Landau-Khalatnikov Modified Model for Predicting ZnO Ferroelectric Properties

Septian Rahmat Adnan

Faculty of Engineering, Universitas Esa Unggul, Jl. Arjuna Utara, Jakarta 11510, Indonesia

Corresponding author: septian.rahmat@esaunggul.ac.id

Abstract. The Dynamic Landau-Khalatnikov (LK) model was modified to calculate polarization hysteresis curve for Zinc Oxide (ZnO) material. Ferroelectric polarization hysteresis of Zinc Oxide (ZnO) were measured by using Sawyer-Tower circuit. Landau Khalatnikov modified model was fitted to experimental data. R-Weighted Pattern (Rwp) factor was used to evaluate the precision of the model compare to experimental data. The results showed that the modified model is in a good precision compare to experimental data with Rwp< 10%.

Keywords : Landau-Devonshire, ZnO, Ferroelectric

INTRODUCTION

The structure of Zinc oxide (ZnO) nanostructures have great potential for applications such as, nano generator, nano sensor, nano storage, and nano memory devices [1−3].due to their unique properties such as optical, electrical, piezoelectric, and ferroelectric-like properties. Gupta and his colleagues showed the existence of enhanced ferroelectricity in V-doped ZnO nanorods at room temperature by using Sawyer−Tower hysteresis bridge, which paved the way for the application as ferroelectric random access memories (FeRAMs) [4]. Ghosh et al. also showed the ferroelectricity in undoped ZnO nano rods and proposed that zinc interstitial defects might be attributed to the existence of ferroelectricity[4].The Ferroelectric properties of materials have been studied theoriticaly or experimentally. The theory of Landau-Devonshire (LD) has been used by many researcher to predict the ferrolectric properties of materials [5,6,7,9,10,11,12]. The theory of Landau-khalatnikov is dynamic theory of Landau theory.

In the present paper, polarization hysteresis (P-E) data of ZnO were obtained from Experimental. It was measured by using Sawyer –Towyer circuit. The Landau - Khalatnikov (LK) model was modified by adding some factor such as scale factor, amplitude and frequency for predicting polarization properties of ZnO[6-12].The differential partial equation of LK model was solved using Runge Kutta Orde 4 on Delphi 6[11,12,14]. The modified theory were compare to experimental data. By adopting Rietvield analysis on General Structure Analysis System (GSAS), R-Weigthed Pattern (Rwp) was calculated to evaluate the precision of the model compare to experimental data[13].

The 6th International Conference on Science & Engineering in Mathematics, Chemistry and Physics
AIP Conf. Proc. 2043, 020007-1–020007-6; https://doi.org/10.1063/1.5080026
Published by AIP Publishing. 978-0-7354-1769-4/$30.00

EXPERIMENTAL PROCEDURE AND SIMULATION

modified theory were compare to experimental data. By adopting Rietvield analysis on General Structure Analysis System (GSAS), R-Weigthed Pattern (Rwp) was calculated to evaluate the precision of the model compare to experimental data[13]. Zinc acetate dehydrates were procured from Aldrich company. Powder ZnO materials were prepared by sol-gel method. The ZnO solutions were prepared by mixing zinc acetate dehydrates in double distilled water and 2-propanol with a volume ratio 1:1. The aqueous solution was kept in a magnetic stirrer while heating at 70oC until become gel. Then the gel was heating at 600 °C for 2 hours to become powder. The powder were compacted with pressure 5 kPa and in cylinder form with diameter 1 cm and thickness 0.3 mm. Hysteresis of Polarization (P-E) was measured by using Sawyer – Tower circuit. Experimental data were compared to model by changing the parameter of the models

SIMULATION

The investigation phenomenaof Free energy of Zinc Oxide (ZnO) material could be calculated by using Landau-Devonshire Theory (LD) [6-10]:

$$F(P,E) = F_0 + \frac{\alpha(T-T_c)}{2}P^2 - \frac{\beta}{4}P^4 + \frac{1}{6}P^6 - EP \tag{1}$$

