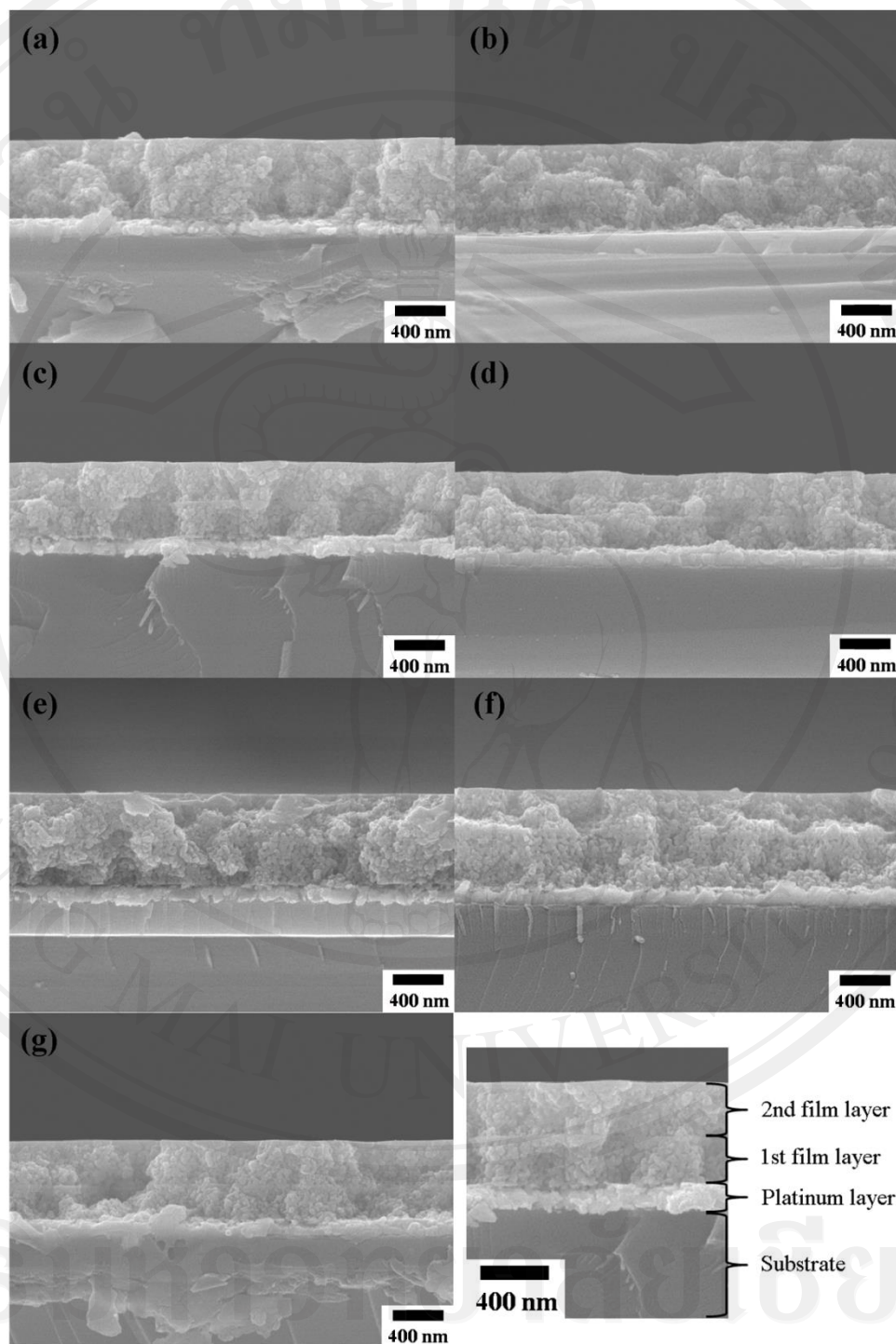


Figure 5.5 SEM micrographs of cross sections of PZT/ x WO₃ films, where x = (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1 wt%, (Magnification = $\times 30,000$).

