CHAPTER 3

METHODOLOGY

In this chapter, the research procedure is described in details i.e. the preparation of ferroelectric hysteresis data, the calculation of hysteresis properties and the analysis of these hysteresis behavior by using the fast Fourier transformation.

3.1 Procedure of the research

In the analysis of ferroelectric hysteresis behavior by using the fast Fourier transformation, ferroelectric hysteresis data in response to temperature T and electric field ($E(t) = E_0\sin(2\pi ft)$ where E_0 and f are amplitude and frequency of electric field, respectively) can be obtained from three methods i.e.

- Ising ferroelectric hysteresis data from mean field calculation: the hysteresis was generated at temperature T in the range 0.01 – 5.00 J/k_B, electric field amplitude E_0 in the range 0.01 – 4.00 J and electric field frequency f in the range 0.001 – 8.000 τ^{-1}.
- Ising ferroelectric hysteresis data from Monte Carlo simulation: the hysteresis was generated at temperature T in the range 0.01 – 3.00 J/k_B, electric field amplitude E_0 in the range 0.01 – 4.00 J and electric field frequency f in the range 0.001 – 8.000 mcs^{-1}.
- $BaTiO_3$ ferroelectric hysteresis data from Sawyer-Tower experiment: the hysteresis was measured at temperature T in the range 25 – 170 ºC, electric field amplitude E_0 in the range 0 – 15 kV/cm and electric field frequency f in the range

1 – 100 Hz.

After that, ferroelectric hysteresis properties i.e. hysteresis area, remnant polarization and coercive field were calculated. The polarization signal was then transformed from time domain to frequency domain to extract the Fourier harmonics. Then, the relationship between hysteresis properties and external perturbation parameters associated to each Fourier harmonic were then investigated. After that, the relationship between hysteresis properties and external perturbation parameters was established. The research procedure is shown in Fig. 3.1.

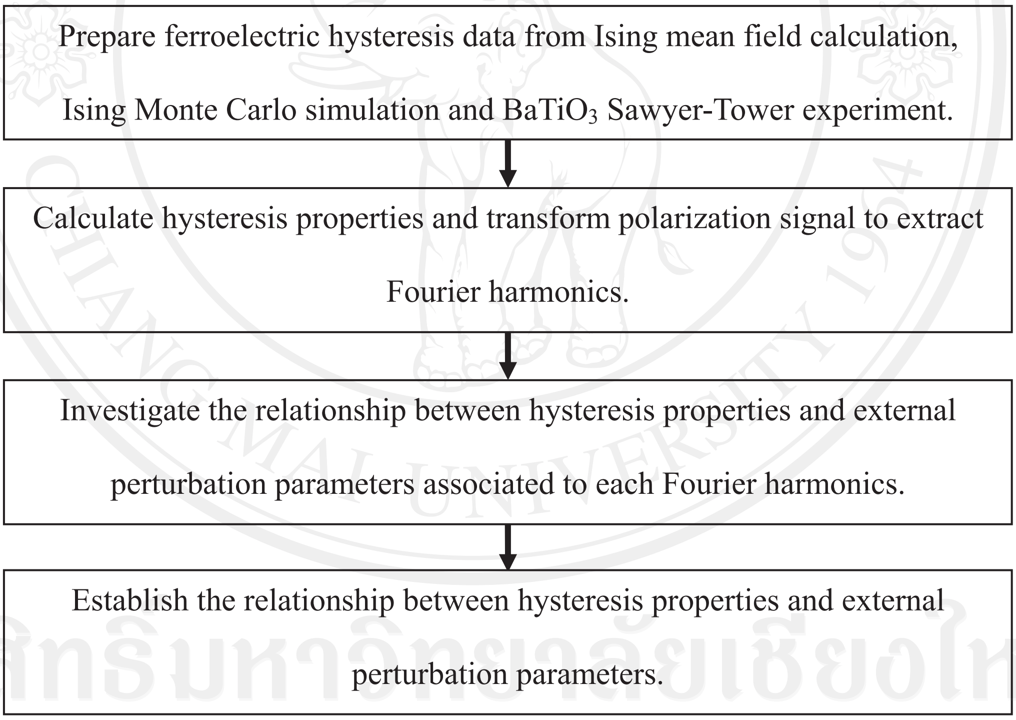

Figure 3.1 The research procedure.

