

CHAPTER 4

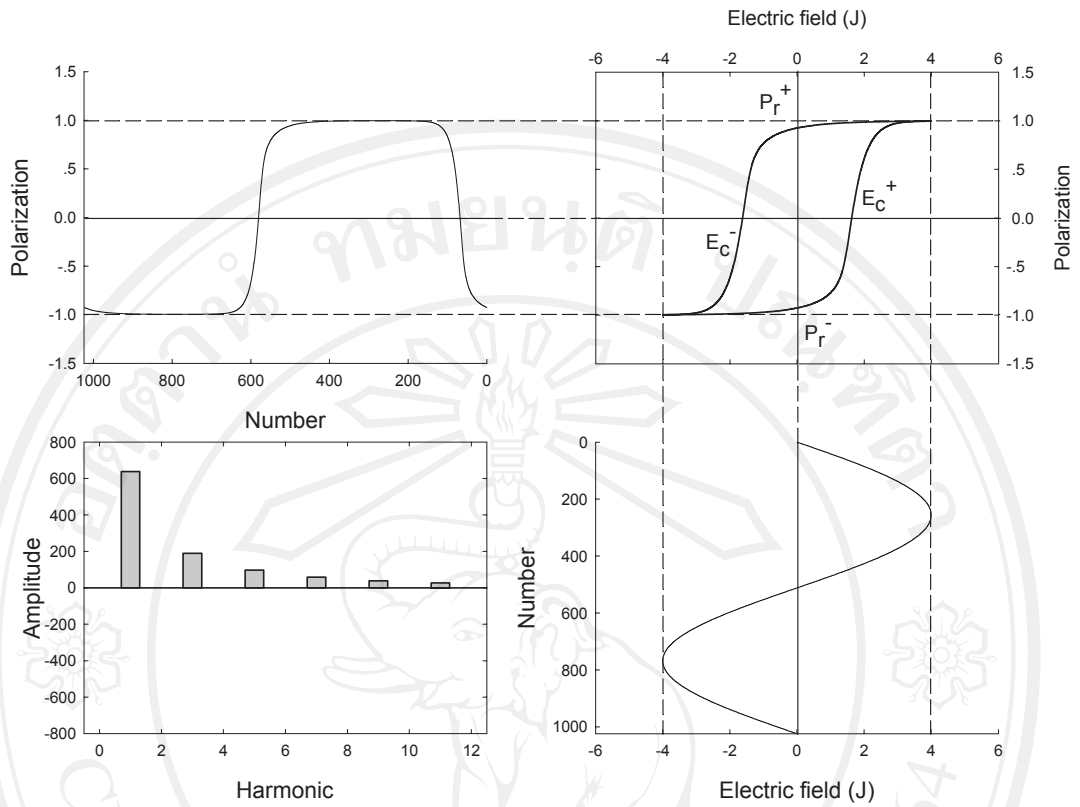
RESULTS AND DISCUSSIONS

In this chapter, the results from Fourier analysis of ferroelectric hysteresis behavior are described in details i.e. the investigation of Fourier spectrum characteristic, the establishing of relationship between hysteresis properties and external perturbation parameters to the amplitude of harmonics of Fourier transformation.

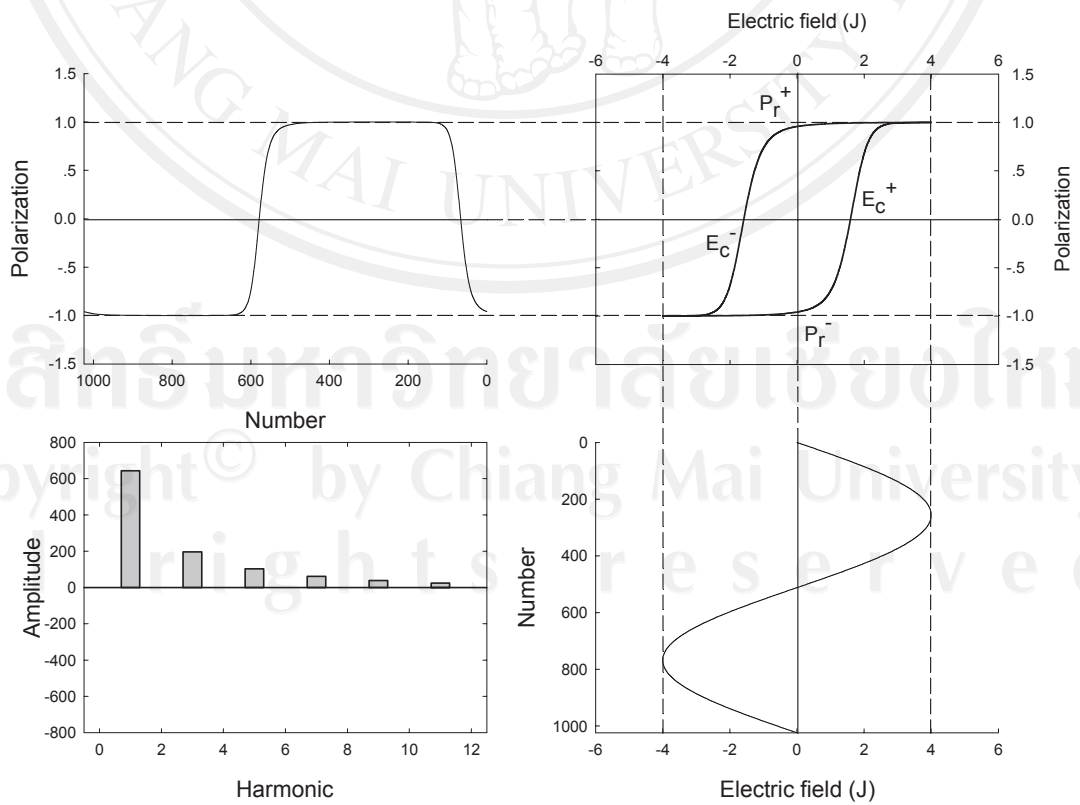
4.1 Fourier spectrum characteristic

In Fourier analysis of ferroelectric hysteresis behavior, Fourier transformation was used to transform polarization data from time domain to frequency domain. Then, the amplitude of harmonics of Fourier transformation (Fourier spectrum) was investigated. It is found that Fourier spectrum $C_k = \sqrt{A_k^2 + B_k^2}$ present only odd harmonics, while all even harmonics equal to zero (see Fig. 4.1). This is expected as symmetric hysteresis is half-wave symmetry.

However, Ising hysteresis from mean field calculation and Monte Carlo simulation is a perfect symmetric hysteresis loop, so the amplitude of even harmonics vanish (with error bar) as shown in Fig. 4.1 (a) and (b). On the other hand, BaTiO₃ hysteresis from Sawyer-Tower experiment is not a perfect symmetric hysteresis loop (due to electric noise), therefore the amplitudes of even harmonics remain but they are comparatively small and can be ignored as shown in Fig. 4.1 (c).



(a)



(b)

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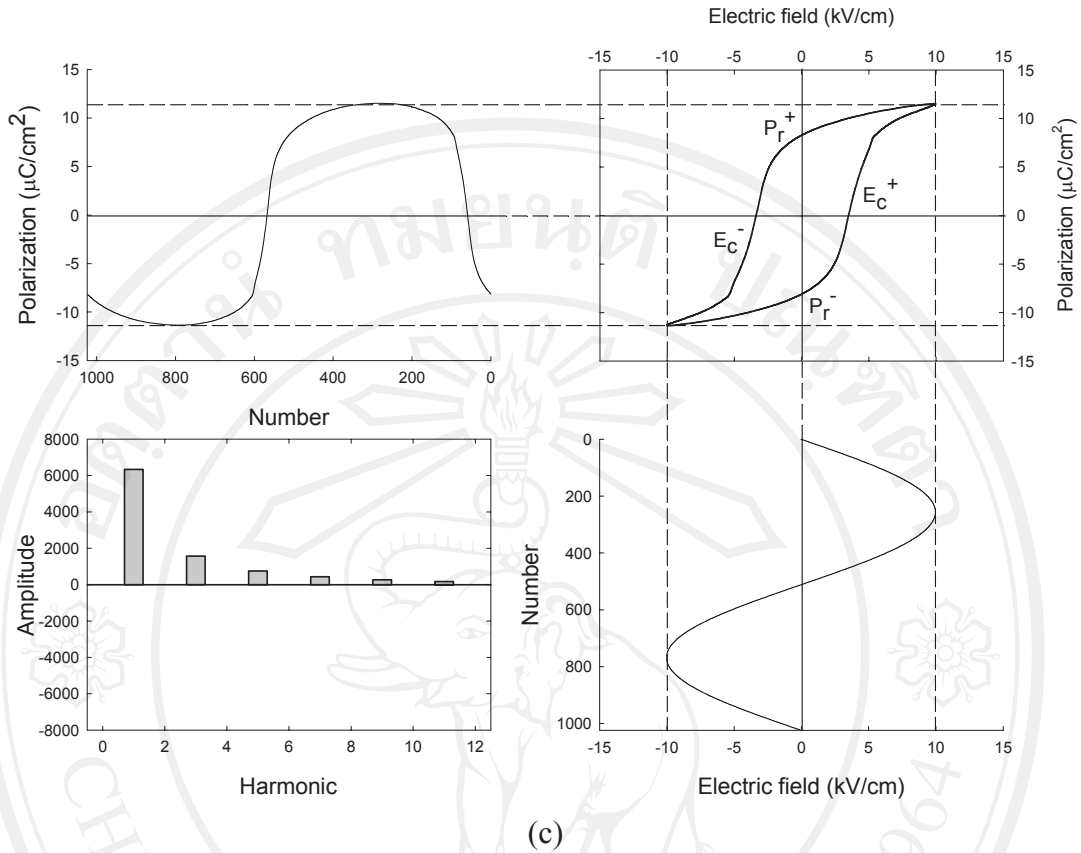


Figure 4.1 The ferroelectric hysteresis (right top) with its corresponding electric field signal (right bottom) and polarization signal (left top), and the spectrum of Fourier transformation (left bottom) for (a) Ising Ferroelectric hysteresis data from mean field calculation that generated at $T = 2.50 J/k_B$, $E_0 = 4.00 J$ and $f = 0.01 \tau^{-1}$, (b) Ising Ferroelectric hysteresis data from Monte Carlo simulation that generated at $T = 2.00 J/k_B$, $E_0 = 4.00 J$ and $f = 0.01 mcs^{-1}$, and (c) BaTiO₃ Ferroelectric hysteresis data from Sawyer-Tower experiment that measured at $T = 25 \text{ }^\circ\text{C}$, $E_0 = 10 \text{ kV/cm}$ and $f = 10 \text{ Hz}$.