The decrease in grain size (Table 5.1) in this system could be due to the B-site donor doping by the substitution of W^{6+} for Ti^{4+} . The substitution is required to maintain the charge neutrality in the lattice by creating cation vacancies. The cation vacancies prefers to exist along grain boundaries rather than inside grains where is thermodynamically more stable [139]. Then the grain boundaries would be pinned by the vacancies, resulting in inhibited grain growth of donor doping system [140-142]. Moreover, the thermodynamic model of previous work concluded that the grain growth is associated with oxygen release [143]. Oxygen was lost at high temperature to establish a thermodynamic equilibrium with the surrounding atmosphere, and the grain growth is accompanied by oxygen release. In addition, it was found that a grain growth was absent in donor doping of this system as shown in Table 5.1. This observation could support that the substitution of W^{6+} for Ti^{4+} reduced oxygen vacancy or prevented the oxygen loss during heat-treatment and thus preventing the grain growth. This ultimately resulted in the reduction of the grain size of the donor dope samples in this work. Moreover, SEM cross sections showed an intergranular fracture for all composition as shown in Fig. 5.5.

5.3 Electrical properties of PZT/ WO_3 thin films

In this part, electrical properties such as dielectric, ferroelectric and fatigue of PZT/ xWO_3 thin films, where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%, were investigated. Among those conditions, the best ferroelectric properties' film was selected, and the ferroelectric fatigue of donor doping compared to the pure PZT thin film was studied.

5.3.1 Dielectric property of PZT/WO₃ thin films

Figure 5.6 shows dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of PZT/ x WO₃ films, where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%, respectively. Capacitance of the films as a function of frequency ($1 - 1000$ kHz) was measured by LCR meter at room temperature. The dielectric constants were then calculated using equation 3.2. The dielectric constant decreased slightly with increasing frequency. However, the dielectric loss showed less dependency on frequency. The enhancement of dielectric constant at low frequency could be attributed to the interfacial polarization, which has a small contribution at high frequency [92]. The room temperature dielectric constant and loss values at 1 kHz are also listed in Table 5.1. It is considered that the dielectric constant reduced when WO₃ was added and further decreased along with an increase in WO₃ concentration. Although the dielectric constant increased at the WO₃ concentration of 1 wt%, the value of dielectric constant was still lower than that found in the pure PZT. The dielectric loss showed less dependency on WO₃ concentration; nevertheless, it was reduced with increasing WO₃ concentration as shown in Fig. 5.6. This phenomenon is described in the next section along with the explanation for ferroelectric properties.

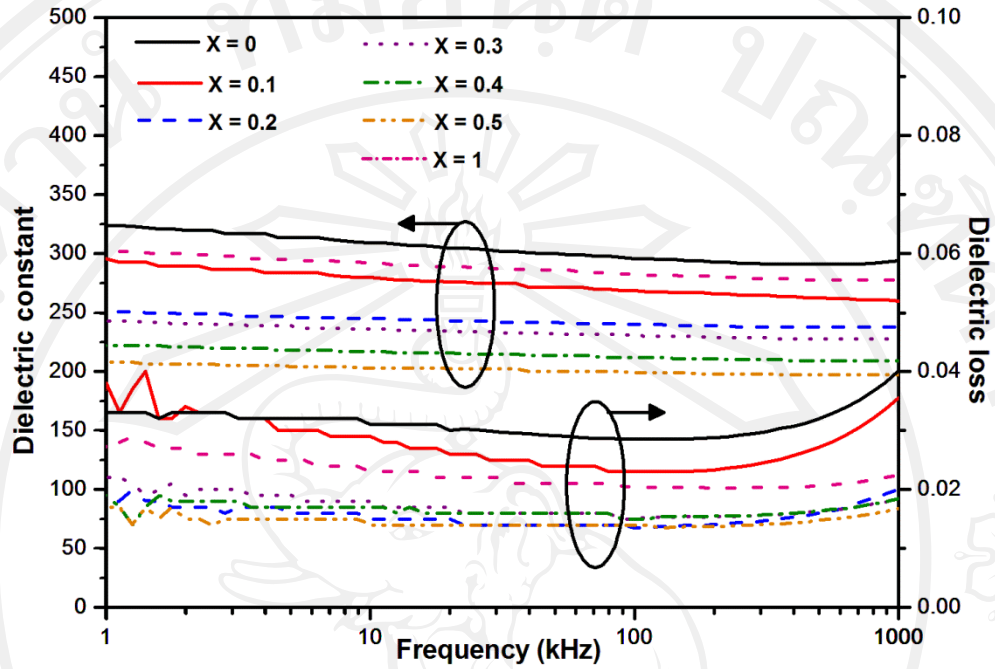


Figure 5.6 dielectric constant and dielectric loss of PZT/ x WO₃ films at room temperature; where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%, plotted as a function of frequency.