3.2 Ferroelectric hysteresis data

In this work, the ferroelectric hysteresis data was obtained from three methods i.e. Ising ferroelectric hysteresis data from mean field calculation, Ising ferroelectric hysteresis data from Monte Carlo simulation and $BaTiO_3$ ferroelectric hysteresis data from Sawyer-Tower experiment. The procedure is obtaining the hysteresis data from each method can be given as the following.

3.2.1 Mean field calculation

In mean field calculation, Ising ferroelectric hysteresis under the affects of electric field was generated by solving mean field equation, Eq. (2.16), $\tau \frac{dP(t)}{dt} = P(t) + \tanh \frac{1}{k_B T}\left(E(t) + \sum_j J_j P(t) \right)$. Since, mean field equation is the first order differential equation $\frac{dP(t)}{dt} = f(t, P(t))$. It was then solved via the fourth order Runge-Kutta, using initial polarization $P(0) = 1$ and the Runge-Kutta parameters (k_1, k_2, k_3 and k_4) were calculated from

$$k_1 = f(t, P(t)), \tag{3.1}$$

$$k_2 = f\left(t + \frac{\Delta t}{2}, P(t) + \frac{k_1}{2} \right), \tag{3.2}$$

$$k_3 = f\left(t + \frac{\Delta t}{2}, P(t) + \frac{k_2}{2} \right), \tag{3.3}$$

$$k_4 = f(t + \Delta t, P(t) + k_3). \tag{3.4}$$

From these k_1, k_2, k_3 and k_4, polarization at time $t + \Delta t$ was calculated from $P(t + \Delta t) = P(t) + \Delta t\left(\frac{k_1}{6} + \frac{k_2}{3} + \frac{k_3}{3} + \frac{k_4}{6} \right)$. In this mean field calculation, the unit of temperature T is J/k_B, where J is the unit of electric field amplitude of E_0, and the unit of simulation time is 1 τ, so τ^{-1} is unit of electric field frequency f. Further, 1,024 data points was recorded in one period of the hysteresis loop, so polarization was recorded every $\Delta t = 1/(1024f)$ τ. For steady state condition, the hysteresis generation is going on until the hysteresis loop is steady in time which can be observed from the dynamic order parameter i.e.

$$Q(n) = \frac{1}{T}\int_0^T P(t)dt, \tag{3.5}$$

where T is the period of electric field and n is the loop index, is no longer depend on time. In this research, hysteresis is assumed steady when $\Delta Q \leq 10^{-6}$ (to compromise computational rounding error) where after that 1,000 hysteresis loops were recorded and averaged.

3.2.2 Monte Carlo simulation

In Monte Carlo simulation, Ising ferroelectric hysteresis under the effect of external perturbation parameters was generated using initial molecular dipole moments $u_i(0) = \pm 1$. Then, a molecular dipole moment was chosen in random and the probability of a molecular dipole moment flipping $p_i(t)$ was calculated from

$$p_i(t) = \exp\left(\frac{-\Delta H_i(t)}{k_B T}\right). \tag{3.6}$$

In Eq. (3.6), $\Delta H_i(t) = 2u_i(t)\left(E_i(t) + \sum_j u_j(t)\right)$ is the energy difference of a molecular dipole moment flipping. After that, a random number $r \in [0, 1)$ was generated and compared with the probability of a molecular dipole moment flipping. If $r \leq p_i(t)$, a molecular dipole moment $u_i(t)$ is allowed to flip to its opposite direction. Conversely, if $r > p_i(t)$, the flip is rejected. In Mote Carlo simulation, the unit of temperature T is also J/k_B, where J is the unit of electric field amplitude of E_0. Nevertheless, the unit of simulation time is 1 mcs (Monte Carlo steps per site), so