In general, it can be derived from Fourier coefficients of the periodic function $f(t)$ with a period T that the half-wave symmetry have only odd harmonics as

$$f(t) = -f\left(t + \frac{1}{2}T\right) = -f\left(t - \frac{1}{2}T\right). \quad (4.1)$$

The coefficient a_0 in Fourier series of the periodic function $f(t)$ is

$$a_0 = \frac{2}{P} \int_{-T/2}^{T/2} f(t) dt. \quad (4.2)$$

Then by separating integral region into 2 parts,

$$a_0 = \frac{2}{T} \left[\int_{-T/2}^0 f(t) dt + \int_0^{T/2} f(t) dt \right]. \quad (4.3)$$

After that, by changing the variable t to $t - \frac{1}{2}T$ in the first integral,

$$a_0 = \frac{2}{T} \left[\int_0^{T/2} f\left(t - \frac{1}{2}T\right) dt + \int_0^{T/2} f(t) dt \right]. \quad (4.4)$$

Next, by replacing $f(t) = -f\left(t - \frac{1}{2}T\right)$ in the first integral,

$$a_0 = \frac{2}{T} \left[- \int_0^{T/2} f(t) dt + \int_0^{T/2} f(t) dt \right], \quad (4.5)$$

and the coefficient a_0 is

$$a_0 = 0. \quad (4.6)$$

On the other hand, the coefficient a_n in Fourier series of the periodic function $f(t)$ is

$$a_n = \frac{2}{T} \int_{-T/2}^{T/2} f(t) \cos(2n\pi f_0 t) dt. \quad (4.7)$$

In a same way, by separating integral region into 2 parts,

$$a_n = \frac{2}{T} \left[\int_{-T/2}^0 f(t) \cos(2n\pi f_0 t) dt + \int_0^{T/2} f(t) \cos(2n\pi f_0 t) dt \right], \quad (4.8)$$

And with changing the variable t to $t - \frac{1}{2}P$ in the first integral,

$$a_n = \frac{2}{T} \left[\int_0^{T/2} f\left(t - \frac{1}{2}T\right) \cos\left(2n\pi f_0\left(t - \frac{1}{2}T\right)\right) dt + \int_0^{T/2} f(t) \cos(2n\pi f_0 t) dt \right]. \quad (4.9)$$

As replacing $f(t) = -f\left(t - \frac{1}{2}T\right)$ in the first integral, so

$$a_n = \frac{2}{T} \left[- \int_0^{T/2} f(t) \cos(2n\pi f_0 t) \cos(n\pi) dt + \int_0^{T/2} f(t) \cos(2n\pi f_0 t) dt \right]. \quad (4.10)$$

In fact, $\sin(n\pi) = 0$, so

$$a_n = \frac{2}{T} (1 - \cos(n\pi)) \int_0^{T/2} f(t) \cos(2n\pi f_0 t) dt, \quad (4.11)$$

where the coefficient a_n is

$$a_n = \begin{cases} 0 & \text{for } n \text{ even} \\ \frac{4}{T} \int_0^{T/2} f(t) \cos(2n\pi f_0 t) dt & \text{for } n \text{ odd.} \end{cases} \quad (4.12)$$

For, the coefficient b_n in Fourier series of the periodic function $f(t)$, it is given by

$$b_n = \frac{2}{T} \int_{-T/2}^{T/2} f(t) \sin(2n\pi f_0 t) dt. \quad (4.13)$$

Again, by separating integral region into 2 parts,

$$b_n = \frac{2}{T} \left[\int_{-T/2}^0 f(t) \sin(2n\pi f_0 t) dt + \int_0^{T/2} f(t) \sin(2n\pi f_0 t) dt \right]. \quad (4.14)$$

With changing the variable t to $t - \frac{1}{2}T$ in the first integral,

$$b_n = \frac{2}{T} \left[\int_0^{T/2} f\left(t - \frac{1}{2}T\right) \sin\left(2n\pi f_0\left(t - \frac{1}{2}T\right)\right) dt + \int_0^{T/2} f(t) \sin(2n\pi f_0 t) dt \right]. \quad (4.15)$$

By replacing $f(t) = -f\left(t - \frac{1}{2}T\right)$ in the first integral,

$$b_n = \frac{2}{T} \left[- \int_0^{T/2} f(t) \sin(2n\pi f_0 t) \cos(n\pi) dt + \int_0^{T/2} f(t) \sin(2n\pi f_0 t) dt \right], \quad (4.16)$$

and since, $\sin(n\pi) = 0$, it given

$$b_n = \frac{2}{T} (1 - \cos(n\pi)) \int_0^{T/2} f(t) \sin(2n\pi f_0 t) dt. \quad (4.17)$$

Therefore, the coefficient b_n is

$$b_n = \begin{cases} 0 & \text{for } n \text{ even} \\ \frac{4}{T} \int_0^{T/2} f(t) \sin(2n\pi f_0 t) dt & \text{for } n \text{ odd.} \end{cases} \quad (4.18)$$

Since the coefficients $a_n = 2A_k / N$ and $b_n = 2B_k / N$, the amplitude of k^{th} harmonic

of Fourier transformation becomes $C_k = \sqrt{A_k^2 + B_k^2}$ where $n = k$ and N is the number

of data points per period. As can be seen, Fourier spectrum presents only odd

harmonics because the symmetric hysteresis is half-wave symmetry. Further, from

Fourier spectrum, polarization signal contains many frequencies different from that of

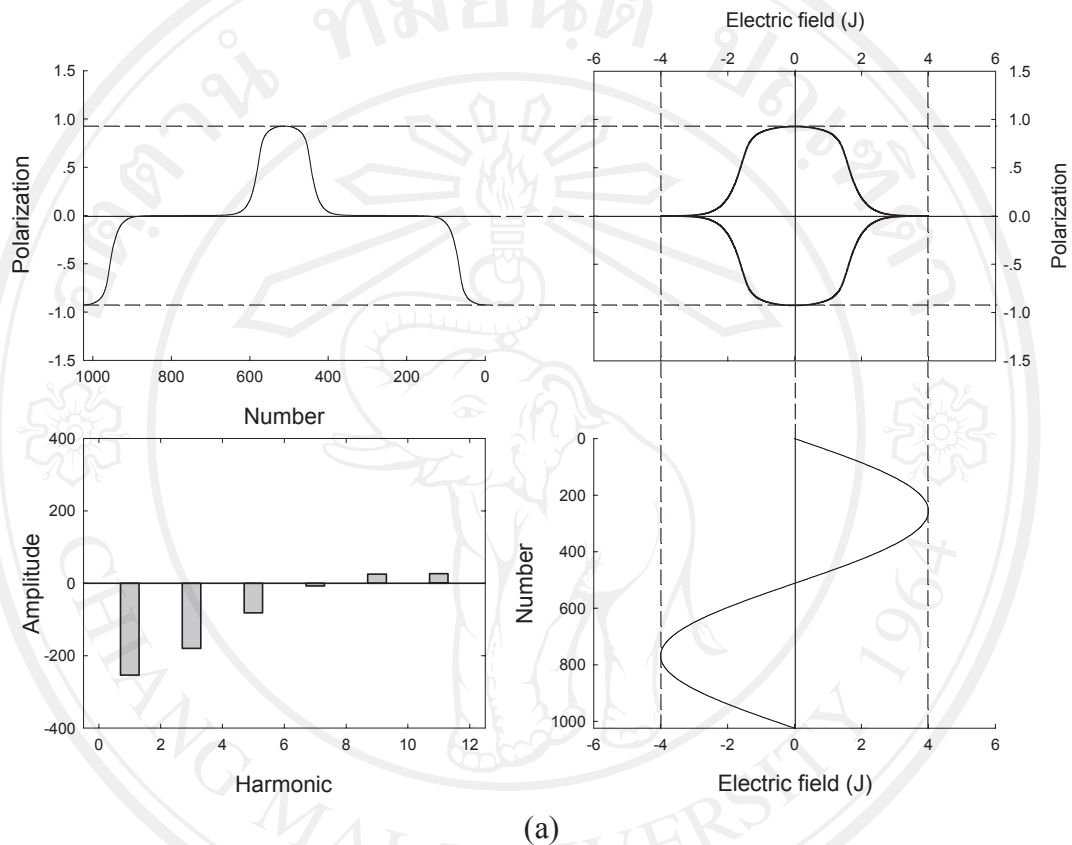
electric field. This is implied that the molecular dipole moments of ferroelectric

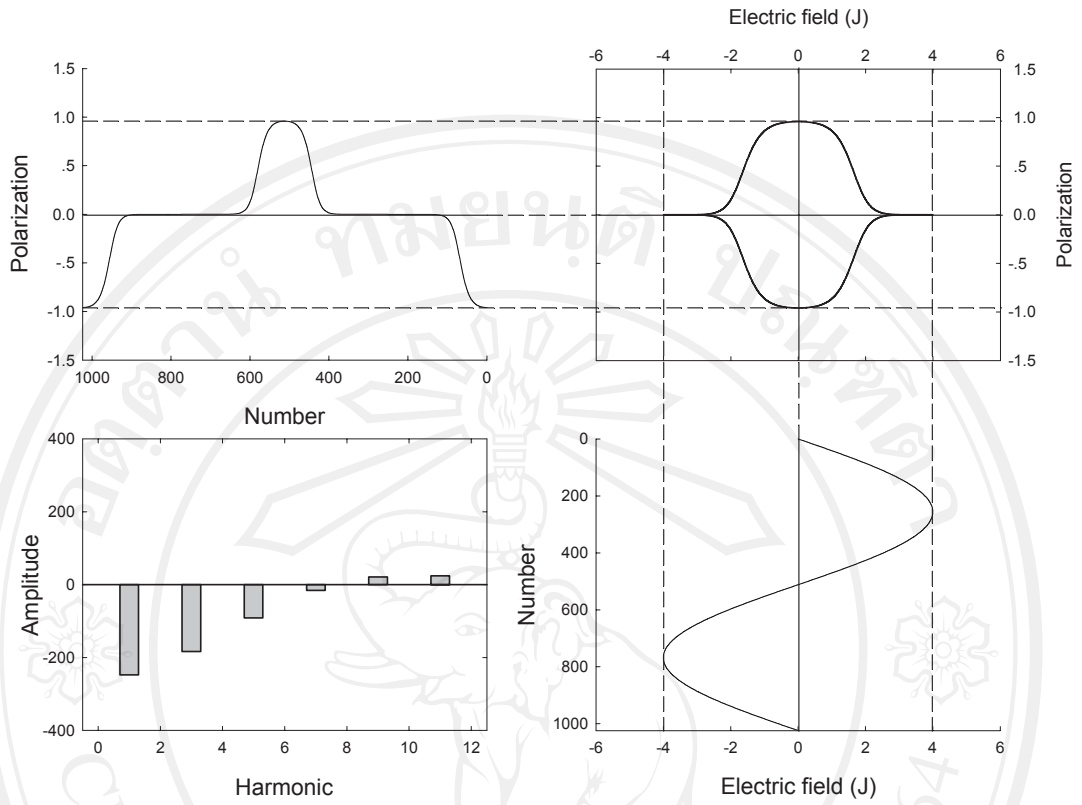
materials do not instantly response to temperature and electric field.