5.3.2 Ferroelectric properties of PZT/WO₃ thin films

Polarization-electric field (P - E) hysteresis loops of PZT/ x WO₃ films; where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%, measured at electric field 1000 kV/cm and a frequency of 1 kHz are presented in Figure 5.7. Ferroelectric results showed a similar trend to that of the dielectric constant. The values of remnant polarization (P_r), maximum polarization (P_{max}) and coercive field (E_c) are also shown in Table 5.1. It was found that the polarization values gradually decreased with the increase in WO₃ concentration up to 0.5 wt%. The reduction in dielectric and ferroelectric properties is believed to be due to the

substitution of WO_3 for PZT, where a ferroelectric phase was replaced by a non-ferroelectric phase. In addition, WO_3 was likely to act as a domain clamping at the interface between PZT and WO_3 to hinder the domain wall motion in PZT films, resulting in the reduction of dielectric and ferroelectric properties of the films. However, with the further increase of WO_3 to 1 wt%, the P_r increased.

It was also found that E_c decreased with an increase in WO_3 concentration. This is explained by a donor doping effect on the B-site substitution of W^{6+} in PZT, which resulted in a reduction of oxygen vacancies upon the substitution of W^{6+} ($r_{\text{W}} = 0.60 \text{ \AA}$) for Ti^{4+} ($r_{\text{Ti}} = 0.61 \text{ \AA}$) ions [29, 144-145] as shown in equation (5.2). However, when the concentration of WO_3 was increased up to 1 wt%, both dielectric and polarization increased. It showed that the donor doping affected by the domain motion was easier to be initiated with a smaller electric field. Thus, this may support the polarization in PZT film, and coercive field of ferroelectric ceramics was also reduced as seen in Fig. 5.8. In addition, the reaction between PbO and WO_3 phases, which formed a PbWO_4 phase on this condition during heat treatment process, was reported to possess good electrical properties [146]. Moreover, the PZT/1wt% WO_3 films are probably closest to morphotropic phase boundary (MPB) of this system which likely to present the mixture of rhombohedral and tetragonal perovskite phases, so called a MPB region [147] as shown in the XRD pattern in the range of 2θ is $\sim 42\text{-}47^\circ$ (Fig. 5.1). It has been well accepted that the MPB phase showed the maximum piezoelectric and ferroelectric properties due to the rhombohedral and tetragonal structures which were enable of each reorientation of domains under the applied field and stress [147]. Not only the intrinsic

condition but also the extrinsic condition contribution to the control of defect chemistry was included, thereby maximizing electrical properties of PZT/1 wt%WO₃ thin film.



Moreover, the ferroelectric characteristics can be observed by the hysteresis loop squarenesss (R_{sq}) [148]. The squareness ratio of the hysteresis loop for ferroelectric materials is commonly understood to be the ratios of the remanent polarization (P_r) at zero electric field to the maximum polarization (P_{max}) at the maximum applied field obtained at some finite field strength below the dielectric breakdown [38]. The used of squareness to measure not only the deviation in the polarization axis but also that in the electric field axis which can be calculate from equation 5.3.

$$R_{sq} = \frac{P_r}{P_{max}} + \frac{P_{1.1Ec}}{P_r} \quad (5.3)$$

$P_{1.1Ec}$ is the polarization at an electric field equal to 1.1 times the coercive field (E_c). For an ideal hysteresis loop, R_{sq} is equal to 2.0 [149].

