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Growth of Glycine Barium Nitrate (GBN) Crystal via Slow Evaporation Method Accompanied by the Application of External Electric Field

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Abstract

Glycine Barium Nitrate (GBN) crystals were grown by slow evaporation method accompanied by the application of an external electric field. The application of external electric field in crystal growth system is expected to align local dipole moments, therefore, it could be expected that it will increase the quality of the grown single crystal. GBN crystals were grown from their saturated solution with slow evaporation method in Pyrex glass tube that was connected with a high voltage power supply (15 kV). Crystal grew over a span of 16-28 days at 50 ^oC with a variation of electric field 0-5 kV/cm. Grown GBN single crystals has tr apezoid-shaped, with an typical dimension of 5x4x3 mm^3. GBN crystals grown with various electric field were characterized with X-Ray powder diffraction method and it was found that higher electric field can cause GBN diffraction peaks shifting to lower 2θ. GBN adopt orthorhombic crystal lattice with space group $P2_12_12_1$. Refinement analysis have been carried out with Le Bail Method using Fullprof program. Results of refinement indicated that lattice parameter a become longer, while b and c decreases along with the increasing of electric field application. The crystal lattice parameter a for GBN 0 kV / cm, 1 kV / cm, 2 kV / cm, 3 kV / cm, 4 kV / cm and 5 kV / cm are 8,2328 (3) Å; 8,2510 (2) Å; 8,2557 (1) Å; 8,2571 (1) Å; 8,2623 (2) Å; and 8,2574 (2) Å respectively, while the lattice parameter b and c were decreased as applied electric field increased.

Keywords: *Slow Evaporation; Glycine Barium Nitrate; Crystal*

INTRODUCTION

Non-linear optical material (NLO) is the latest field of research in science and technology that is known to be applicable in the fields of telecommunications, optical information, and optical storage media. One of the materials that has been developed is semi-organic compounds. The semi-organic compounds refers to amino acid salts. Crystals from amino acids have non-linear optical properties, one of which is Second Harmonic Generation (SHG). One of the amino acids that can form salt is glycine. Much research has been done on the growth of crystalline glycine salts. One of the newly developed is Glycine Barium Nitrate (GBN)[1]. The advantages of GBN crystals as NLO material include (1) high laser damage thresholds; (2) good optical transparency; and (3) the presence of inorganic elements (Ba^{2+} and NO^{3-}) can increase the NLO properties of the crystals, which will result in high SHG efficiency [2]. In order for this material to show optimum non-linear optical properties, the

crystal must be highly ordered. However, growing larger, better quality and highly ordered crystals are very difficult.

Crystallization is one of the purification processes and taking results in solid form. Recently, crystallization is a very important industrial process, because more chemical products are marketed in crystal form. Crystal forms are increasingly in demand because of their high purity, with attractive shapes and easy packing and transportation. Crystallization is a solid particle formation in a homogeneous phase. Crystallization of a solution is a very important process because there are various types of materials marketed in crystalline form. In general, the purpose of crystallization is to obtain high purity products and with a high level of yield. In order to harvesting crystals with high purity, the right technique is needed.

There are several crystal growth techniques that allow to produce highly ordered crystal. Growing crystals from the seeds obtained from the recrystallization process and slow evaporation techniques for three days was successfully carried out by Robert [3]. Growing crystals without seeds by giving ultrasonic power to saturated solutions and crystals obtained separated by vacuum filtration has been reported by Sayan [4]. One technique that is relatively easy is the slow evaporation method. In this technique the saturated solution of the crystallized compound is evaporated at low temperatures until the desired crystal is obtained. The principle of this technique is regulating the rate of evaporation and heating assistance.

Crystals that can be grown with slow evaporation method include crystals of ionic compounds that are easy to make its saturated solutions. On GBN there is a local dipole moment due to the presence of two types of charge in the zwitter ion: $^{+}$NH3 and COO^{-}. The local dipole moment will affect the polarization properties of a material, thus contributing to the quality of the material applied in the electro-optical field. The direction of polarization from a previously random local dipole moment can be uniformed by adding an external electric field into the material [5, 6].

In this research, the effect of applied external electric field toward the grown crystal parameters was studied. GBN crystals are grown with a slow evaporation method accompanied by the application of an external electric field to the crystal growth system. The crystals that were successfully grown then were characterized by powder X-Ray Diffraction (XRD) instrumentation and Scanning Electron Microscopy (SEM) as the morphology study

stage. The crystal parameters were refined using refinement software *Fulprof*, then the correlation between the values of electric field toward crystal parameters were analyzed.