mcs^{-1} is unit of electric field frequency f. Similarity, there are 1,024 data points per period in hysteresis loop, so the polarization was calculated every $\Delta t = N/(1024f)$ mcs from

$$P(t) = \frac{1}{N}\left\langle \sum_{i=1}^{N} u_i(t) \right\rangle, \tag{3.7}$$

where N is the total number of molecular dipole moments. For steady state condition, the first 1,000 hysteresis loops will be discarded and the next 10,000 hysteresis loops will be recorded and averaged.

3.2.3 Sawyer-Tower experiment

In this research, hysteresis data from $BaTiO_3$ bulk ceramics was considered as an application. The ceramics were prepared by a conventional mixed-oxide method having diameter = 8.16 mm, thickness = 1.20 mm and T_c = 124.5 ºC. Its dynamic hysteresis was measured by Sawyer-Tower circuit with electric field signal (sine waveform) generated by a function generator (HP 3310A). The hysteresis loop of each condition (temperature, amplitude and frequency of electric field) was recorded after reaching steady state. Details of the experimental setup were explained elsewhere [6].

However, due to electronic noises, electric field signal may not be perfect sine waveform i.e. electric field data in each time interval is not equal to that of the electric field data of perfect sine waveform even with the same amplitude and frequency. It can be implied that the time intervals between electric field and polarization data tend to vary so the numbers of data points in each loop also vary, and this limits the direct use of Fourier analysis. Additionally, in this research, the fast Fourier transformation was used to transformed polarization data in time domain to frequency domain so the number of data point is required to be a power of two (e.g. N = 1,024 data points per period). Therefore, the hysteresis data (the set of electric field (n, E) and polarization (n, P), Δn are equal) has to be manipulated as the following.

3.2.3.1 Hysteresis data averaging

The polarizations having the same electric field data in each interval of each loop wave averaged because the hysteresis is caused by that polarization signal is out of phase with electric field signal. The electric field and its corresponding polarization data were divided into 3 intervals (see Fig. 3.2) i.e.

- The interval that electric field increases from zero to positive (interval I)
- The interval that electric field decreases from positive to negative (interval II)
- The interval that electric field increases from negative to zero (interval III).

After averaging, the new set of electric field $(n_{averaged}, E_{averaged})$ and polarization $(n_{averaged}, P_{averaged})$ data in one period were drawn, where $N_{averaged}$ is the number of data points per period after averaging that may unequal to $N/2$ but $\Delta n_{averaged}$ between data points are equal.