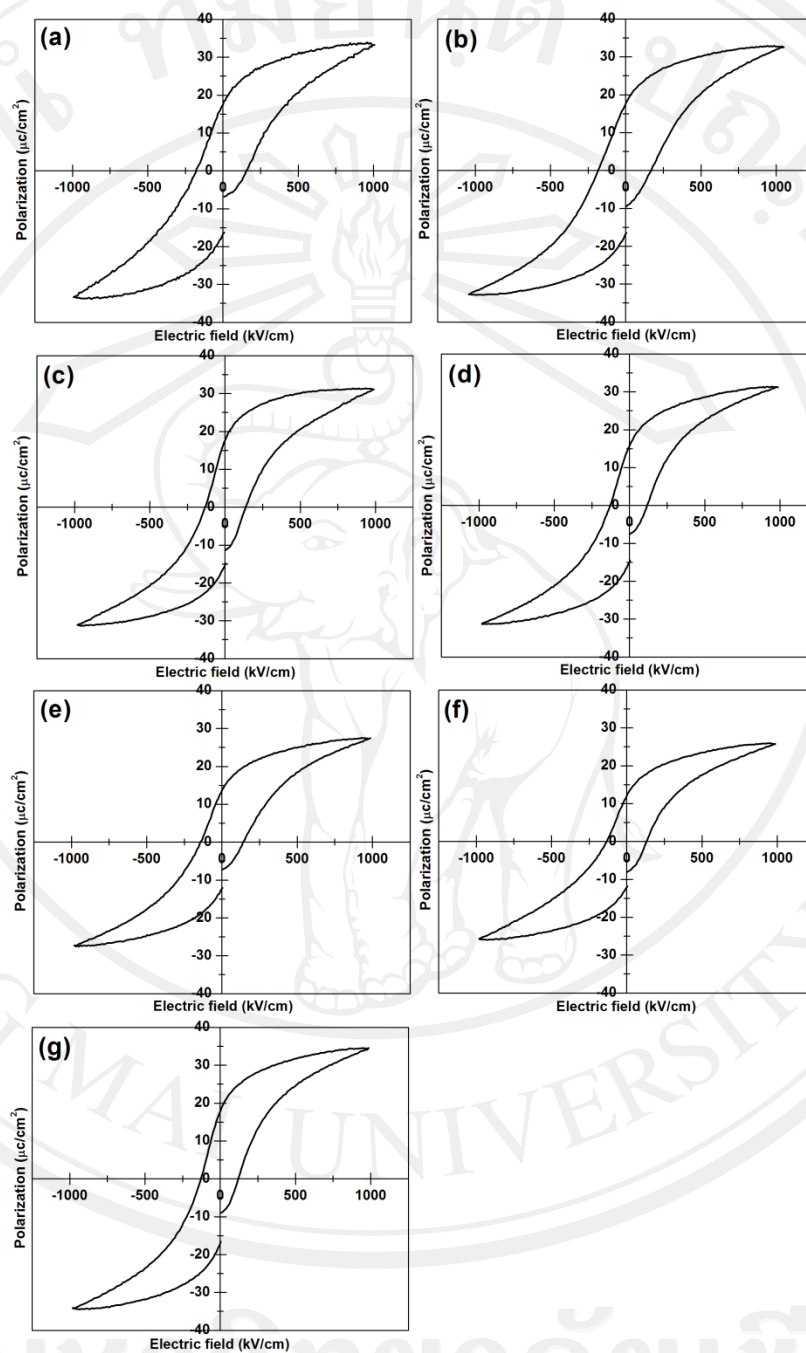


Figure 5.7 *P-E* hysteresis loops of PZT/ $x\text{WO}_3$ films; where x = (a) 0, (b) 0.1, (c) 0.2, (d) 0.3, (e) 0.4, (f) 0.5 and (g) 1 wt%, respectively.