EXPERIMENT AND METHODS

A. Materials

The equipment used in this research were a set of customized 30 mL Pyrex glass tubes along with its cover as a place of crystal growth, high voltage power supply (DC 15 kV), stainless steel electrodes, 100x100 mm customized Teflon insulator, glassware, magnetic stirrer, analytical balance, Fischer oven, Bruker Powder XRD instrumentation, and Phillips Scanning Electron Microscopy (SEM). All reagents used in this study were analytic grades and were used without any further refining in the whole process. Deionized water also used in the preparation of all solutions.

B. Procedure

a. Saturated Solution of Glycine Barium Nitrate (GBN)

Making a saturated solution of GBN is done by dissolving 3,375 grams of Glycine (H_2NCH_2COOH) and 11,755 grams of Barium Nitrate ($Ba(NO_3)_2$ respectively in 50 mL aqua dm as a solvent (molar ratio 1: 1). The solution is stirred using a magnetic stirrer for 6 hours. The solution was made under ambient temperature conditions, so that a saturated solution of GBN was obtained.

b. The Growth of GBN Crystals

The GBN saturated solution is poured into customized glass tube that has been made before. The glass tube is closed by leaving a small gap so that evaporation can occur slowly. Furthermore, a glass tube that already contains a GBN saturated solution is attached to a customized 100x100 mm Teflon plate that has a stainless steel electrode attached inside and connected to a high-voltage power supply. This power supply is capable of producing varying electrical voltages (0-15 kV). This crystal growth set is inserted into the oven with temperature setting at 50^oC. If the evaporation rate is faster than the crystal growth rate, then the saturated solution is added again until the macro-size crystal is obtained. The growth of GBN crystals in this way is repeated for growth with the application of 1-5kV / cm external electric field.

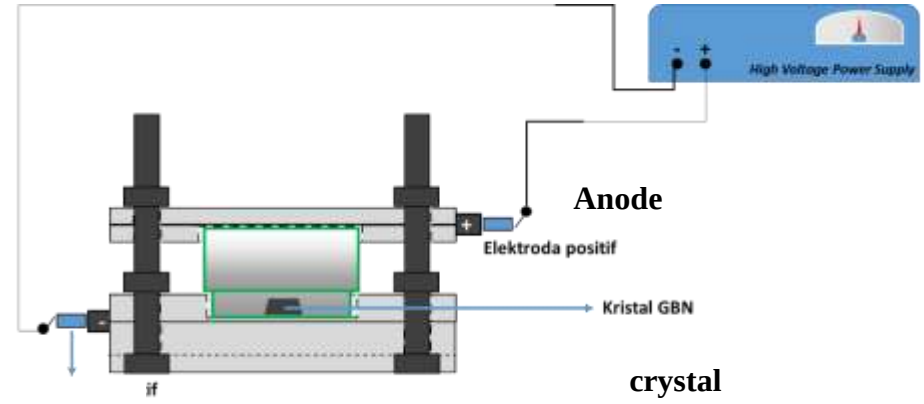


Figure 1. The GBN's Crystal Growth Scheme

c. Characterization

Crystals that have been successfully grown are seen through a microscope through 10 times of magnification to confirm its shape and size. Some of the crystals harvested via various external electric field application were crushed with mortar and pestle until its homogeneous in size and each of them were characterized by XRD-powder Instrumentation to determine its structure and crystallinity. The structural parameters are then analyzed using Fulprof Refinement Software using Le Bail Method. GBN crystals that grown without electric fields was characterized by SEM to confirm the morphological surface of the crystals.

RESULT AND DISCUSSION

A. The Growth of GBN Crystal

GBN crystals were successfully grown with variations electric field applied. The six types of crystals were grown from saturated solutions in turns, with 30 mL volume of each at 50^{o}C. Then the solution was left until the remaining solution is half and gradually added by saturated solution of GBN as much as 5-10 mL dropwise. This step was done because the solvent's evaporation rate in the saturated solution of GBN is faster than the crystal's growth itself. On GBN crystal growth, the higher application of the electric field, the evaporation time of the solvent was faster. This relationship can be seen in Table 1 and Figure 2.