Where T is temperature of sample and in this work we assumed it was at room temperature, Tc is Currie Temperature and F0 is Free energy on paraelectric phase. E is electric field which applied on sample and P is polarization. Hence the equation 1 can be rewritten as [11] :

$$F = \frac{\alpha}{2}P^2 - \frac{\beta}{4}P^4 + \frac{1}{6}P^6 - EP \tag{2}$$

Dipole polarization on Zinc Oxide (ZnO) material can be explained by using dynamic model of Landau - Khalatnikov (LK), which is a differential partial equation shown in eq 3[11].

$$\gamma\frac{dP}{dt} = -\frac{\partial F}{\partial P} \tag{3}$$

where γ is constant and F is Free energy of material. The relation between the free energy as function of its polarization can be drawn using the Eq.2 to get its behavior. This equation, therefore [11] :

$$\gamma\frac{dP}{dt} = -\alpha P + \beta P^3 - P^5 + E \tag{4}$$

where α and β is Landau coefficient which calculated with experimental data, and E is Electric field that is applied on materials , the value of α and β could be calculated from experimental data as Eq. 4and Eq. 5. Electric field is a function of frequency and it could be rewritten as eq. 7.

$$\alpha = \beta P_s^2 \tag{5}$$

$$\beta = \frac{3\sqrt{3}E_C}{2P_s^3} \tag{6}$$

$$\gamma \frac{dP}{dt} = -\alpha P + \beta P^3 - P^5 + E_0 Sin\omega t \tag{7}$$

Where E_c is coercive electric field, P_s is spontaneous Polarization, E_0 is amplitude of applied electric field, w is frequency and $E = V/t$ where t is thickness of material. The solution of Eq. 7 can be solved using Runge-Kutta orde 4. The result of the model then evaluated with experiment data. Similar to analysis method for powder diffraction on General Structure Analysis System (GSAS), R-Weighted Pattern (Rwp) was calculated to evaluate agreement between model and experiment result, R-Weighted Pattern (Rwp) the shown in eq. 8[11].

$$R_{wp} = \left[\frac{\sum_{i=1}^{n} \left(P_{\exp} - P_{\text{mod}}\right)^2}{\sum_{i=1}^{n} P_{\exp}^2} \right] \times 100\% \tag{8}$$

where Pexp is experiment result and Pmodel is model result of Polarization. Some of the variables are frequency (w), Electric Field Amplitude (E0) and Scale Factor (Sf) then adjust to see the influence [11,12]. The calculation is performed by Delphi running program on Windows. We used Delphi program for calculation and performed graphic based routine to me easier for visual analysis. Flow chat calculation is shown in fig 1.

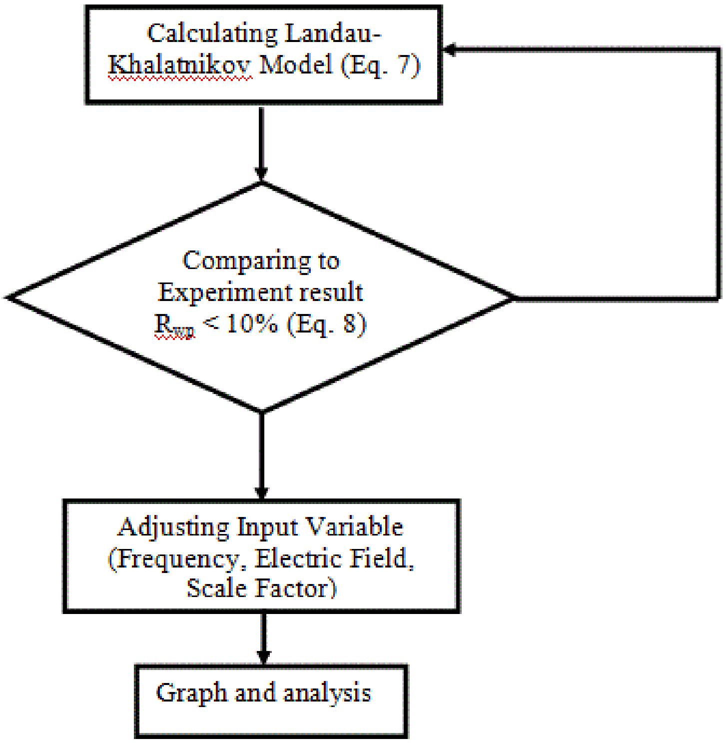

FIGURE 1. Simulation Method

RESULT AND DISCUSSION

Hysteresis curve model using LK model and ZnO experiment were shown in figure 2 and figure 3. To fitting the model to the experimental results, frequency (with constant amplitude) or amplitude (with constant frequency) were varied until the curve as close as possible. R-weighted Pattern (Rwp) were used to evaluate the agreement between model and experiment. Figure 2 show the curve of the model with different frequency (with constant amplitude) and the experiment and Table 1 show polarization and coercive electric field calculation with different frequency. If Rwp is less than 10%, the models satisfy with the experiment data [6,7,11,12].