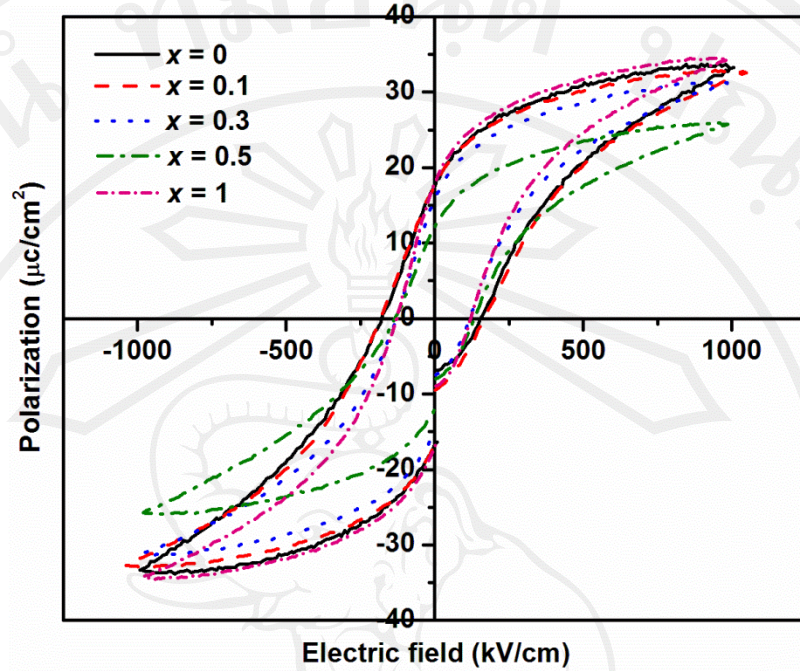


Figure 5.8 Comparison of P - E hysteresis loops of PZT/ x WO₃ films; where $x = 0, 0.1, 0.3, 0.5$ and 1 wt%.

According to equation 5.3, the squareness of the films were calculated and given in Table 5.1. It was found that the squareness of this system were not dependent on WO₃ concentration. The squareness of this system is about 0.6 and it was much lower compared to the ideal square loop which is 2.0. This may cause by the loops did not get saturated electric fields due to the high saturation field of these PZT thin films and a limitation of the equipment. However, It is well known that the films for memory applications are required to possess the following properties such as a large remanent polarization (P_r), a low coercive field (E_c) and high degree of loop squareness (R_{sq}) [38, 45, 150]. Within the WO₃ added films, the PZT/1 wt% WO₃ film showed the largest

remanent polarization, lowest coercive field and good loop squareness compare to the other compositions. Thus, it showed the best donor doping effect (easier to be reoriented under a small applied field). This may support the polarization in PZT films but reduced coercive field of ferroelectric ceramics as shown in Table 5.1.

Table 5.1 Structural and electrical properties of PZT/xWO₃ films

WO ₃ contents (wt%)	Grain size (nm)	Electrical properties at room temperature.					
		ϵ_r	$\tan \delta$	$P_r(\mu\text{C}/\text{cm}^2)$	$P_{\max}(\mu\text{C}/\text{cm}^2)$	$E_c(\text{kV}/\text{cm})$	R_{sq}
0	56.99 ± 10.00	325	0.037	17.63	33.86	175	0.61
0.1	54.88 ± 07.00	296	0.038	17.22	32.74	169	0.61
0.2	51.64 ± 07.00	251	0.017	16.39	31.33	138	0.61
0.3	50.83 ± 05.00	243	0.022	15.31	31.29	126	0.74
0.4	48.78 ± 08.00	222	0.019	13.03	27.47	139	0.53
0.5	48.35 ± 06.04	208	0.017	12.12	24.94	130	0.59
1	49.05 ± 06.06	302	0.027	17.39	34.53	122	0.62

From the ferroelectric properties of PZT/WO₃ thin films, PZT/1wt% WO₃ thin films were found to be the best representative for donor doping compared to other conditions in this system. Therefore, this work used this condition to further investigate the effect of donor doping on fatigue properties in PZT thin films.

5.3.3 Fatigue property of PZT/WO₃ thin films

Ferroelectric fatigue is a loss of switchable polarization (P_{sw}) with repeated polarization reversal [151]. In this study, hysteresis loops of PZT and PZT/WO₃ films before and after 10⁸ polarization switching cycles were compared. The samples were electrical fatigued under an applied field of higher than about 3 times of a switching