After that, Fourier spectrums of the real and imaginary parts were then

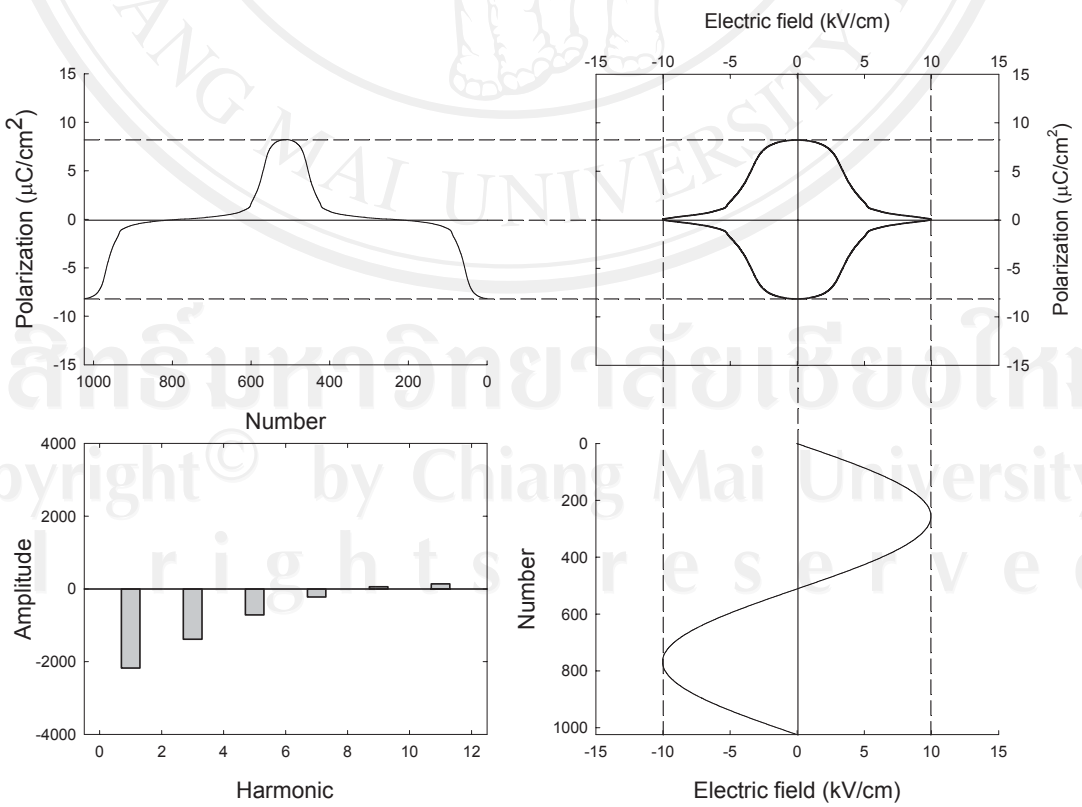
investigated in details. The hysteresis re-calculated from inverse Fourier

transformation of the real and imaginary parts were used to observe the relation of the amplitude of Fourier harmonics of the real and imaginary parts to hysteresis characteristic.



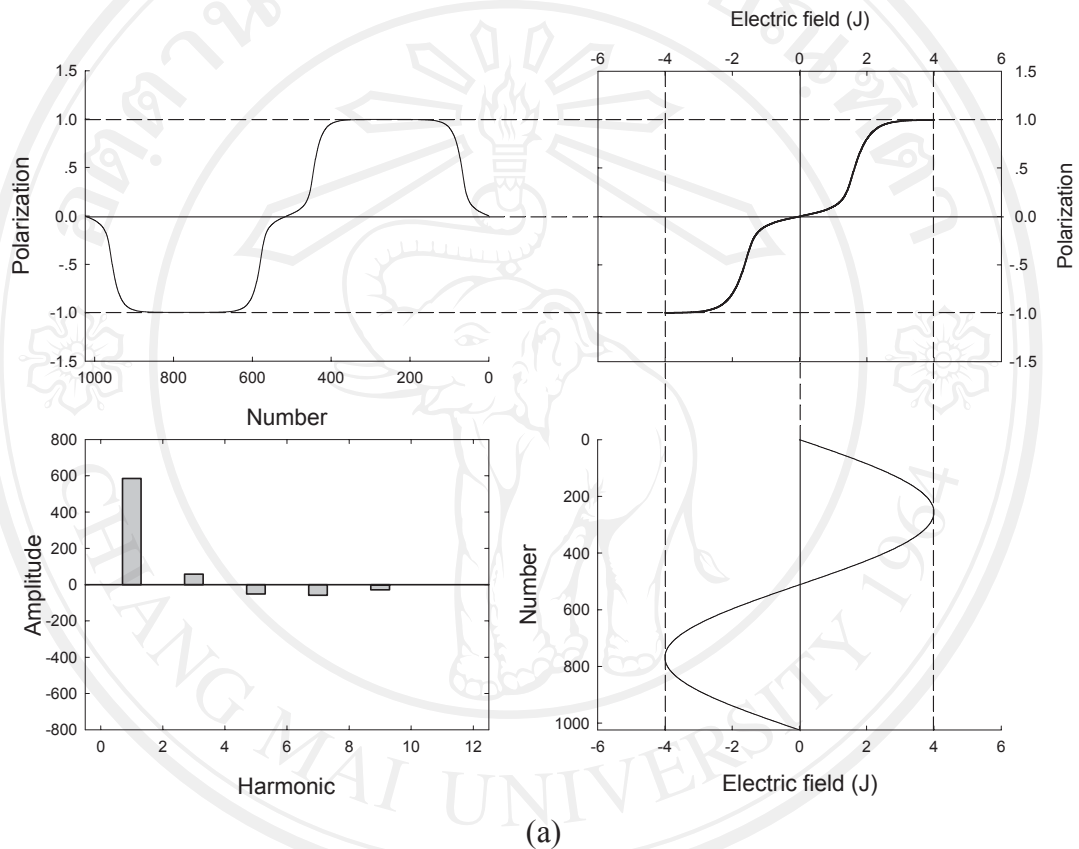


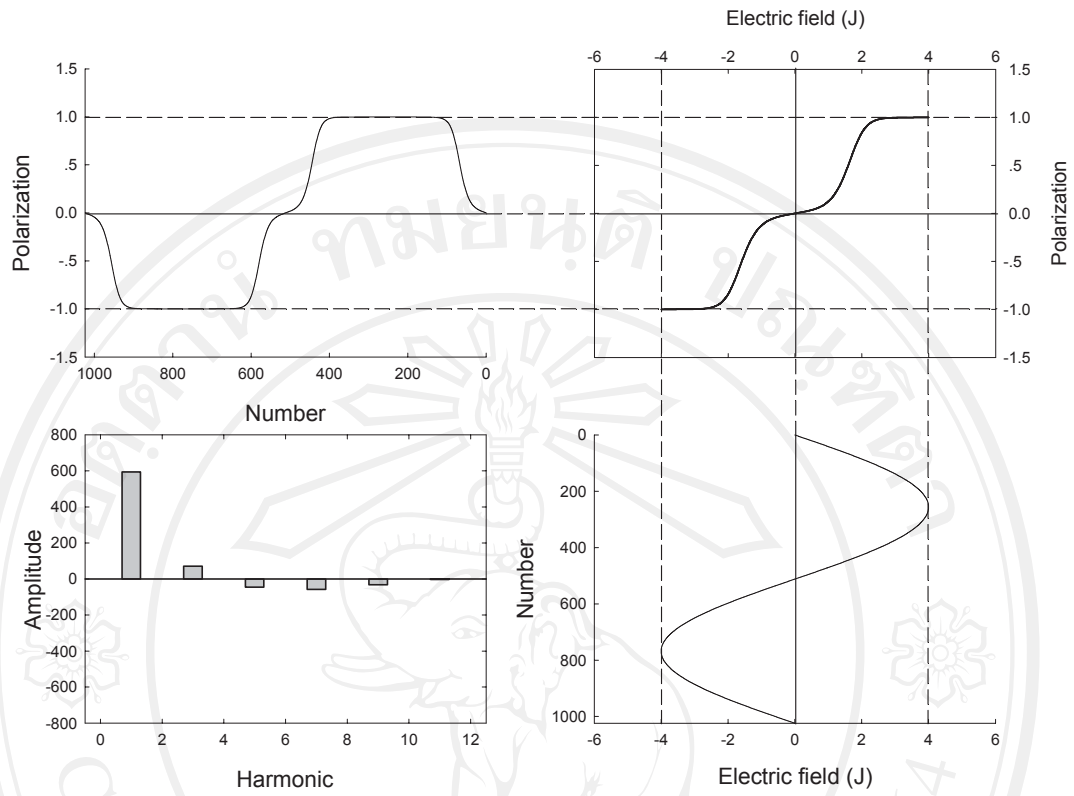
(b)



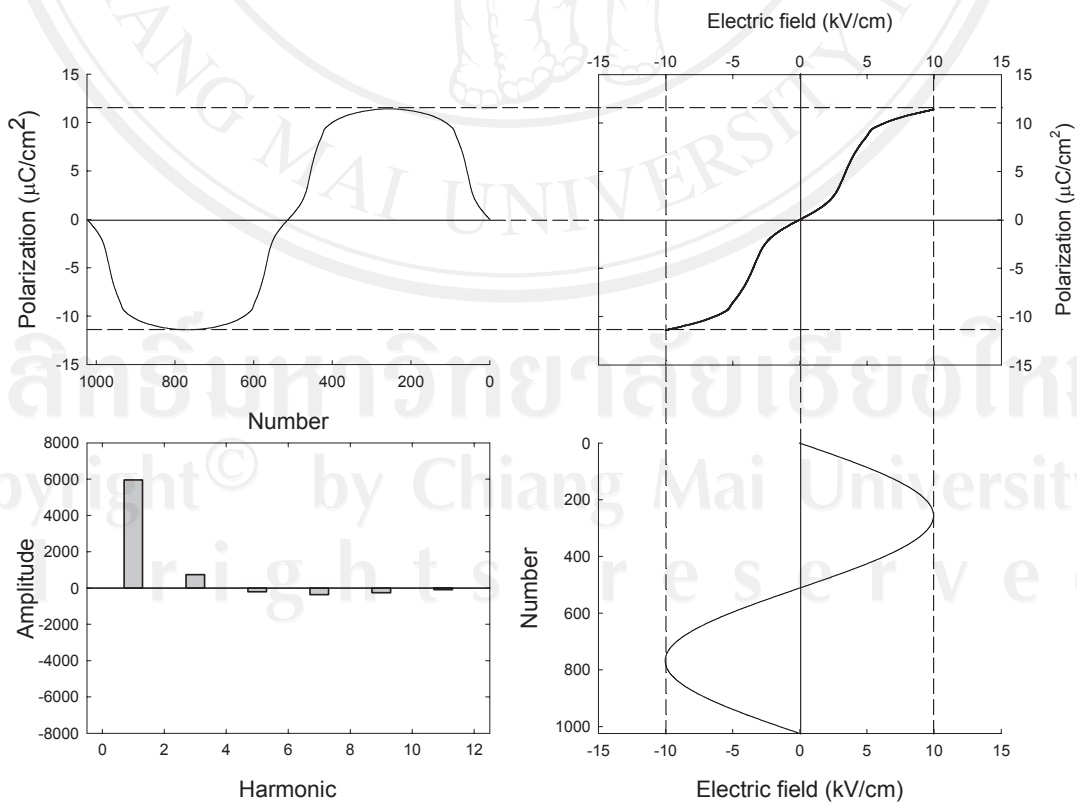
(c)

Figure 4.2 The ferroelectric hysteresis (right top) re-calculated from inverse Fourier transformation of the real part with its corresponding electric field signal (right bottom) and polarization signal (top left) and the spectrum of Fourier transformation of real part (left bottom) from Fig. 4.1.