Figure 2.Hysteresis curve Model with variation of frequency and Experiment result of ZnO with constant amplitude 100 kV/m

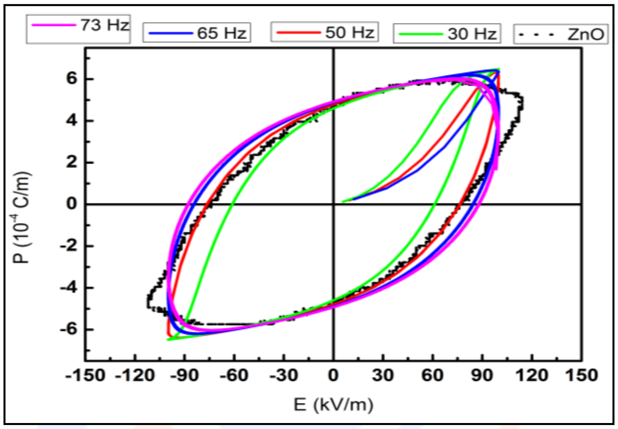

FIGURE 2. Hysteresis curve Model with variation of frequency and Experiment result of ZnO with constant amplitude 100 kV/m

TABLE 1. Polarization and Coercive Electric Field Result at Various Frequencies and constant amplitude 100 kV/m

Material ZnO	**Saturated Polarization (Ps) x10^{-4} (C/m^2)**	**Remanent Polarization (Pr) x10^{-4} (C/m^2)**	**Coercive Electric Field (Ec) (kV/m)**	**R_{wp}**
Experiment	6.0	4.5	70	-
Model at 30 Hz	6.2	4.3	60	3.47
Model at 50 Hz	6.2	4.6	70	3.12
Model at 65 Hz	6.0	4.8	88	3.68
Model at 73 Hz	5.8	4.85	90	5.97

Table 1 show that saturated polarization and remanent polarization are almost the same value [5-6]. But coercive electric field are influenced markly by frequency. From simulation, the value of R_{wp} are less than 10%, it could be concluded that the model are in a good agreement with the experiment. But among the model, for frequency 50 Hz and amplitude 100 kV/m, the value of R_{wp} is the smallest one. Table 2 show landau coefficient for different frequency and constant amplitude 100 kV/m. From equation 5 and 6, it show that the landau coefficient depend on coercive electric field. The value of α and β are optimum at frequency 65 Hz.

Table 2. Landau Coefficient (α and β)

Materials and Model	Result	
	α (V/m) x10^7	β(m/F) x 10^{10}
ZnO	235.69	6.54
Model at 30 Hz	230.40	5.98
Model at 50 Hz	268.730	6.99
Model at 65 Hz	296.305	8.23
Model at 73 Hz	264.610	7.86