Table 2 Growth of GBN Crystal in Influence of Electric Field Variation

Crystal	Applied Electric Field (kV/cm)	Evaporation Timespan (days)	Evaporation rates (mL/day)	Dimension (mm)
GBN	0	27	1,16	5x4x1
GBN-1	1	25	1,25	5x5x2
GBN-2	2	23	1,36	4x4x2
GBN-3	3	20	1,57	5x4x3
GBN-4	4	15	2,09	5x4x2
GBN-5	5	13	2,41	5x5x3

This result is interesting to be explored further. It is well known that water as a universal solvent has hydrogen bonds between its molecules. This hydrogen bond causes water to have a high boiling point (100^oC, P = 1 atm). Likewise with evaporation, water requires relatively long timespan to evaporate without the aid of heat, or heating with low temperatures (50^oC). However, with the presence of an external electric field, the evaporation span of water at the same temperature turns out to be shorter. This is probably due to the presence of an increasingly strong electric field causing the hydrogen bonds between water molecules to be disrupted. That is, without the presence of an electric field, the hydrogen bonds between water molecules form a multi-layered tetrahedral formation, so that strong hydrogen bonds between water molecules become the same in all directions. This phenomenon implicates that high amount of energy was needed to break the attraction that tends to strengthen each other. When an external electric field is applied, the tetrahedral formation between water molecules changes according to the direction of the field which causes the formation of water molecules to tend to be nematic. This effect causes the hydrogen bonds between water molecules tend to be oriented only along the direction of the electric field. The collective hydrogen bond between water molecules that is only oriented towards the field direction will weaken so that with a little help from the heating element (50^oC) the water becomes more volatile. Another possible explanation is the change of entropy (ΔS) involved in the water evaporation process. The presence of an external electric field causes a change in entropy in the water evaporation process increased, in which results that water become more volatile relatively at low heating temperatures (50^oC).

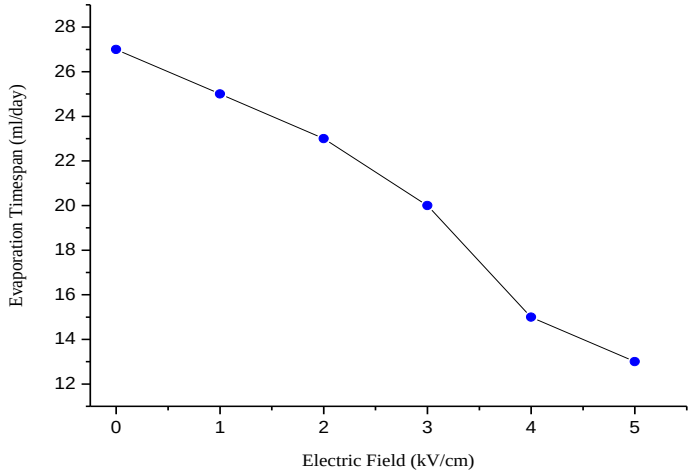
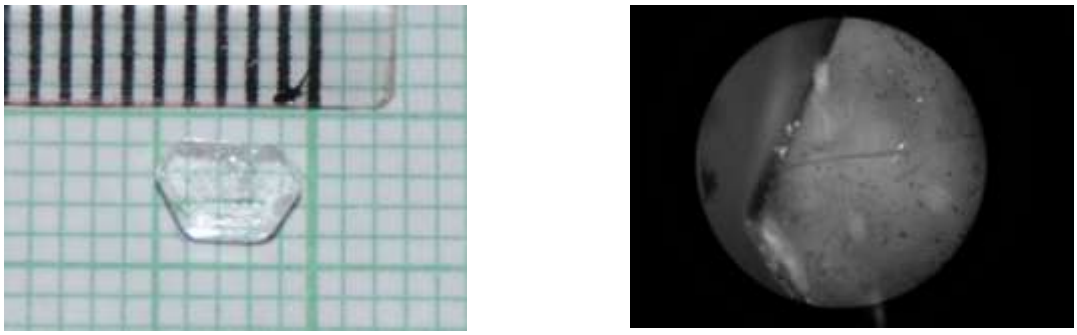


Figure 2 The Relationship between external electric field application toward solvent evaporation span on the growth of GBN crystal

The grown GBN crystal's dimensions are around 5x4x3 mm^3. In GBN crystals, growth was dominant in (231) plane. The appearance of GBN crystals and its magnification using a microscope and SEM can be seen in **Figure 2** and **3**.