electric field (E_{sw}) and a fixed frequency at 1 kHz. The results showed that a dramatic drop of polarization value was observed for pure PZT film. An addition of small amount of WO_3 into PZT thin film could improve a degradation of remanent polarization. Figure 5.9 shows fatigue behavior of PZT and PZT/1 wt% WO_3 thin films measured as a function of polarization switching cycles with 500 kv/cm electric field. For the PZT films (Fig. 5.9(a)), the switchable polarization started to decrease after 10^6 cycles and reduced by about 17% at 10^8 cycles. For the PZT/1 wt% WO_3 films (Fig. 5.9(b)), 5% decrease of switchable polarization was observed after 10^7 cycles as shown in Fig. 5.10. This indicated that an addition of WO_3 could improve fatigue behavior of ferroelectric PZT thin films. There are two basic models regarding the mechanisms for the fatigue behavior of ferroelectric films [35]. The first mechanism is the formation of internal field by space charge segregation at both electrode interfaces. Oxygen vacancies are transported to the negative electrode interface during repeated switching of electric fields to set up a space charge layer which reduces the electric field in the ferroelectric. This reduction causes the polarization of films to decrease, which results in the fatigue behavior. The second mechanism is a pinning of the domain walls by defects, such as electronic carriers or oxygen vacancies which segregate the domain walls. The domain wall pinning reduces domain movement and results in a degradation of ferroelectric switching ability. Furthermore, during a reorientation of ferroelectric domains in the fatigue process, oxygen vacancies are driven toward the ferroelectric domain walls or grain boundaries and captured by the space charge there. The heavy pile-up of captured oxygen vacancies at these sites would lead to an increase in a domain wall pinning rate, thereby preventing

a further domain switching [152]. Thus, in order to alleviate the ferroelectric fatigue, it is vital to suppress the creation of oxygen vacancies by, for example, adding some donor-dopant such as WO_3 as done in this study [153].

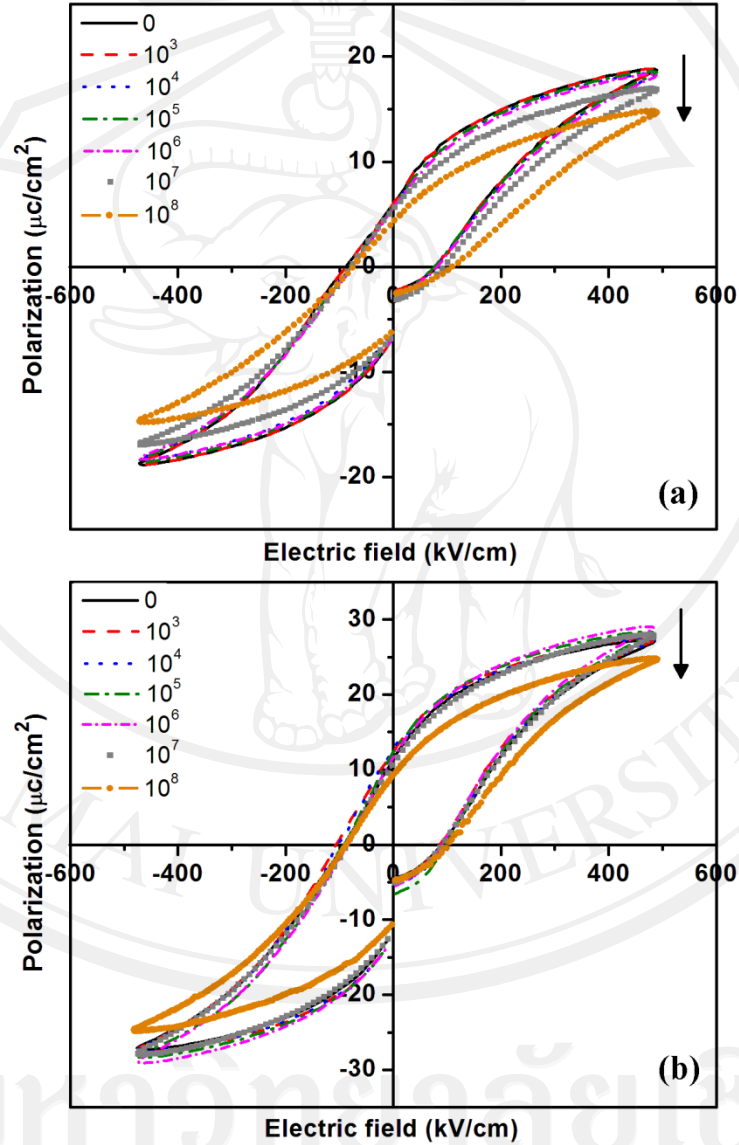


Figure 5.9 Hysteresis loops of (a) PZT and (b) PZT/1 wt% WO_3 films with the number of bipolar fatigue cycles under 500 kV/cm at 1 kHz.