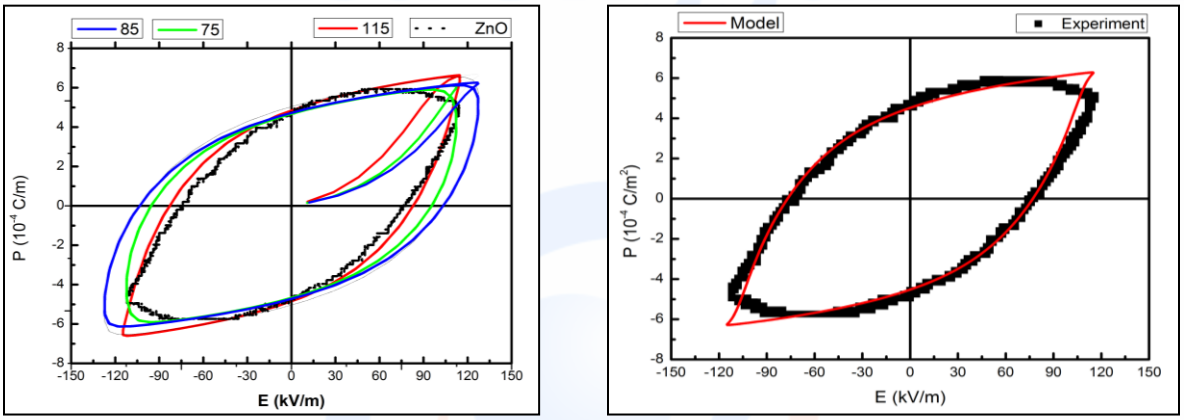

FIGURE 3. (a) Hysteresis curve Model with variation of Amplitude and Experiment result of ZnO (b) Landau-Khalatnikov (red line) Model and Experiment polarization Hysteresis curve (black dash line) of ZnO

Table 3. Polarization and Coercive Electric Field Result at Various Electric Field Amplitudes (E_0) and constant frequency 50 Hz

Material ZnO	Saturated Polarization (Ps) x10^{-4} (C/m^2)	Remanent Polarization (Pr) x10^{-4} (C/m^2)	Coercive Electric Field (Ec) (kV/m)	R_{wp}
Experiment	5.12	4.9	75	-
Model (E_0 = 75 kV/m)	5.3	4.89	103	3.55
Model (E_0 = 85 kV/m)	6.0	4.93	115	3.60
Model (E_0 = 100 kV/m)	6.2	4.6	70	3.12
Model (E_0 = 115 kV/m)	7.1	4.93	88	3.73

It can be explained that increasing amplitude increase the energy to polarize the dipole. However, an increasing frequency do not influence the value of remanent polarization (P_r) because it's characteristic value of each materials [6-7]. Figure 3 (b) show the hysteresis curve of the optimum model (f = 50 Hz and E_0 = 100 kV/m) and the experiment. It show that modified model propose in this paper is a one good model. In the future we will further examine the behaviour of ZnO using Landau-Khalatnikov (LK) by adding more variable such as atomic position and type of input wave signal and also use quantitative model by Miller *et al* and dipole polarization model by J. Yu *et al* as comparison to develop the new model.

CONCLUSION

From calculation using Landau - Khalatnikov (LK) dynamic model for ZnO, we obtained R-Weighted Pattern (R_{wp}) model for ZnO is less than 10% and statistically the results have the smallest and acceptable error. Frequency and amplitude parameter involved in the model have significant influence on the model to fitting with the experiment data.

REFERENCES

1. M. Joseph, H. Tabata, T. Kawai, Appl.Phys. Lett. Vol. 74 pp 2534−2536 (1999).
2. Ö zgür Ü, Y. I. Alivov, C. Liu, A. Teke, M. Reshchikov, S. Doğan, V. Avrutin , S. J. Cho, H. Morkoc, J. Appl. Phys. Vol. 98 041301(2005).
3. I. C. Yao, D.Y. Lee, T. Y. Tseng, P. Lin, Nanotechnology Vol 23 145201 (2012).
4. M. Ghosh, G. M. Rao, Adv. Mater. Vol. 5 pp 733−739 (2013).
5. H. H. Wu, S. G. Cao, J. M. Zhu, T. Y. Zhang, Act. Mechanica Vol 228 pp 811-2817 (2017).
6. M. H. Kuok, S. C. Ng, H. J. Fan, M. Iwata,Y. Ishibashi, Y, Solid State Comm. Vol 118 pp 169-172(2001).
7. L. Cui, Z. Qiu, Z, Han, R. Li, J. Che, Adv. Mater. Research Vol 936 pp 269-275 (2014).
8. J. F. Scott, ISRN Materials Science p 1(2013).
9. A. F. Devonshire, Advance in Phys Vol 3:10 pp 85-130 (1954)
10. C. B. Sawyer and C. H. Tower, Phys Rev pp 35 (1930).
11. T. K. Song. J. Korean Phys. Society Vol 46 pp 5-9 (2005).
12. M. Hikam and S.R. Adnan, J. Phys.: Conf. Ser pp 012008 (2014).
13. Young A. G (Ed.)1993 The Rietveld Method. (Oxford : Oxford University Press)
14. M. Hikam, S. R. Adnan, B. Soegijono, A. Sudarmaji, G. Sanhaji and L. Husein ZT, Spektra Vol 15 pp 2 (2014).