(b)



(c)

Figure 4.3 The ferroelectric hysteresis (right top) re-calculated from inverse Fourier transformation of the imaginary part with its corresponding electric field signal (right bottom) and polarization signal (left top) and the spectrum of Fourier transformation of imaginary part (left bottom) from Fig. 4.1.

Additionally, it is found that the polarization re-calculated from inverse Fourier transformation of the real part is out of phase with electric field (see Fig. 4.2). On the other hand, the polarization re-calculated from inverse Fourier transformation of the imaginary part is in phase with electric field (see Fig. 4.3). These imply that hysteresis area depends on the harmonics of real part, but hysteresis shape depends on the harmonics of imaginary part. Consequently, it is useful to find the relationship between hysteresis properties and external perturbations parameters to the amplitude of each harmonic of Fourier transformation.

4.2 The relationship between hysteresis properties and amplitude of Fourier harmonic

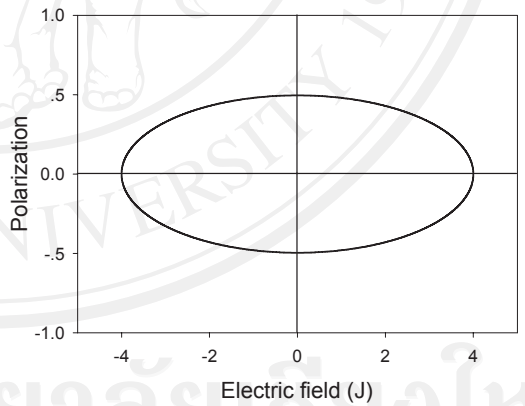
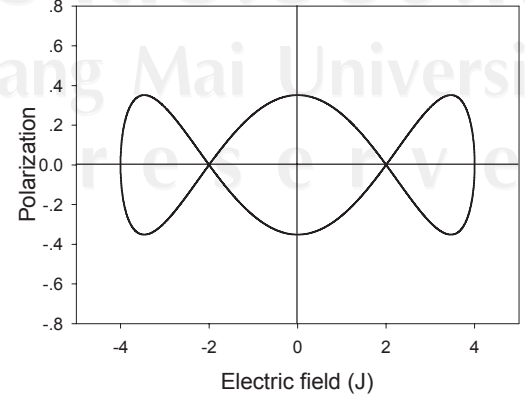
After that with the understanding of Fourier spectrum characteristic, the relationship between hysteresis properties and amplitude of each Fourier harmonics was investigated.

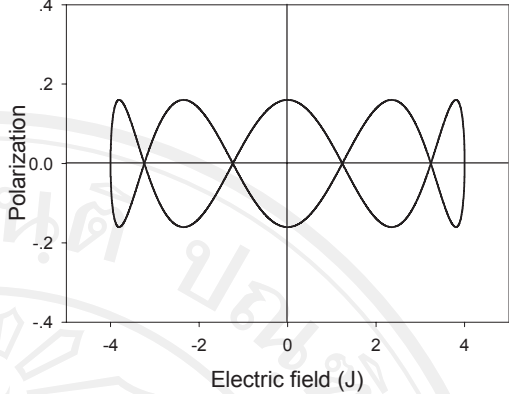
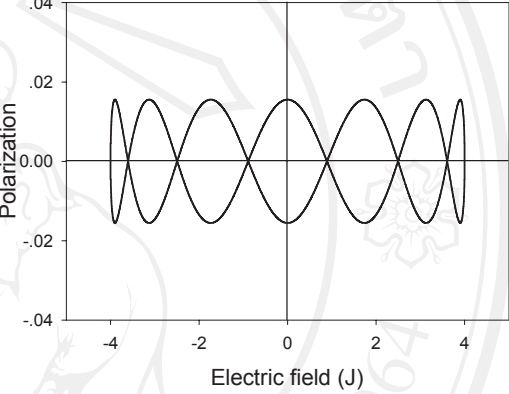
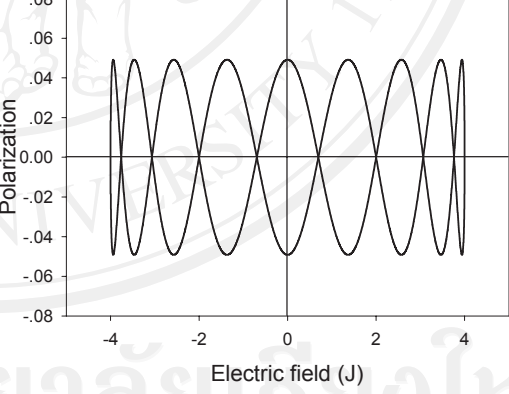
4.2.1 Hysteresis area

The hysteresis area (A) refers to the external energy requires to cycle the molecular dipole moments in ferroelectric materials. Since, the polarization re-calculated from inverse Fourier transformation of the real part is out of phase with electric field, so hysteresis area may be nonzero. On the other hand, the polarization re-calculated from inverse Fourier transformation of the imaginary part is in phase

with electric field, so hysteresis area is equal to zero. Therefore, it is safe to imply that the hysteresis area can be extracted from inverse Fourier transformation of odd harmonics of the real part. Then, the hysteresis area re-calculated from inverse Fourier transformation of the real part was investigated in details as shown in Table 4.1 for Ising hysteresis from mean field calculation, Table 4.2 for Ising hysteresis from Monte Carlo simulation and Table 4.3 for BaTiO₃ hysteresis from Sawyer-Tower experiment.

Table 4.1 The hysteresis area ($A_k^{real\ part}$) re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for Ising hysteresis from mean field calculation in Fig. 4.1 (a).

k^{th}	A_k	$A_k^{real\ part}$	$A_k^{real\ part}$
1	-253.8517	6.2304	
3	-179.9873	8.35×10^{-15}	

5	-82.0658	4.77×10^{-15}	
7	-7.9538	3.42×10^{-16}	
9	25.1853	-1.50×10^{-15}	

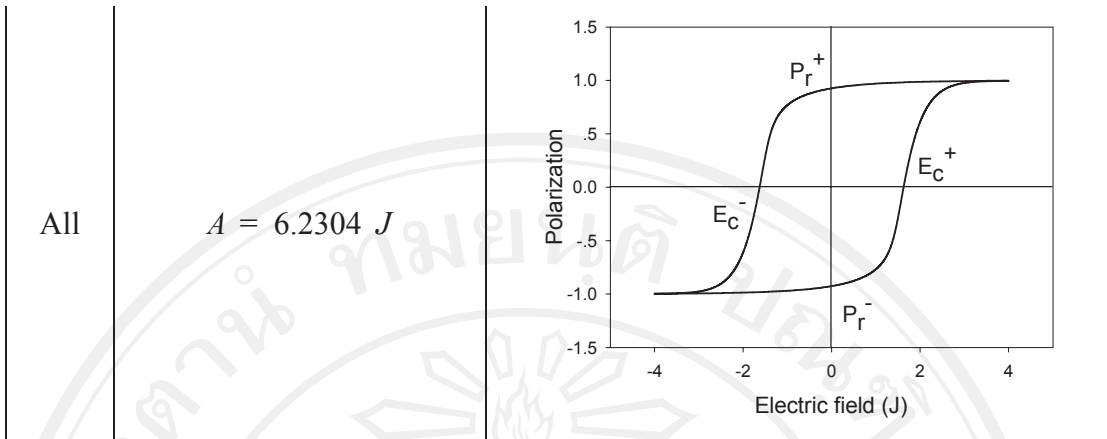
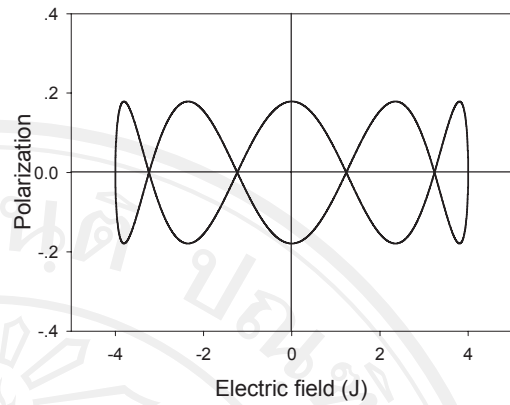


Table 4.2 The hysteresis area ($A_k^{real part}$) re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for Ising hysteresis from Monte Carlo simulation in Fig. 4.1 (b).

k^{th}	A_k	$A_k^{real part}$	$A_k^{real part}$
1	-247.5941	6.0768	
3	-183.3343	6.26×10^{-8}	

