International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 05 Issue: 03 | Mar-2018 www.irjet.net p-ISSN: 2395-0072

Synthesis, Growth and Characterization of Nonlinear optical Ammonium 4- Methylbenzenesulfonate single crystal

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Abstract - *Good optical quality single crystal of Ammonium 4-Methylbenzenesulfonate (A4MBS) was grown by slow evaporation technique using water as solvent. Single crystal X-ray diffraction study was performed on the title compound. The presence of functional groups and modes of vibrations for A4MBS was interpreted using FT-IR and Raman spectrum. The crystalline perfection of grown crystal was evaluated by high-resolution X-ray diffractometry. The optical quality and percentage of transmission was assessed using UV-Vis analysis. Second order nonlinear optical property of the crystal was examined using Kurtz–Perry powder test. The surface laser damage threshold value of A4MBS crystal was measured by using Nd:YAG laser. The TG-DTA studies were performed in order to evaluate the thermal stability. Etching study was carried out to reveal the growth mechanisms*

***Key Words*: Crystal growth, X-Ray Diffraction, Spectral analysis, SHG**.

1. INTRODUCTION

Non Linear Optical (NLO) materials play a vital role in the aspect of materials science and many research groups have been abundantly studying its necessity in day to day life all around the world. While, In comparison with inorganic counterparts, organic nonlinear optical materials dominate its superiority with higher and faster nonlinearity. It is well known that materials with high nonlinearity are widely studied for the second harmonic generation (SHG) applications such as information processing, optical communication etc. Therefore fundamental research on the frame work of organic NLO materials has been in progress for several decades [1, 2]. Organic NLO crystals should meet several requirements, such as large phase –matchable non-linear optical co-efficient, a wide optical and chemical stability and a high damage threshold. The organic compounds with electron sufficient (donor) and electron deficient (acceptor) counterparts, provide the asymmetric charge distribution in the π electron system and shows large non-linear optical responses. The cationic part, ammonia is found to be basic in nature readily available to react with acids and are protonated easily thereby forming new compounds. The anionic counterpart, 4-methyl benzenesulfonic acid monohydrate plays a vital role in the formation of non-centrosymmetric crystal structure in organic crystals. [3]. Hence, the realization and importance of designing and developing such materials are precisely overlooked by scientific and engineering communities. In this present investigation ammonium 4-methyl benzenesulfonate crystal was grown by slow evaporation method and the grown material was subjected for various characterizations techniques. The obtained results are discussed here.

2. EXPERIMENT

2.1 Material Synthesis

Ammonium 4-methylbenzene sulfonate (A4MBS) was synthesized by reacting the stoichiometric ratio of Ammonium chloride (NH_4Cl) and 4-Methylbenzenesulfonic acid monohydrate ($C_7H_8SO_3.H_2O$) in 1:1 ratio. The calculated amount of Ammonium chloride and 4-Methylbenzenesulfonic acid monohydrate were dissolved using deionized water as solvent. The separate solutions of acid and base were allowed to stir continuously using an immersible magnetic stirrer for 3 hours at room temperature. Then the basic solution of ammonium chloride was added drop by drop to the acidic solution of 4-methylbenzenesulfonic acid monohydrate. While adding Ammonium chloride solution into 4-Methylbenzenesulfonic acid monohydrate, white precipitate was formed with exothermic reaction thereby confirming the product formation. The white precipitate was dissolved by adding excess of water as solvent until the solution was clear. This clear solution was stirred for 6 hours to obtain homogeneity. A4MBS was synthesized according to the synthesis scheme shown below in Fig.1.

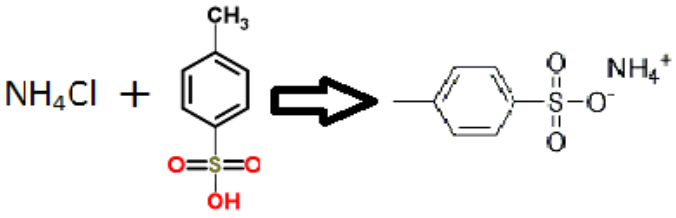

Fig -1: Synthesis Scheme of A4MBS

2.2 Solubility study

Solubility is an important parameter, which converses the growth procedure. If the solubility is too high, it is difficult to grow bulk single crystals with optical quality and too low solubility restricts the size and growth rate of the crystals. In order to evaluate and optimize the growth parameters, the solubility of A4MBS in water was determined using

gravimetric analysis for different temperatures namely 30, 35, 40, 45 and 50°C. The solubility of A4MBS exhibits good and positive temperature gradient solubility in water as a function of temperature as shown in Fig.2.