(a) *(b)*

Figure 3 The appearance of (a) GBN crystal); (b) 10 x magnification of GBN crystal's edge

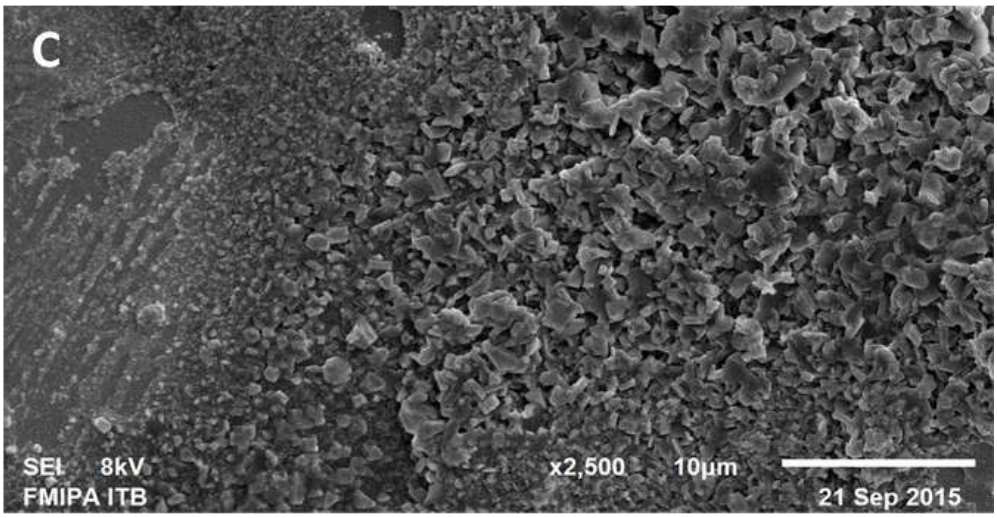


Figure 4 SEM Morphological Image Of GBN Crystal At 2500 X Magnification

In Figures 3 (a) and (b), the GBN crystal evenly surface is macroscopically visible, but when enlarged using SEM with 2500x magnification (Figure 4), there is both diffused and evenly surfaced morphology seen. This is probably the effect of the humidity of the crystal growing environment which causes crystal growth to experience defects on the outside. High humidity affects the equilibrium of transporting anionic-cationic species in the solution to the crystal surface by diffusion progressively faster. This causes the crystal growth rate to be high. A high crystal growth rate causes anionic-cationic species to not have enough time to organize themselves properly. This is what causes the crystal surface to become uneven [8, 12].

B. GBN Crystal XRD Analysis

GBN crystals are grown with a variety of external electric field applications, namely 0 kV / cm, 1 kV / cm, 2 kV / cm, 3 kV / cm, 4 kV / cm, and 5 kV / cm. Then each crystal is grinded homogeneously then characterized using powder XRD instruments with Cu-Kα radiation (λ = 1.54056 Å). Measurements were made from diffraction angle (2θ) between 0^o to 80^o. The diffraction pattern is shown in **Figure 5.**

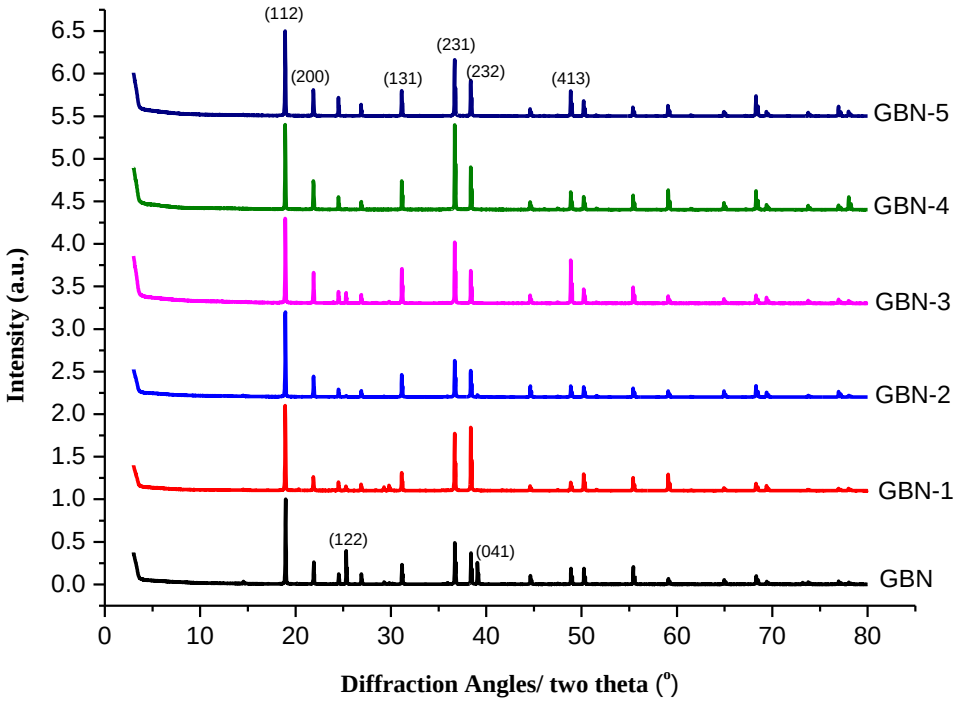


Figure 5 Diffraction pattern of each GBN crystal with its corresponding Miller indices