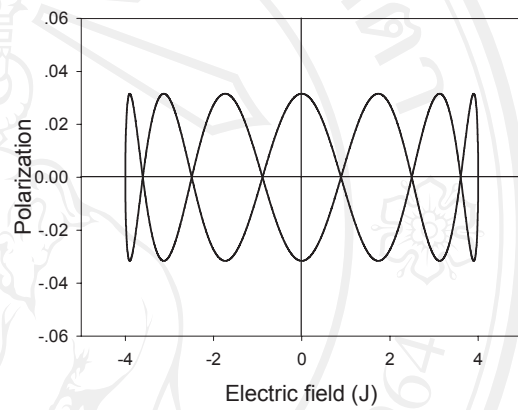
5

-91.6445

 1.53×10^{-7} 

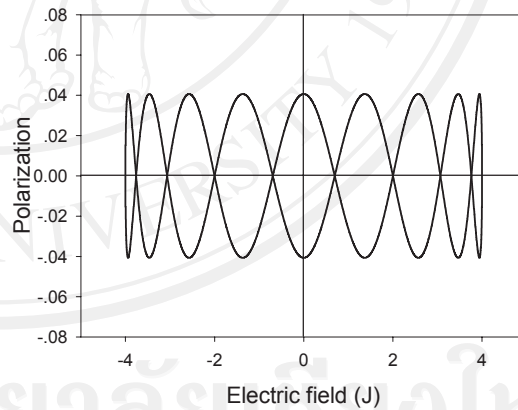
7

-16.1722

 1.03×10^{-8} 

9

20.8371

 -3.36×10^{-8} 

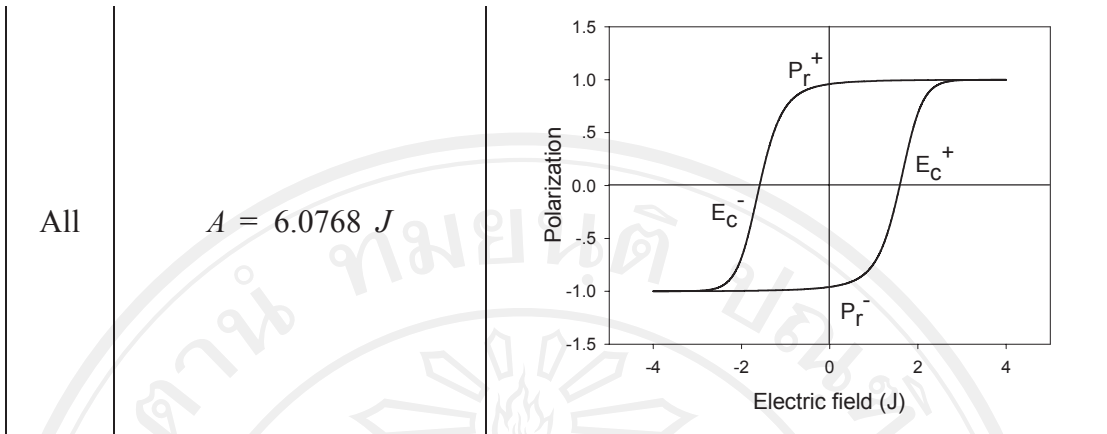
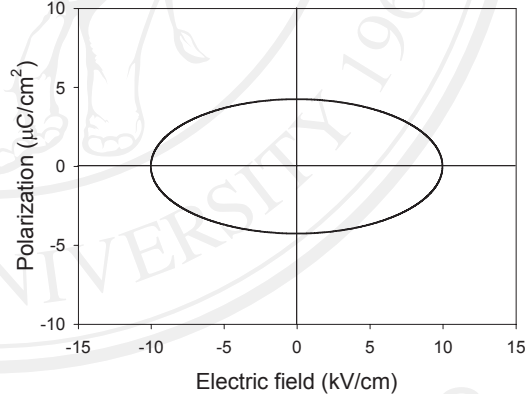
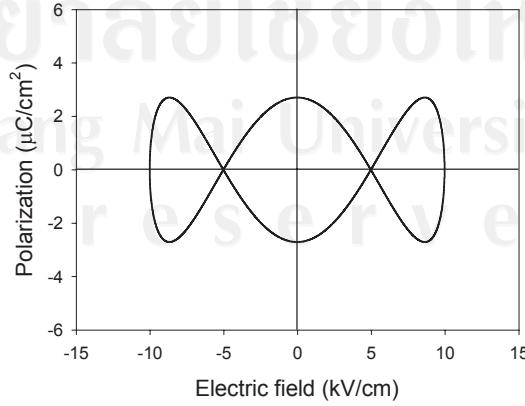
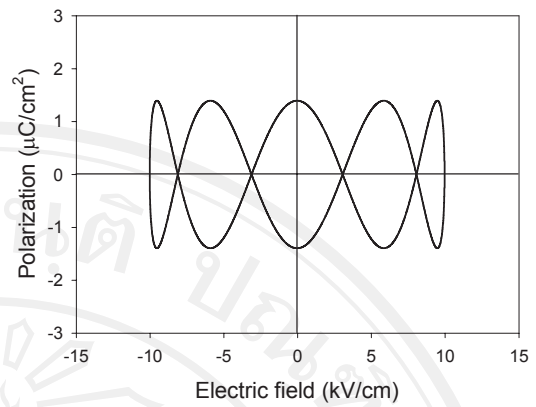


Table 4.3 The hysteresis area ($A_k^{real\ part}$) re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for BaTiO₃ hysteresis from Sawyer-Tower experiment in Fig. 4.1 (c).

k^{th}	A_k	$A_k^{real\ part}$	$A_k^{real\ part}$
1	-2178.1042	133.5459	
3	-1385.0301	-9.52×10^{-8}	

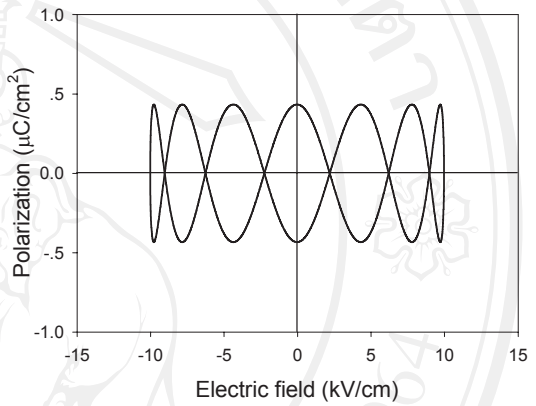
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-713.9643

 -1.39×10^{-7} 

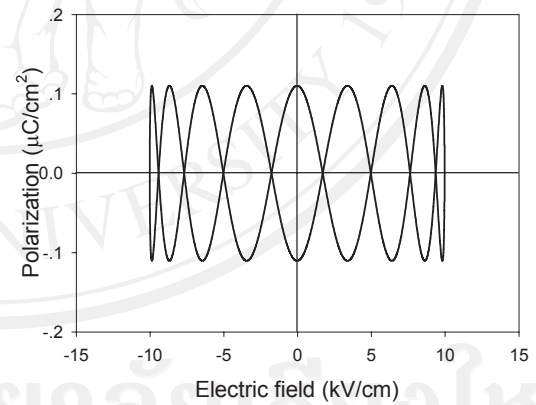
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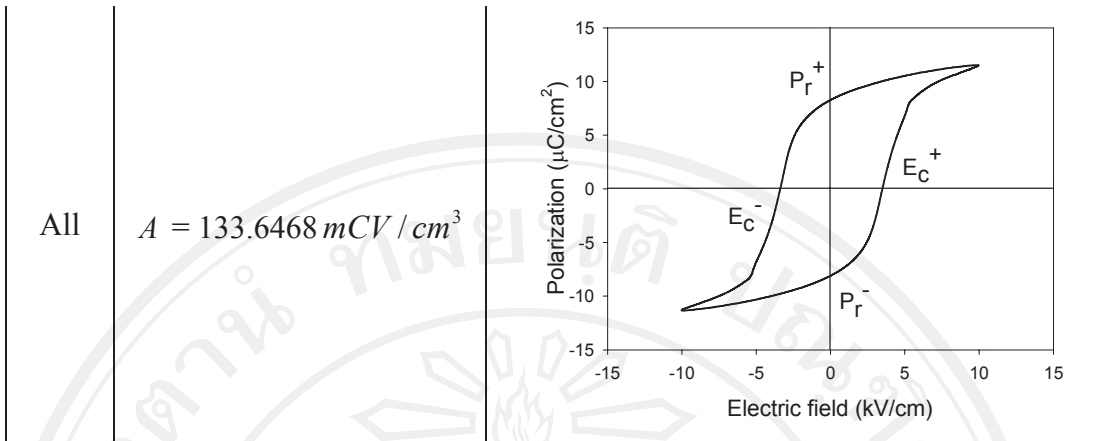
-221.9601

 -8.38×10^{-8} 

9

56.4744

 3.56×10^{-8} 



As can be seen from Table 4.1, 4.2 and 4.3, the hysteresis area re-calculated from inverse Fourier transformation of the first harmonic of real part is almost equal to the real hysteresis area. On the other hand, the hysteresis areas from inverse Fourier transformation of all other harmonics of real part nearly cancel out and are very small in comparison to the real hysteresis area. Further, it is also found that the hysteresis re-calculated from inverse Fourier transformation of the first harmonic of the real part is ellipse-like. Since the area of typical ellipse equal to πab where a is length of major axis and b is length of minor axis, the hysteresis area is then compound with quantity $\pi E_0 P_1^{real\ part}$ (where E_0 is the electric field amplitude and $P_1^{real\ part}$ is the polarization amplitude re-calculated from inverse Fourier transformation of the first harmonic of the real part), and it was found that they are equal (with less than one percent different). Additionally, $P_1^{real\ part}$ can be written in the term of the first harmonic of real part (A_1) i.e. $P_1^{real\ part} = -2A_1/N$ where N is the number of data points per period, hysteresis area can then be rewritten as

$$A = -\frac{2\pi}{N} E_0 A_1 \quad (4.19)$$

To verify the validity of Eq. (4.19), numerical comparison was evaluated. In Fig. 4.1, the hysteresis loop has $A = 6.2304 J$, $6.0768 J$ and $133.6468 mCV/cm^3$ but from Eq. (4.19), $A = 6.2304 J$, $6.0768 J$ and $133.5459 mCV/cm^3$, which agree very well. As a result, this emphasizes that the hysteresis area depends on the amplitude of electric field and the amplitude of the first harmonic of real part.

4.2.2 Remnant polarization

On observation of the remnant polarization (P_r) which is the magnitude of polarization that remains at the vanishing of the electric field. Since, the polarization re-calculated from inverse Fourier transformation of the real part is out of phase with electric field, so electric field and polarization magnitudes do not vanish at the same time. On the other hand, the polarization re-calculated from inverse Fourier transformation of the imaginary part is in phase with electric field, so electric field and polarization magnitude vanishes together. Therefore, the remnant polarization re-calculated from the inverse Fourier transformation of odd harmonics of the real part was investigated in details as shown in Table 4.4 for Ising hysteresis from mean field calculation, Table 4.5 for Ising hysteresis from Monte Carlo simulation and Table 4.6 for BaTiO₃ hysteresis from Sawyer-Tower experiment.

Table 4.4 The remnant polarization $P_{r_k}^{real\ part}$ re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for Ising hysteresis from mean field calculation in Fig. 4.1 (a).

k^{th}	A_k	$P_{r_k}^{real\ part}$	$P_k^{real\ part}$
1	-253.8517	0.4958	
3	-179.9873	0.3515	
5	-82.0658	0.1603	