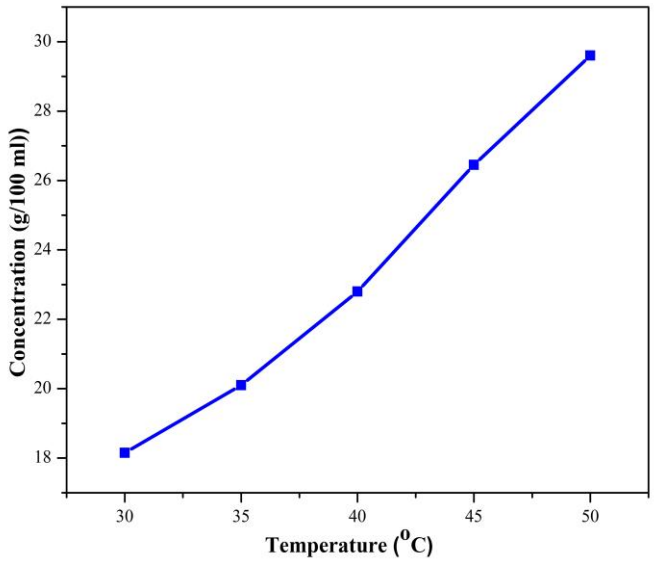

Fig - 2: Solubility curve of A4MBS

2.3 Crystal Growth

The synthesized product was purified by successive recrystallization process. Slow evaporation solution growth technique is employed to grow good quality single crystal at room temperature. Single crystal of dimension 13 mm × 7 mm × 2.5 mm has been harvested after 32 days. The photograph of the as-grown A4MBS crystal is shown in Fig.3.

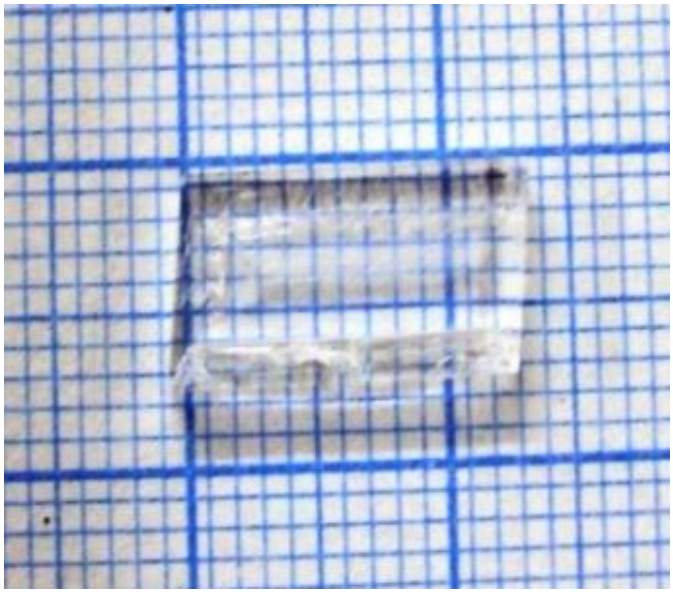

Fig – 3: Photograph of as grown A4MBS

3. RESULTS AND DISCUSSION

3.1 Single crystal X-ray diffraction study

Single crystal X-ray diffraction data of A4MBS was elucidated using ENRAFNONIUS CAD-4 single crystal X-ray diffractometer. X-ray diffraction analysis was carried using the good quality single crystal of A4MBS in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the A4MBS crystal belongs to orthorhombic crystal system with $Pna2_1$ non- centro symmetric space group. The unit cell parameters are found to be, a = 20.41 (3) Å, b = 7.05 (1) Å, c = 6.28 (4) Å, V = 904 Å^3 and is found to be in good agreement with the reported data [4].

3.2 Spectral analyses

FT-IR and FT-Raman spectra was recorded to interpret the chemical bonding and modes of vibration of A4MBS in the range 4000–400 cm^{-1} by PERKIN–ELMER spectrometer using KBr pellet technique and FT-RAMAN spectrometer (BRUKER RFS 27: Stand-alone FT-Raman Spectrometer)with a resolution of 1.0 cm^{-1}and 2.0 cm^{-1} respectively. The spectral analysis of A4MBS was carried out on the characteristic vibrations of ammonium group, sulfonate group, methyl group and benzene rings. The FT-IR and FT-Raman spectra of A4MBS compound were presented in Fig.4 and Fig.5 respectively.

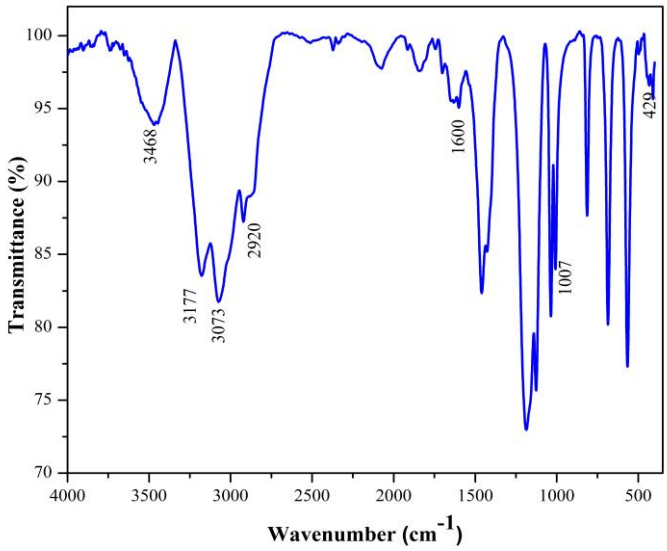

Fig.4: FT-IR spectrum of A4MBS

Ammonium cation vibrations

The peak at 3468 cm^{-1}is assigned to the O...H stretching of title compound via the strong hydrogen bonding between the cation and anion which enhances SHG generation. The absorption bands of the NH_4^+ group corresponding to stretching vibration are in the range 3300–3030 cm^{-1} [5].The