In **Figure 5**, it can be seen that the number of diffraction peaks in the GBN crystals decreases with increasing application of the external electric field. The peak profile (122) and (041) which originally appeared on the GBN crystals decreased in intensity. Furthermore, there is also intensity change in specific peak. The peak profile (231) has the highest relative intensity on GBN-4 crystals, while the peak (232) and (413) have the highest relative intensity in a row on GBN-1 and GBN-3 crystals.

If each peak is enlarged, each peak will be seen shifted towards a smaller diffraction angle with greater electric field strength. In accordance with Bragg's law, this peak shift means that the distance between the lattice plane is getting bigger. This explanation proved that the electric field affects the local dipole moment which arises from two types of charge in zwitter ions: $^{+}NH_3$ and COO^{-}. **Figure 6** shows magnification at the peak (231).

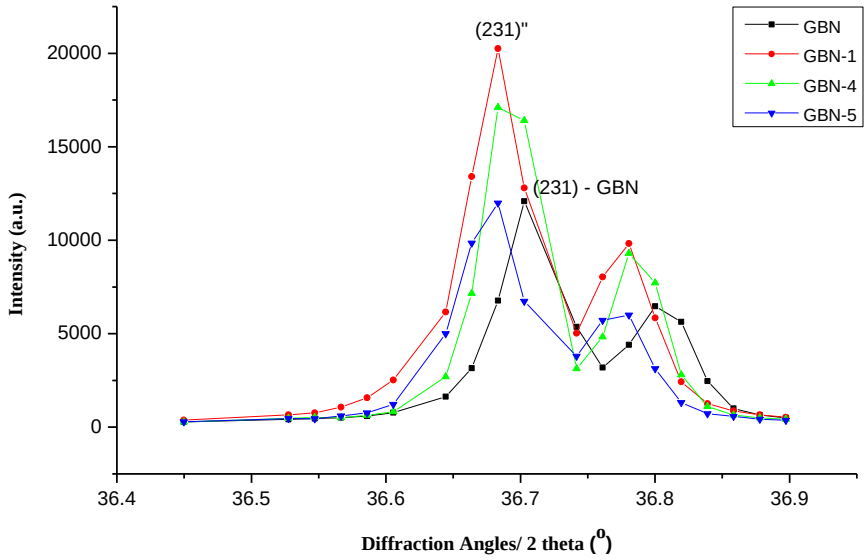


Figure 6. Peak shifting (231) for each GBN Crystal series

The existence of an external electric field will rearrange crystal growth orientation by means of the electric field at the negative pole will attract zwitter ion (NH_3^+)"tail (+)", while (COO^-) "head (-)"on the zwitterion leads to the positive pole. This causes each zwitter ions would moved away by one another.

The zwitter ion shift due to the effect of external electric field causes the distance between zwitter ions to move farther at one of the crystallography axes indicated by length extension of the lattice parameter *a*. The existence of screw 2_1 operation on each axis causes an extension of one axis to be followed by a shortening of the other lattice parameters. This is due to the electrostatic attraction between the zwitter ions glycine on each axis. When the zwitter ions on the *a* axis get extended from each other, the zwitter ions on the *b* and *c* axes approach each other due to the tensile force between the $^+$NH3 and COO^- group. In detail, the vaue of the lattice parameters *a, b*, and *c* can be seen from the results of the diffraction pattern refinement.

Refinement of the XRD diffraction pattern was carried out via Le Bail method using Fullprof refinement software. In conducting refinement, standard data for cell parameters such as space groups and lattice parameters are used as a comparison. The accuracy of this

refinement process can be seen from the value of *Rp* (*residue of profile calculation*) and χ^2 (*chi-square*) in **Table 2**. Refinement parameters are uses least square benchmark and straight depended by the value of *Rp* and *goodness of fit* (GOF). GOF is represented by χ^2 (chi^2). The smaller *Rp* , the smaller the residual calculation and it is said that the refinement went well. The refinement results of GBN crystal at 15-22% shows a large calculation residual factor. The bigger profile residual factor may be due to a mismatch in the selection of peak functions in the refinement process. This thing undoubtly interferes further calculations, so the value of χ^2 can be used as a reference. The smaller χ^2, the better quality of refinement, meanwhile its also indicates that the difference between the peak of diffraction pattern (of the sample) and the refinement peak were small to be comparized. This result can be seen more clearly in **Figure 7** below.