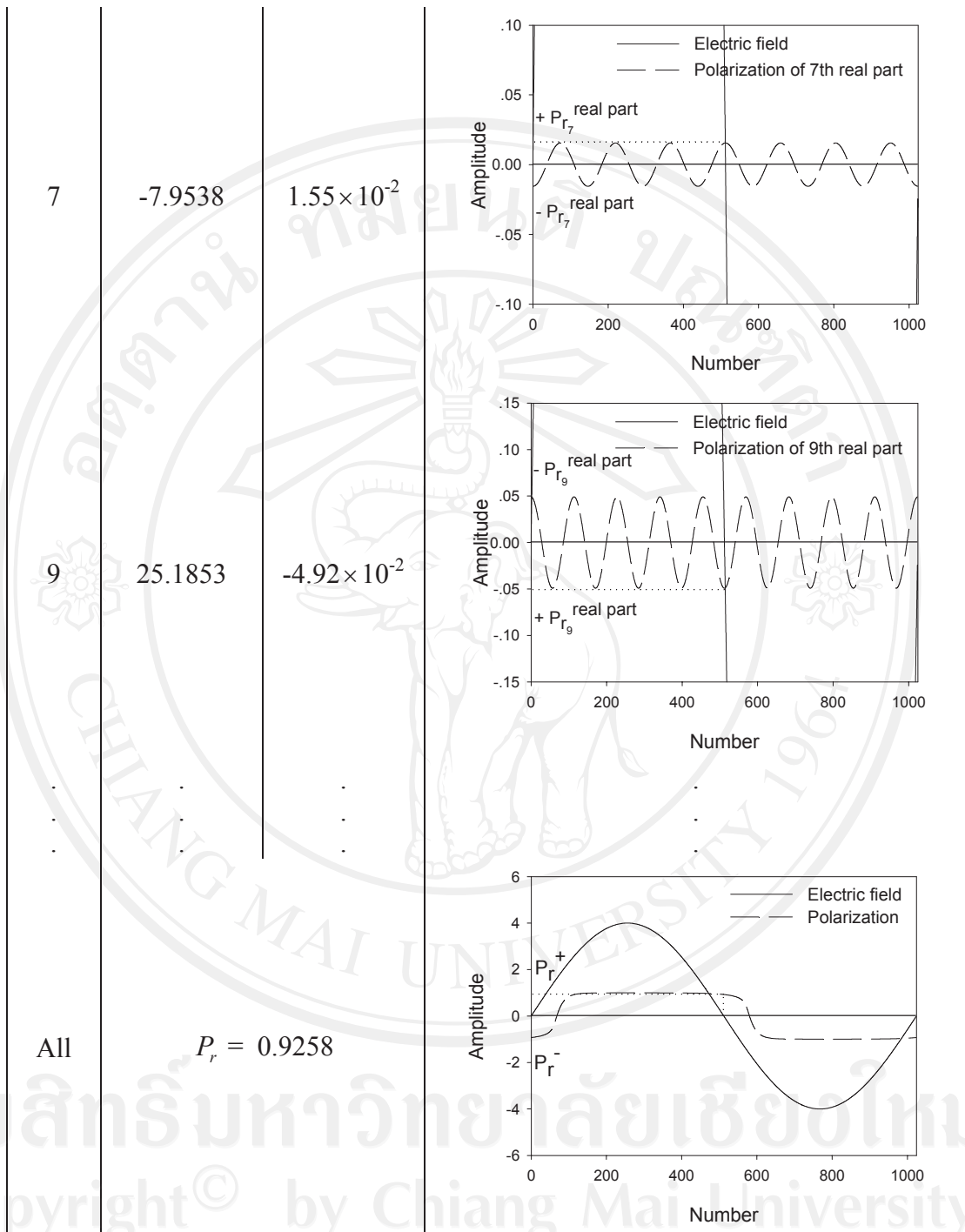


Table 4.5 The remnant polarization $P_k^{real\ part}$ re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for Ising hysteresis from Monte Carlo simulation in Fig. 4.1 (b).

k^{th}	A_k	$P_{r_k}^{real\ part}$	$P_k^{real\ part}$
1	-247.5941	0.4836	
3	-183.3343	0.3581	
5	-91.6445	0.1790	

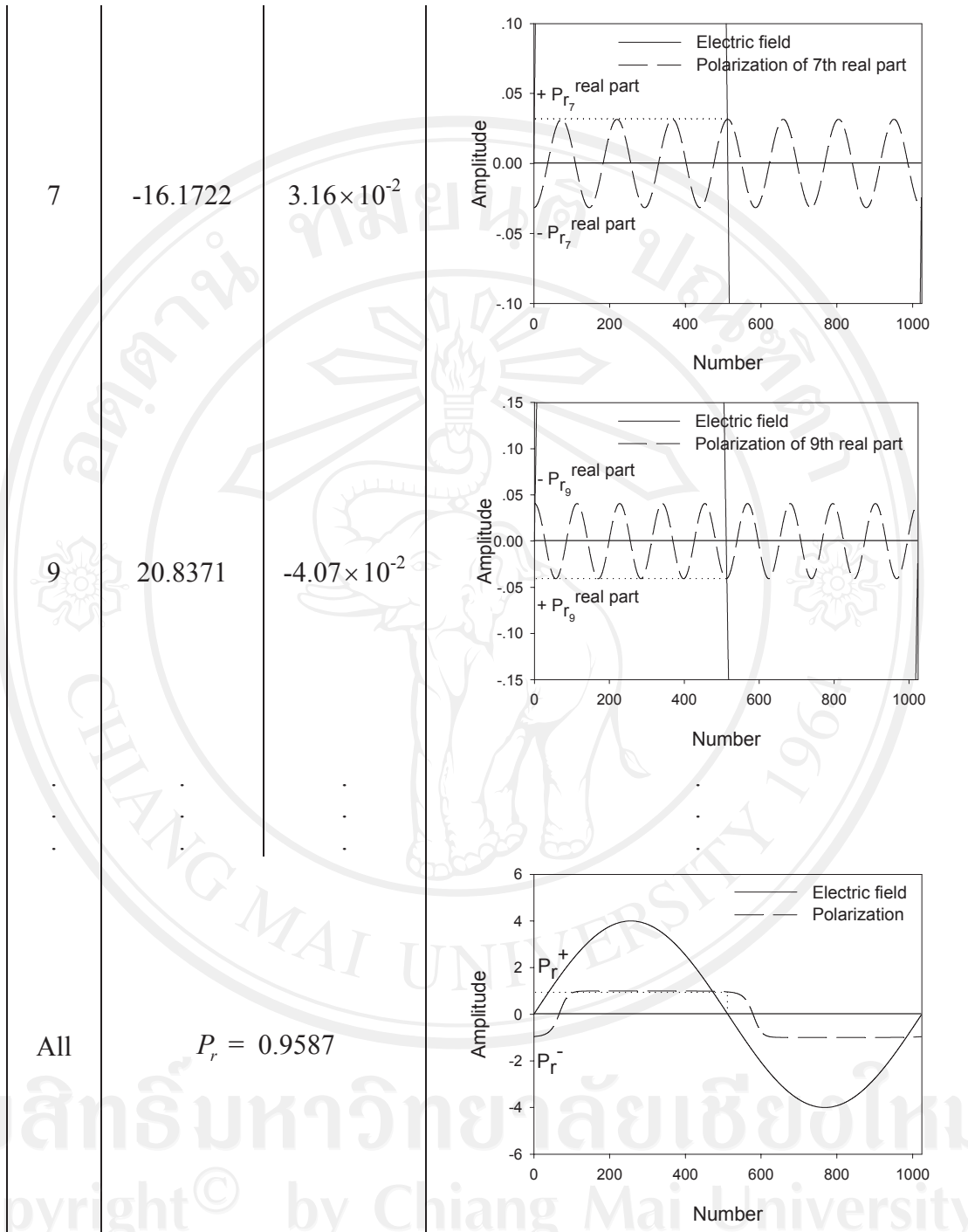
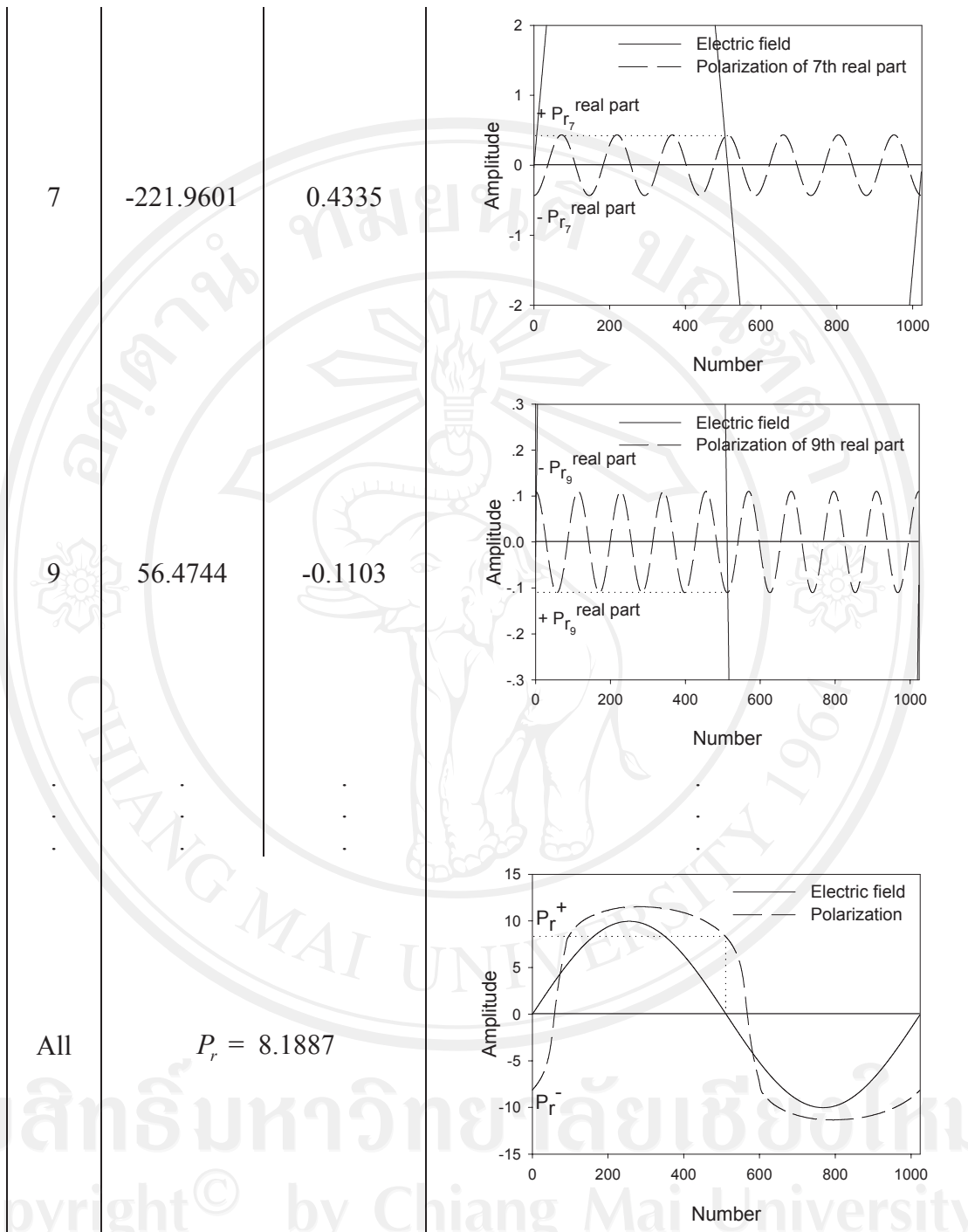


Table 4.6 The remnant polarization $P_{r_k}^{real\ part}$ re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) for BaTiO₃ hysteresis from Sawyer-Tower experiment in Fig. 4.1 (c).

k^{th}	A_k	$P_{r_k}^{real\ part}$	$P_k^{real\ part}$
1	-2178.1042	4.2541	
3	-1385.0301	2.7051	
5	-713.9643	1.3945	



As can be seen from Table 4.4, 4.5 and 4.6, the remnant polarization can be calculated from the sum of the polarization amplitude re-calculated from inverse Fourier transformation of odd harmonics of the real part ($P_k^{real\ part}$), so it can be written as

$$P_r^\pm = \mp \frac{2}{N} \sum_{k=1}^{N/2} P_k^{real\ part} . \quad (4.20)$$

Since, $P_k^{real\ part}$ can be written in terms of the amplitude of odd harmonics of the real part (A_k) i.e. $P_k^{real\ part} = -2a_k/N$ where N is number of data points per period and k are odd integers. Therefore, the remnant polarization can be rewritten as

$$P_r^\pm = \mp \frac{2}{N} \sum_{n=1}^{N/2} A_n . \quad (4.21)$$

To verify this, the hysteresis loop in Fig. 4.1 has the average remnant polarization $(P_r^+ - P_r^-)/2$ of 0.9258, 0.9588 and $8.1887 \mu\text{C}/\text{cm}^2$ while the average remnant polarization calculated from Eq. (4.21) is 0.9258, 0.9588 and $8.1887 \mu\text{C}/\text{cm}^2$, which are exactly the same (up to 4 digits). Therefore, it can be concluded that the remnant polarization depends on the amplitude of odd harmonics of real part.