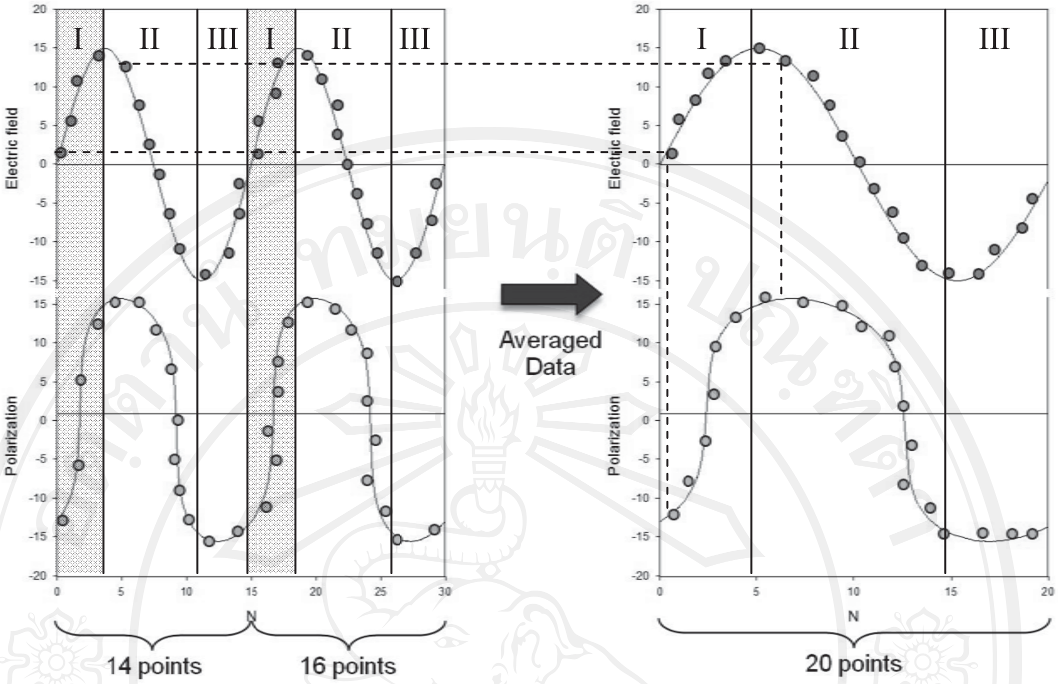

Figure 3.2 The averaging of polarizations having the same electric field data obtained from many hysteresis loops where the target number of data points per period is N = 32.

3.2.3.2 Hysteresis data arranging

The electric field and its corresponding polarization data were arranged relative to the perfect sine waveform having the same electric field amplitude and frequency (see Fig. 3.3) i.e.

$$n = \begin{cases} \dfrac{N}{2\pi}\sin^{-1}\left(\dfrac{E}{E_0}\right) & \text{for interval I} \\ \dfrac{N}{2}\left(1-\dfrac{1}{\pi}\sin^{-1}\left(\dfrac{E}{E_0}\right)\right) & \text{for interval III} \\ N\left(1+\dfrac{1}{2\pi}\sin^{-1}\left(\dfrac{E}{E_0}\right)\right) & \text{for interval III.} \end{cases} \quad (3.8)$$

From Eq. (3.8), the two sets of electric field $(n_{arranged}, E_{arranged})$ and polarization $(n_{arranged}, P_{arranged})$ data were redrawn, where $N_{arranged}$ is the number of data points per period after arranging that equal to $N_{averaged}$ where $\Delta n_{arranged}$ between data points may not be equal at this stage.