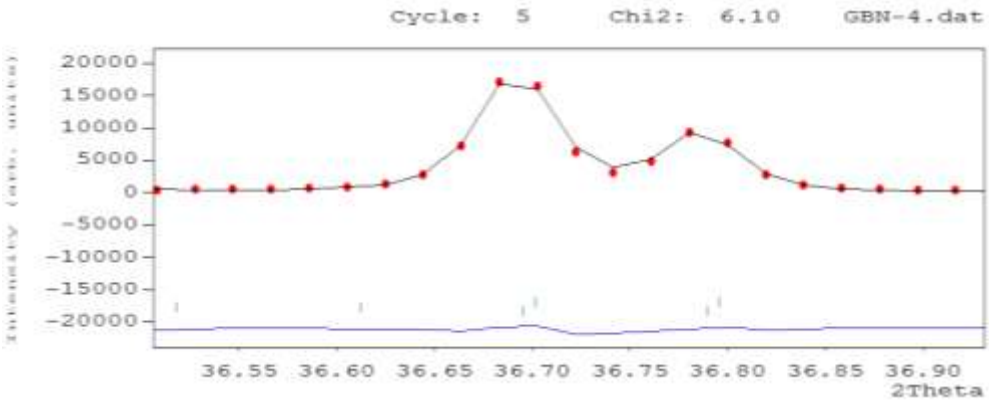


Figure 7. Enlargement Of Refinement Results At Peak (231). Red Dots Indicate The Diffraction Pattern Of The Sample, While The Black Line Through The Red Dot Shows The Pattern Of The Calculation Results. The Blue Line Shows The Difference Between The Peak Of The Diffraction Pattern Of The Sample And The Peak Calculated By The Refinement (X^2).

The GBN crystalline powder refinement results are shown in **Table 2**. Between the cells parameters *a, b*, and *c* experience different shift patterns toward the application of the electric field. Clear fully, this pattern is shown in **Figure 8.**

Table 2 GBN Crystall Refinement Results

Crystal	Applied Electric Field (kV/cm)	Lattice Parameter (Å)			Rp	χ^2
		a	*b*	*c*		
GBN	0	8,2328 (3)	9,3214 (2)	14,8441 (3)	18,4	6,37
GBN-1	1	8,2510 (2)	9,3188 (2)	14,8469 (4)	15,2	5,31
GBN-2	2	8,2557 (1)	9,3142 (2)	14,8454 (2)	20,1	6,56
GBN-3	3	8,2571 (1)	9,3113 (2)	14,8438 (3)	19,5	4,81
GBN-4	4	8,2623 (2)	9,3082 (2)	14,8433 (2)	21,3	6,10
GBN-5	5	8,2574 (2)	9,3096 (2)	14,8437 (2)	18,8	4,31