4.2.3 Coercive field

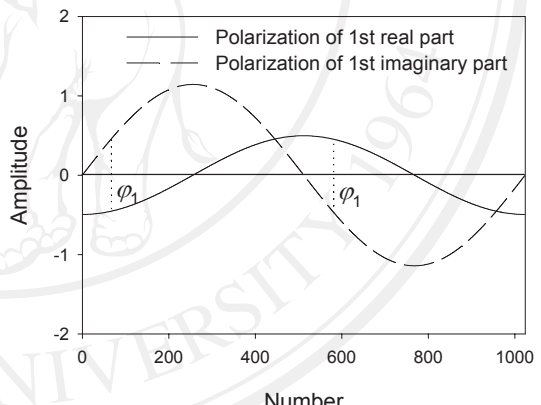
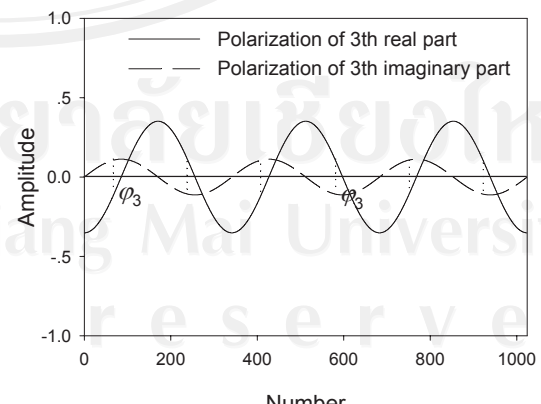
On investigation of the coercive field (E_c) which describes the magnitude of the electric field that cancels the polarization in ferroelectric materials. Therefore, the coercive field can be found from the electric field magnitude at the phase-lag (ϕ) between electric field and polarization signals, so it can be written as

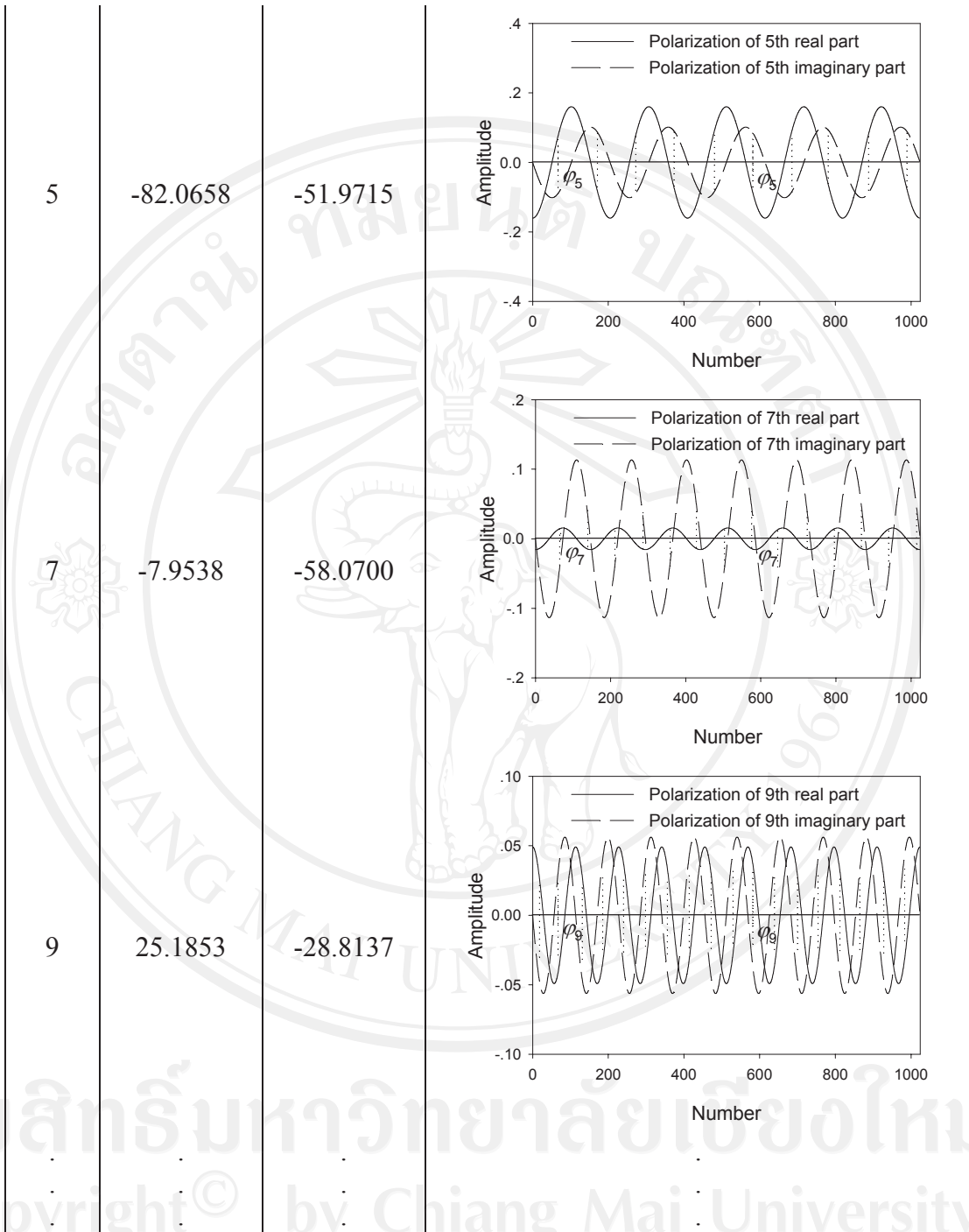
$$E_c^\pm = \pm E_0 \sin(\phi) . \quad (4.22)$$

Further, this phase-lag (ϕ) is also equal to the phase-angle (ϕ_k) that the combinations of polarizations of all k^{th} harmonics (polarization re-calculated from inverse Fourier transformation of the real and imaginary part) are cancelled. Since, the Fourier coefficients of symmetric hysteresis presents only odd harmonics, so the polarizations re-calculated from inverse Fourier transformation of each harmonic of real and

imaginary part are cancel at two phase-angles as shown in Table 4.7 for Ising hysteresis from mean field calculation, Table 4.8 for Ising hysteresis from Monte Carlo simulation and Table 4.9 for BaTiO₃ hysteresis from Sawyer-Tower experiment.

Table 4.7 The phase-angles φ_k that the combination of polarizations re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) and imaginary (B_k) part are cancelled for Ising hysteresis from mean field calculation in Fig. 4.1 (a).

k^{th}	A_k	B_k	φ_k
1	-253.8517	584.9039	
3	-179.9873	57.7073	



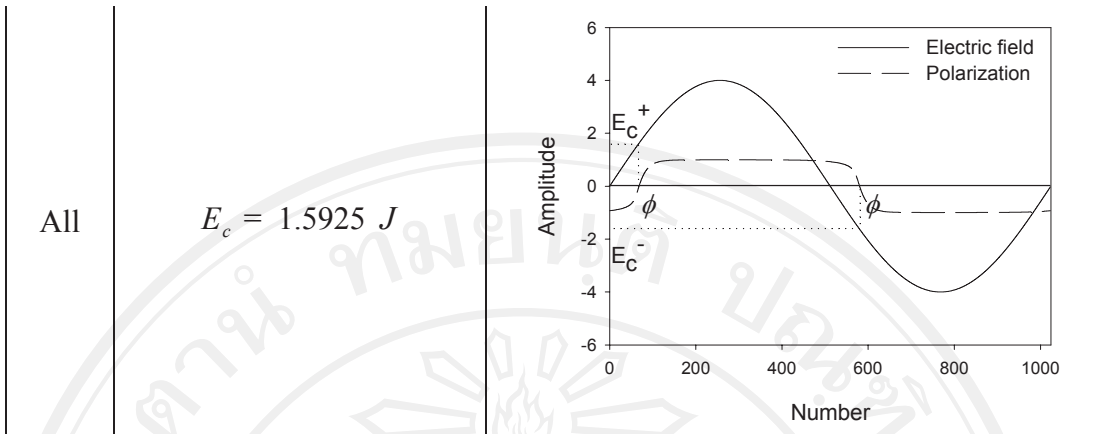
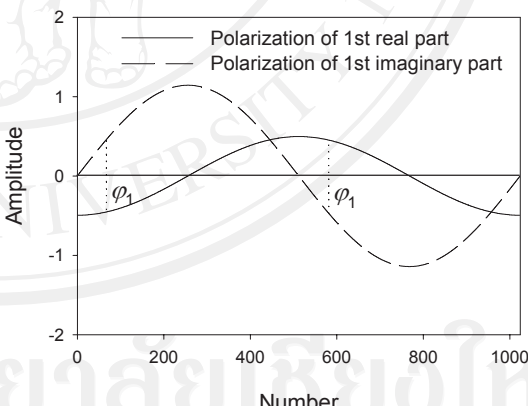
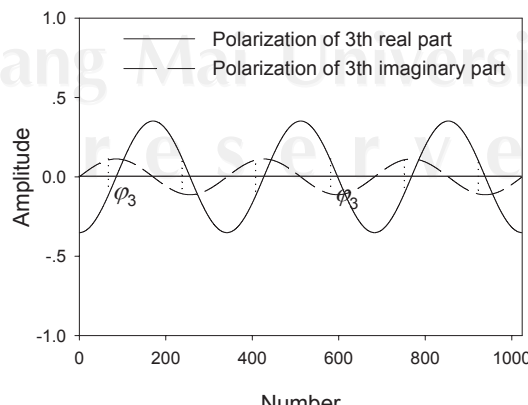
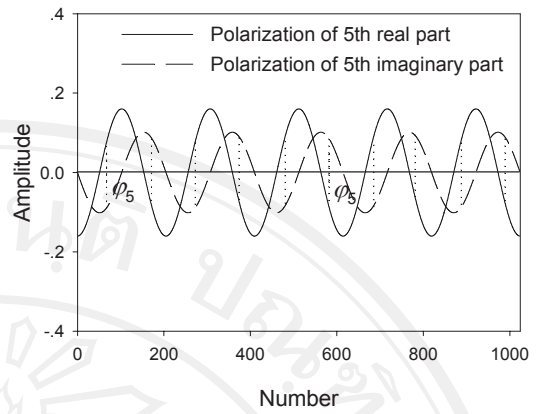


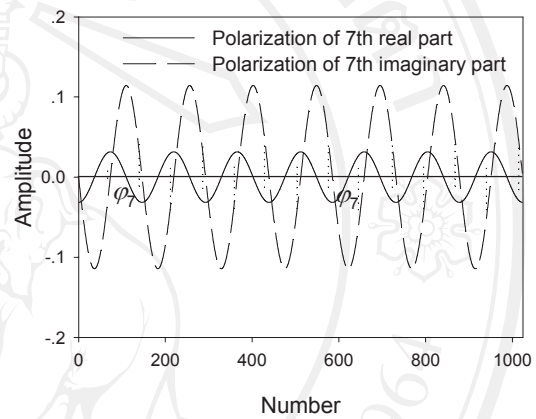
Table 4.8 The phase-angles φ_k that the combination of polarizations re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) and imaginary (B_k) part are cancelled for Ising hysteresis from Monte Carlo simulation in Fig. 4.1 (b).