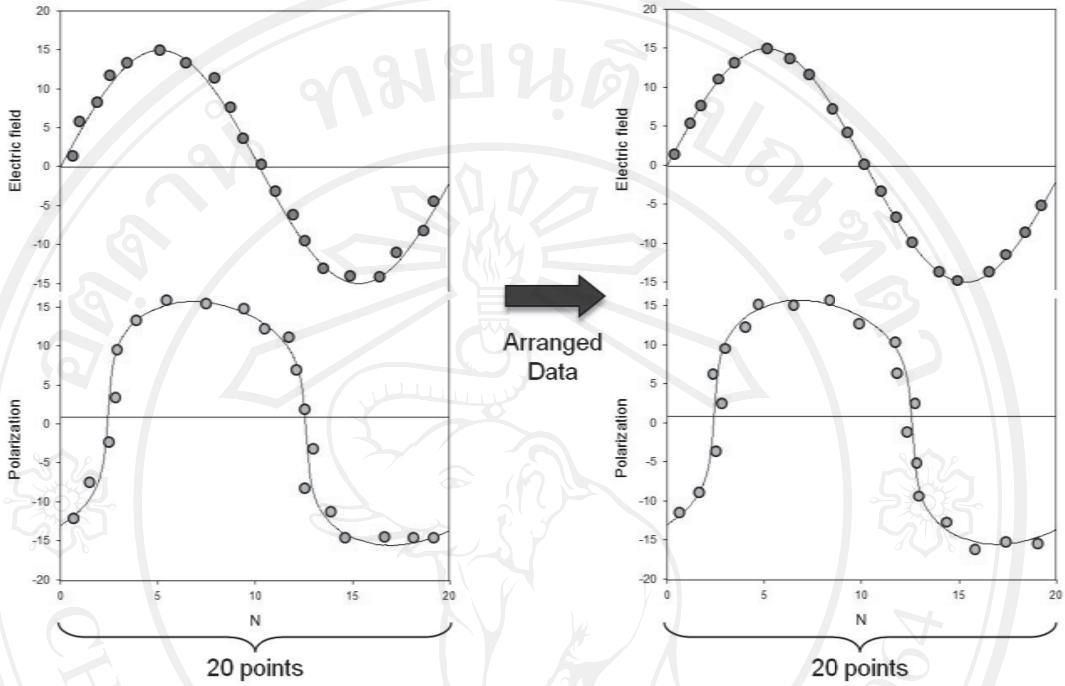

Figure 3.3 The arranging of electric field and it corresponding polarization data relative to the perfect sine waveform having the same electric field amplitude and frequency where the target number of data points per period is $N = 32$.

3.2.3.3 Hysteresis data smoothing

The polarization data were then smoothed using the Loess smoothing method [31, 32] to adjust polarization data as fluctuation from a perfect sine waveform have strong effect to electric field and its corresponding polarization data interpolation (see Fig. 3.4). After smoothing, the new set of electric field $(n_{smoothed}, E_{smoothed})$ and polarization $(n_{smoothed}, P_{smoothed})$ data in one period were again drawn, where $N_{smoothed}$ is the number of data points per period after smoothing that equal to $N_{arranged}$ and $\Delta n_{smoothed}$ between data points are still not equal.

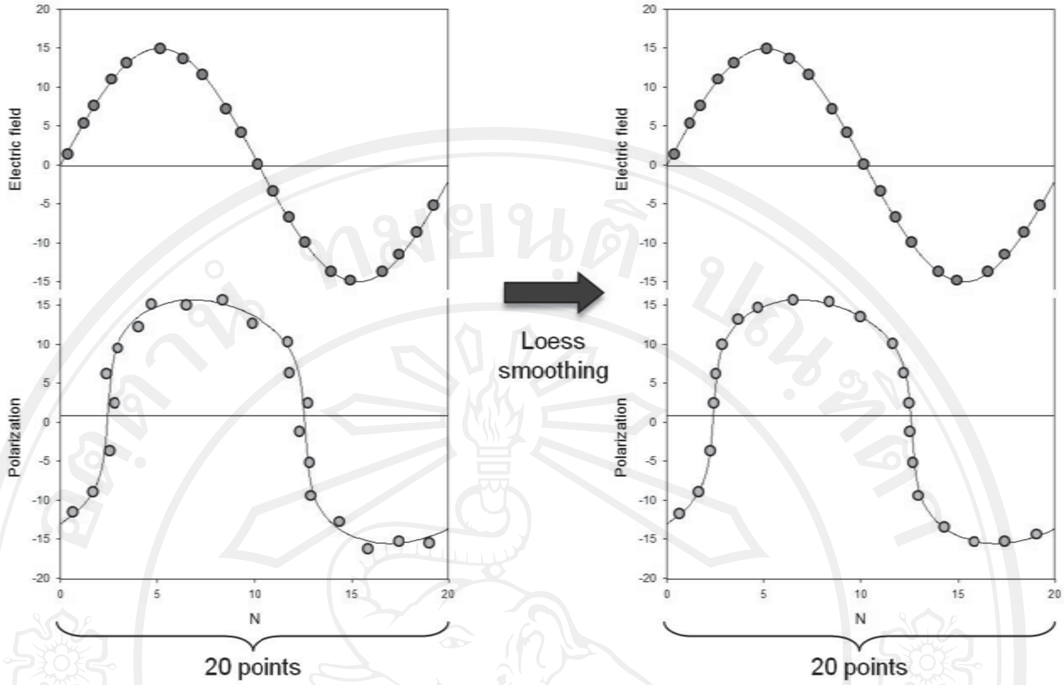

Figure 3.4 The Loess smoothing of polarization data where the target number of data points per period is $N = 32$.