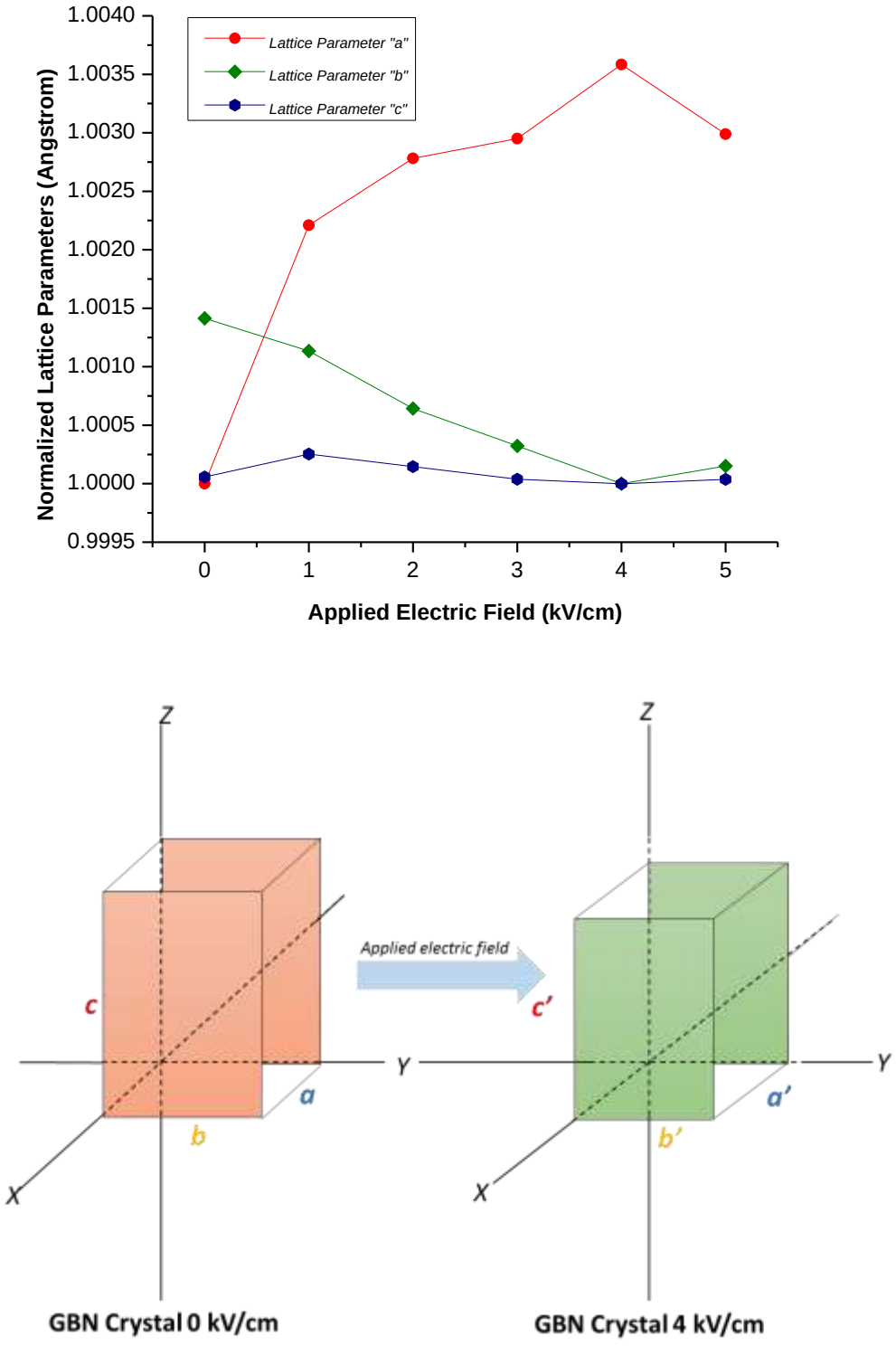


Figure 8. Lattice Parameter graphic of grown GBN crystal toward Application of External Electric Field and its tendencies in 3D model.

Based on the picture above, it can be seen that there is a tendency of length extension of *a* cell parameter on external electric field of 4 kV/cm, but again shorten at 5 kV/cm. This pattern is very different from *b* and *c* parameters which actually experience a length reduction until application of electric field at 4 kV/cm, but extends back on the 5 kV / cm. This means that there is a shift in the diffraction plane formed by zwitter ions glycine along with the Ba^{2+} and NO_3^- anions. This shift tends to move away from each other in which results in *a* cell parameters extension, while *b* and *c* shorten. When a 5 kV / cm electric field is applied, this field becomes too high for the system, that results distance between planes became shorten which may due to the zwitter ion that approaching each other in the lattice. This condition also causes why on the electric field 5 kV / cm the lattice parameter *a* is shortened, while *b* and *c* are increase in length.

CONCLUSION

The conclusion that can be drawn from this research is that the electric field accelerates the evaporation of water from saturated solutions. The peak shift towards a smaller diffraction angle occurs until the application of the electric field is 5 kV / cm. In GBN crystals, the external electric field causes the peak to shift towards a smaller diffraction angle, so that the lattice parameter *a* becomes longer, while the lattice parameters b and c are shorten. Based on the results of the refinement using the Fullprof program, the lattice parameters for GBN crystals are 0 kV / cm, 1 kV / cm, 2 kV / cm, 3 kV / cm, 4 kV / cm, and 5 kV / cm with space group $P2_12_12_1$ and $a \neq b \neq c$ in a row is *a* = 8.2328 (3) Å; 8,2510 (2) Å; 8.2557 (1) Å; 8,2571 (1) Å; 8,2623 (2) Å; 8,2574 (2) Å, *b* = 9,3214 (2) Å; 9.3188 (2) Å; 9.3142 (2) Å; 9.3113 (2) Å; 9,3082 (2) Å; 9,3096 (2) Å, and *c* = 14,8441 (3) Å; 14,8469 (4) Å; 14,8454 (2) Å; 14,8438 (3) Å; 14,8433 (2) Å; 14,8437 (2) Å.