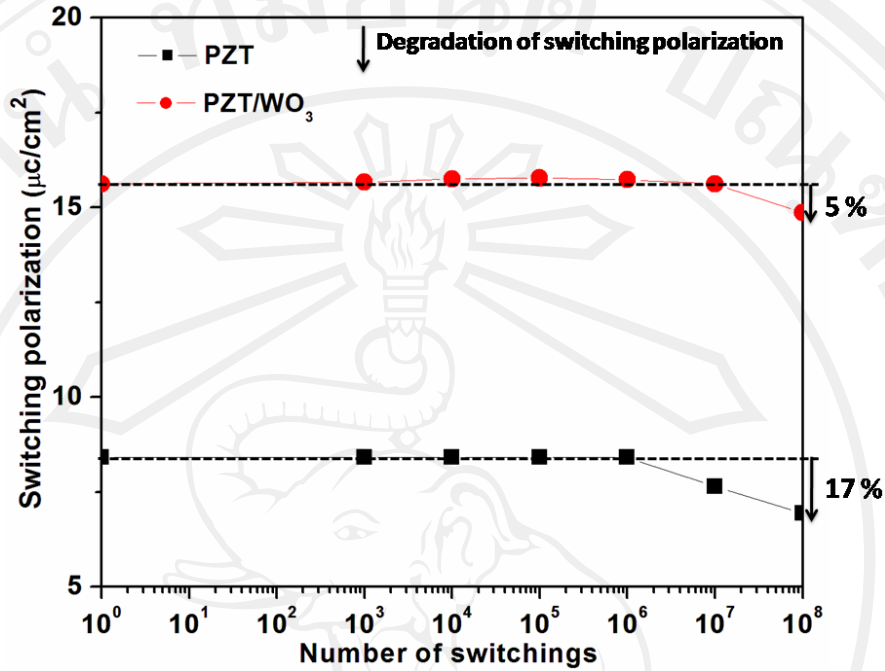


Figure 5.10 Switchable polarization of PZT and PZT/1 wt% WO₃ films with the number of bipolar fatigue cycles.

In this work, WO₃ nanoparticles were added into PZT thin films as a donor doping to reduce the oxygen vacancies as shown in equation 5.2. This equation helps to consume oxygen vacancies and reduces the possibilities of their segregation at the electrode interface or the pinning of the domain walls during the repeated switching cycles. However, the maximum polarization of PZT/1 wt% WO₃ thin films as shown in Fig. 5.9(b) was found to increase with increasing the switching cycles to 10⁶ and then reduced again with the further increase of the switching cycles. It could be attributed to the fact that the as-deposited polycrystalline films had random orientations as shown in Fig. 5.5. This led to a reduction of the maximum possible total polarization while this

phenomenon was not found in the PZT films. This is possibly due to the substitution of Ti^{4+} with W^{6+} into PZT crystal lattice making the film more disorganized; therefore, the polarization was increased after applying the electric field.

5.4 Conclusions

The effects of WO_3 nanoparticles on phase and electrical properties of PZT thin films were investigated. The $\text{PZT}/x\text{WO}_3$ films (where $x = 0, 0.1, 0.2, 0.3, 0.4, 0.5$ and 1 wt%) were prepared by a hybrid chemical solution deposition technique. The perovskite phase was formed in the films annealed at 600°C . However, the reaction between PbO and WO_3 which formed PbWO_4 was observed at high concentration of WO_3 (> 0.5 wt%). Microstructure of films showed crack-free, dense and equiaxed grains for all the films. The increase in WO_3 concentration reduced a grain size of PZT films. The dielectric and ferroelectric properties of PZT films were found to reduce when WO_3 was added. However, when WO_3 concentration was increased to 1 wt%, the electrical properties were improved. The W^{6+} doping could enhance the electrical properties of PZT by reducing of the oxygen vacancies in the PZT system. However, some WO_3 particles remaining in films is believed to prohibited the domain wall motion and reduced the electrical properties of PZT films. The donor doping and the mixture of rhombohedral and tetragonal phases, which were closest to MPB region, is believed to be the key to improve in the electrical properties of $\text{PZT}/1$ wt% WO_3 films. Compared to a 17% reduction of polarization found in PZT films at 10^8 cycles, the improvement in PZT

fatigue behavior was obtained when 1 wt% of WO_3 was added into PZT thin films, resulting in a 5% reduction of switchable polarization up to 10^8 switching bipolar pulses.