3.2.3.4 Hysteresis data interpolation

The electric field and its corresponding polarization data were then interpolated using Cubic spine interpolation [33] to form the perfect sine waveform having the same electric field amplitude and frequency with equal time intervals among data points (see Fig. 3.5). After interpolation, the new set of electric field $(n_{interpolated}, E_{interpolated})$ and polarization $(n_{interpolated}, P_{interpolated})$ data in one period were ready for Fourier analysis, where $N_{interpolated}$ is the number of data points per period after interpolation that equal to power of two (1,024 data points per period) and $\Delta n_{interpolated}$ between data is finally equal.

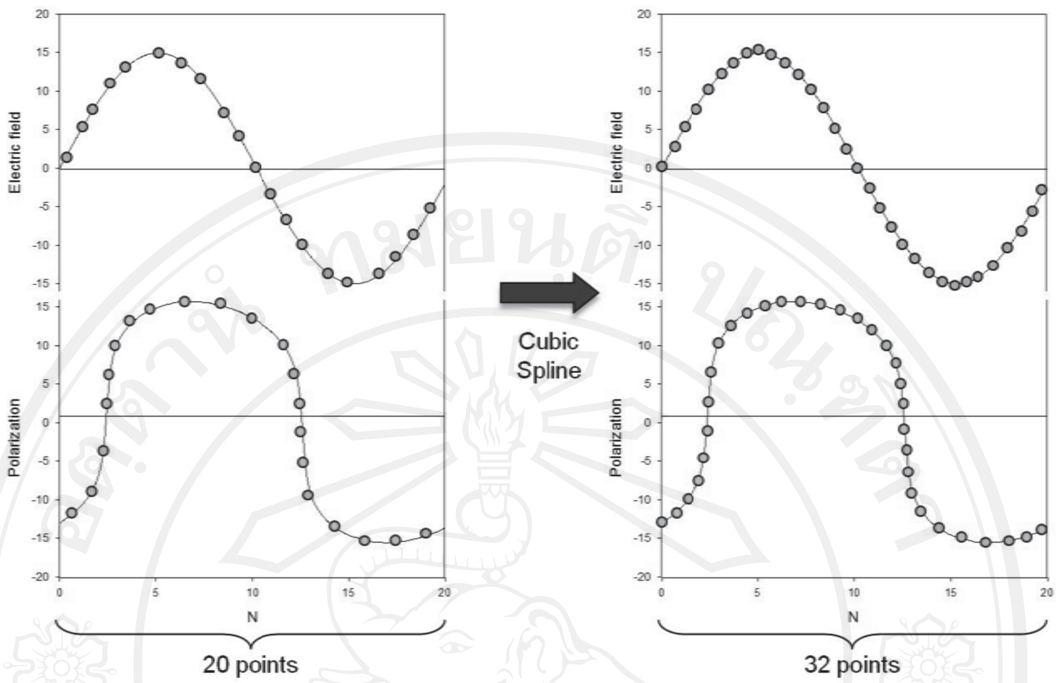

Figure 3.5 The Cubic spine interpolation of electric field and its corresponding polarization data where the target number of data points per period is $N = 32$.

After ferroelectric hysteresis data modifying, the electric field and its corresponding polarization having equal time intervals and the number of data points period equal to 1,024 (power of two), were paned to the Fourier analysis.

3.3 Ferroelectric hysteresis properties

With the modified ferroelectric hysteresis data, the hysteresis properties i.e. hysteresis data, remnant polarization and coercive field were then extracted using the following method.

3.3.1 Hysteresis area

Hysteresis area refers to the external energy requires to cycle the molecular dipole moments in ferroelectric materials, which can be calculated from $A = \oint PdE$, where E is the electric field signal and P is the polarization signal. Since, the obtained ferroelectric hysteresis is discrete data. Hysteresis area can then be found from the sum of small trapezoid area between electric field data points, the so called trapezoidal integration. Therefore, the hysteresis area is given by

$$A = \frac{1}{2}\sum_{i=1}^{N-1}\left(P_{i+1} + P_i\right)\left(E_{i+1} - E_i\right), \tag{3.9}$$

or

$$A = \frac{\Delta E}{2}\sum_{i=1}^{N-1}\left(P_{i+1} + P_i\right), \tag{3.10}$$

where P_{i+1} and P_i are the lengths of the parallel sides and $\Delta E = E_{i+1} - E_i$ is the width of the trapezoid.