REFFERENCES

1. Varalakshmi, S., Kumar, S.M., Elango, G., Ravisankar, R. (2014): Synthesis, growth and characterization of semi-organic non-linear optical crystal glysine barium nitrate (GBN), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, **133**, p677-682.
2. Vijayakumar, T., Joe, H., Reghunadhan, C. P., Jayakumar, V. S. (2008). Non-bonded interactions and its contribution to the NLO activity of glycine sodium nitrate: a vibrational approach, *Journal of Molecular Structure***, 877**, p20-p35.

3. Robert, R., Raj, C.J., Krishnan, S., dan Das S.J. (2010) : Growth, theoretical and optical studies on potassium dihydrogen phosphate (KDP) single crystals by modified Sankaranarayanan-Ramasamy (mSR) method, *Physica B*, **405**, 20-24.
4. Sayan, P., Sargut, S.T., dan Kiran, B. (2011) : Effect of ultrasonic irradiation on crystallization kinetics of potassium dihydrogen phosphate, *Ultrasonics Sonochemistry*, **18**, 795-800.
5. Lumsdon, S. O., Kaler, E. W., Velev, O. D. (2004). Two-dimensional crystallization of microspheres by a coplanar AC electric field, *Langmuir***, 20**, p2108-p2116.
6. Nogueira, E. M., Gomes, E. M., Belsley, M. S. (2001). Re-crystallization of MNA under a strong DC electric field, *Solid State Sciences*, **3**, p733-p740.
7. Tilley, Richard. (2006). *Crystals and Crystal Structures*.Chichester: John Willey and Sons. Ltd., 86.
8. De Yoreo, J.J., dan Vekilov, P.G. (2003): *Principles of Crystal Nucleation and Growth 3*, Livermore, California, 58.
9. Seyedhosseini, E., Ivanov, M., Bystrov, V., Bdikin, I., Mishina, E. D. (2014). Growth and non-linear optical properties of β-glycine crystals grown on Pt Substrates, *Crystal Growth and Design*, **14**, p2831-p2837.
10. Azhagan, S.A.C., dan Ganesan, S. (2013) : Crystal growth, structural, optical, thermal and NLO studies of γ-glycine single crystals, *Optik - International Journal for Light and Electron Optic*, 1-5.
11. Kavitha, P., Shanti, J., Deepthi, P.R. (2012). Optical properties and density functional theory study of single crystal glycine, *International Journal of Applied Physics and Mathematics*, **Vol. 2**, p293-295.
12. Mullin, J. (2001). *Crystallization*. London: Butterworth-Heinemann, 260-280.
13. Linet, J. M., Das, S. J. (2012). Optical studies on glycine sodium nitrate: a semiorganic non-linear optical crystal, *Optic*, **123**, p1895-p1899.
14. Wöhlecke, Manfred. (2005). *Non-linear Optics*. Osnabruck: University of Osnabrück Press, 29-47.
15. Loewen, E., Palmer, C. (2005). *Difraction Grating Handbook*. New York: Newport Corporation, 20-28.
16. Ghotbi, M., Zadeh, M., E. (2004). Optical second harmonic generation properties of BiB_3O_6, *Optics Express*, **Vol. 12**, p32-50.
17. Parikh, K. D., Dave, D. J., Joshi, M. J. (2010). Growth and characterization of L-alanine doped KDP crystals, *Cryst. Res. Technol*, p1-8.
18. Goryainov, S.V., Boldyreva, E. V., Kolesnik, E. N. (2006). Raman observation of a new polymorph of glycine, *Chemical Physics Letters***, 419,** p496-500.
19. Devi, K. R., Srinivasan, K. (2013). The role of charge compensation on the nucleation of α and γ polymorph of glycine from aqueous solution, *Journal of Crystal Growth*, **364,** p88-p94.

20. Remko, M., Rode, B. M. (2006). Effect of metal ions (Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) and water coordination on the structure of glycine and zwitterionic glycine, *J. Phys. Chem. A*, **110**, p1960-p1967.
21. Siska, Musiam. (2014). *Studi Pengaruh Medan Listrik terhadap Pertumbuhan Kristal Senyawa Ionik Dengan Metode Evaporasi Lambat.* Thesis. Bandung: ITB.
22. Blake, Alexander J. (2009). *Crystal Structure Analysis: Principles and Practice*. Oxford: Oxford University Press, 9-23.
23. Newnham, Robert E. (2005). *Properties of Materials*. Oxford: Oxford University Press, 30-36.