k^{th}	A_k	B_k	φ_k
1	-247.5941	593.9259	
3	-183.3343	71.0047	

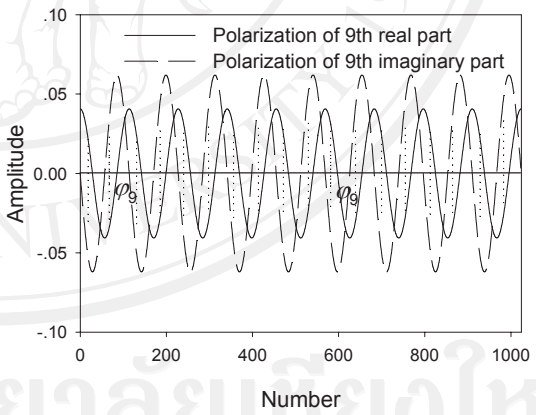
5 -91.6446 -45.2983



7 -16.1722 -58.5428



9 20.8371 -31.7729



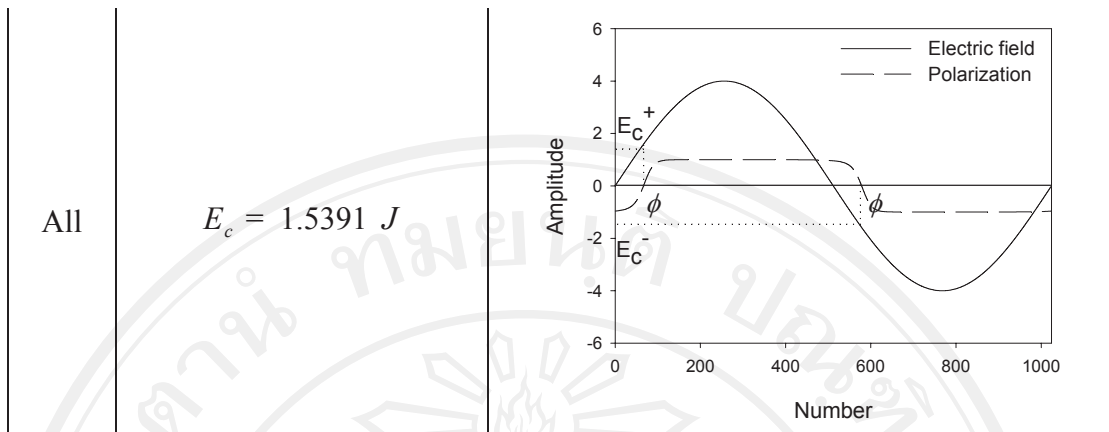
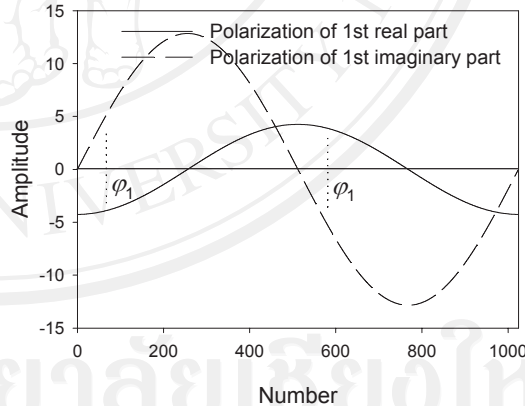
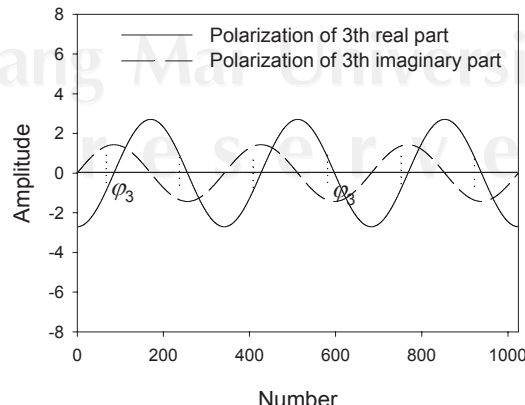
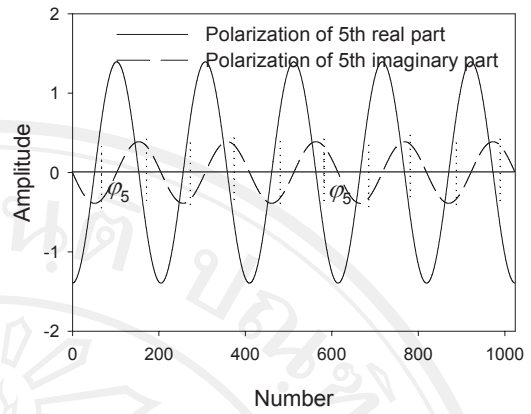


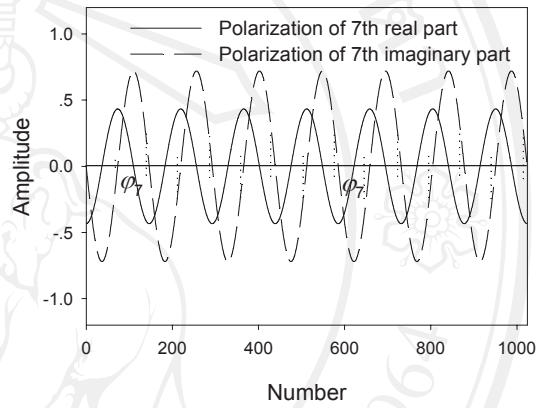
Table 4.9 The phase-angles φ_k that the combination of polarizations re-calculated from inverse Fourier transformation of the amplitude of odd k^{th} harmonic of real part (A_k) and imaginary (B_k) part are cancelled for BaTiO₃ hysteresis from Sawyer-Tower experiment in Fig. 4.1 (c).

k^{th}	A_k	B_k	φ_k
1	-2178.1042	5951.7470	
3	-1385.0301	731.8969	

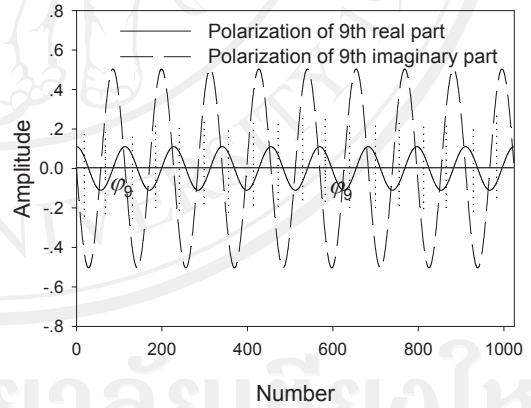
5 -713.9643 -198.7143

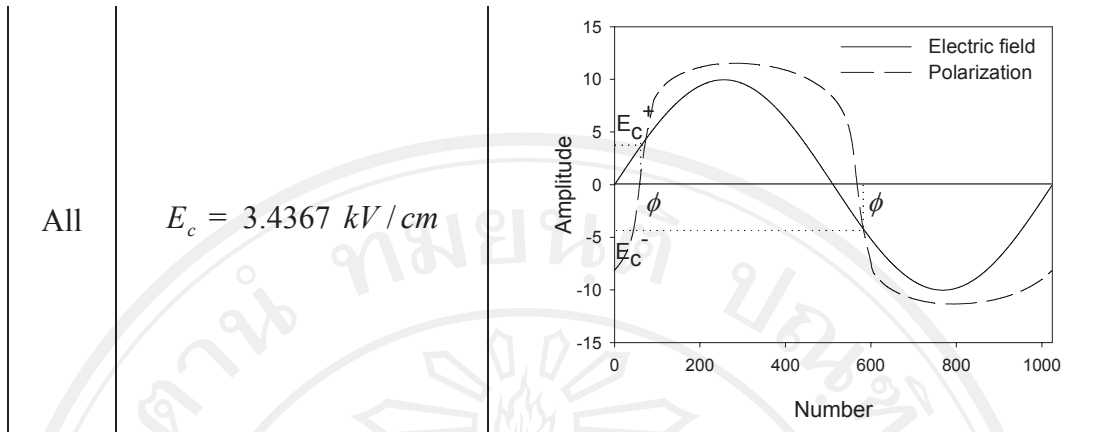


7 -221.9601 -368.8424



9 56.4744 -257.8738





As can be seen from Table 4.7, 4.8 and 4.9, these two phase-angles can be found from where the magnitude of the polarization re-calculated from inverse Fourier transformation of the first harmonic of real part equal to that of imaginary part but with opposite sign i.e.

$$-P_1^{real\ part} \cos(\varphi_1) = P_1^{imaginary\ part} \sin(\varphi_1) \quad (4.23)$$

where $P_1^{real\ part}$ and $P_1^{imaginary\ part}$ are amplitude of polarizations re-calculated from inverse Fourier transformation of the first harmonic of the real and imaginary part respectively. Since, $P_1^{real\ part}$ and $P_1^{imaginary\ part}$ can be written in the term of the first harmonic of real A_1 and imaginary B_1 part respectively i.e. $P_1^{real\ part} = -2A_1/N$ and $P_1^{imaginary\ part} = 2B_1/N$, where N is number of data points per period, Eq. (4.23) can be

rewritten as $A_1 \cos(\varphi_1) = B_1 \sin(\varphi_1)$, i.e. $\varphi_1 = \tan^{-1}(A_1 / B_1)$. Therefore, the coercive field can be rewritten as

$$E_c^\pm = \pm E_0 \sin(\tan^{-1}(A_1 / B_1)). \quad (4.24)$$

Note that the hysteresis loop in Fig. 4.1 has the average coercive field $(E_c^+ - E_c^-)/2$ is 1.5925 J, 1.5391 J and 3.4367 kV/cm while the average coercive field calculated from Eq. (4.24) is 1.5925 J, 1.5391 J and 3.4594 kV/cm for Ising hysteresis from mean field calculation and Monte Carlo simulation, and BaTiO₃ hysteresis from

Sawyer-Tower experiment, respectively. These therefore confirm that the coercive field depends on amplitude of the electric field and amplitude of the first harmonic of real and imaginary part.

4.3 The relationship between external perturbations parameters and amplitude of Fourier harmonics

After that with the relationship between hysteresis properties and amplitude of Fourier harmonics, the relationship between external perturbations parameters and amplitude of Fourier harmonics that relate to hysteresis properties was investigated e.g.

- The hysteresis area depends on amplitude of the first harmonic of real part in following the relationship by Eq. (4.9).
- The remnant polarization depends on amplitude of odd harmonics of real part in following the relationship by Eq. (4.21).
- The coercive field depends on amplitude of the first harmonics of real and imaginary part in following the relationship by Eq. (4.24).

The relationship between external perturbation parameters and amplitude of these Fourier harmonics may establish some power law scaling relation, leaving a window of opportunities for future investigation.