3.3.2 Remnant polarization

Remnant polarization is the magnitude of polarization that remains is the vanishing of the electric field in ferroelectric materials. It can be calculated by using linear approximation at where a sign of electric field changes. The positive remnant polarization P_r^+ is therefore given by

$$P_r^+ = P_{above}^+ - E_{above}^+\left(\frac{P_{above}^+ - P_{below}^+}{E_{above}^+ - E_{below}^+}\right), \tag{3.11}$$

where P_{above}^+ and P_{below}^+ are positive polarizations above and below P_r^+ corresponding to the electric fields E_{above}^+ and E_{below}^+ (with $E_{above}^+ E_{below}^+ \leq 0$), respectively. The negative remnant polarization P_r^- is then given by

$$P_r^- = P_{above}^- - E_{above}^-\left(\frac{P_{above}^- - P_{below}^-}{E_{above}^- - E_{below}^-}\right), \tag{3.12}$$

where P_{above}^- and P_{below}^- are negative polarizations above and below P_r^- corresponding to the electric fields E^-_{above} and E^-_{below} (with $E^-_{above}\, E^-_{below} \le 0$), respectively.

3.3.3 Coercive field

Coercive field is the magnitude of electric field in the opposite direction required to cancel polarization in ferroelectric materials. Similarly, it can be calculated by using linear approximation at where the sign of polarization change. Therefore, the positive coercive field E^+_c is given by

$$E^+_c = E^+_{above} - P^+_{above}\left(\frac{E^+_{above} - E^+_{below}}{P^+_{above} - P^+_{below}}\right), \tag{3.13}$$

where E^+_{above} and E^+_{below} are positive electric fields above and below E^+_c corresponding to the polarizations P^+_{above} and P^+_{below} (with $P^+_{above}\, E^+_{below} \le 0$), respectively. On the other hand, the negative coercive field E^-_c is given by

$$E^-_c = E^-_{above} - P^-_{above}\left(\frac{E^-_{above} - E^-_{below}}{P^-_{above} - P^-_{below}}\right), \tag{3.14}$$

where E^-_{above} and E^-_{below} are negative electric fields above and below E^-_c corresponding to the polarizations P^-_{above} and P^-_{below} (with $P^-_{above}\, P^-_{below} \le 0$), respectively.

3.4 Fourier analysis of ferroelectric hysteresis

After that with the obtained ferroelectric hysteresis data and their properties, the fast Fourier transformation was used to transform polarization data from time domain (n) to frequency domain (k) i.e.

$$F(k) = \sum_{n=0}^{N-1} f(n)\exp(-i2\pi nk/N). \tag{3.15}$$

Since, exp(-$i\theta$) = cos(θ) - $i$sin(θ), it is found that

$$F(k) = \sum_{n=0}^{N-1} f(n)\cos(2\pi nk / N) - i\sum_{n=0}^{N-1} f(n)\sin(2\pi nk / N). \tag{3.16}$$

In Eq. (3.16), the cosine term is the amplitude of k^{th} harmonic of the real part (A_k) and the sine term is the amplitude of k^{th} harmonic of the imaginary part (B_k) i.e. $F(k) = A_k + iB_k$, where N is the total number of data points per period. The Fourier harmonics of real and imaginary parts can be extracted from this transformation. Then, polarization re-calculated from inverse Fourier transformation of each harmonic of real and imaginary parts were use to relate the Fourier coefficients to the hysteresis properties. The relationship between hysteresis properties and external perturbation parameters to these Fourier coefficients were then elaborated where the relationship between hysteresis properties and external perturbation parameters will be proposed in the next chapter.