sharp peak at 3177 cm^{-1} is assigned to the asymmetric vibration of ammonium cation. The band at 3073 cm^{-1} in IR and a band at 3063 cm^{-1} in Raman are assigned to NH_4^+ symmetric stretching vibrations, respectively.The band at 1600 cm^{-1} observed in Raman and IR corresponds to the asymmetric deformation of the NH_4^+ion.

4-Methylbenzenesulfonate anion vibrations

The strong and sharp peak at 2920 cm^{-1} in IR and 2928 cm^{-1}in Raman spectrum are assigned to the symmetric stretching vibration of C-H bonds there by confirming the presence of methyl groups. The sharp peak observed at 1007 and 1013 cm^{-1} in IR and Raman spectra are attributed to in-plane and out of plane bending of aromatic ring C–H bonds, respectively [6,7]. The sharp intense peaks observed at 429and 397 cm^{-1} in IR and Raman are assigned to the stretching of the sulfonate group.

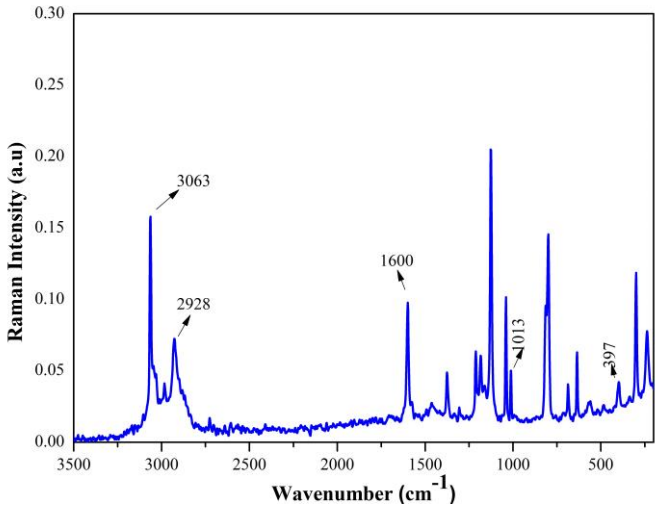

Fig.5: FT-Raman spectrum of A4MBS

3.3 High Resolution X-Ray Diffraction

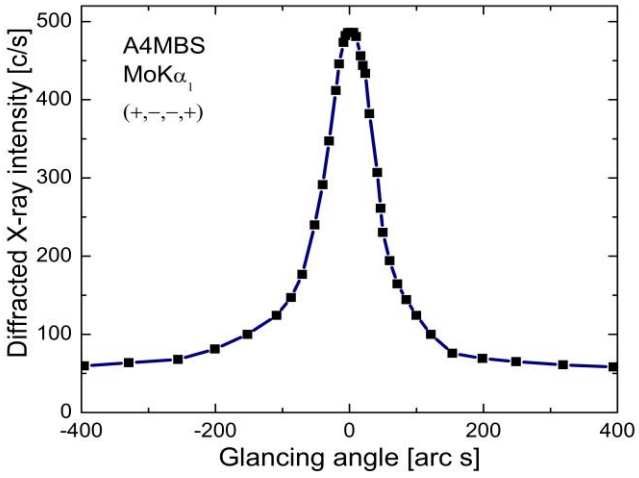

Fig – 6: HRXRD spectrum of A4MBS

Figure 6 shows the high-resolution diffraction curve (DC) for A4MBS recorded using symmetrical Bragg geometry. From the obtained spectrum it is noticed that the DC contains a single peak and indicates that the specimen is free from any structural grain boundaries. The FWHM of the curve is found to be 23 arc s which is slightly more than that expected value for an ideal crystal from the plane wave theory of dynamical X-ray diffraction [8], but it is close to that expected value for a nearly perfect real life crystal. The absence of additional satellite peaks and the single DC peak showed that, the crystalline perfection of the grown A4MBScrystal is fairly good without having any internal structural grain boundaries. Hence it is depicted that the crystalline perfection is good [9].

3.4 UV-Vis spectral analysis

The optical transparency and cut-off wavelength are the most important optical parameters to tailor the materials for various applications. The UV-vis transmission spectrum of A4MBS crystal was recorded in the wavelength range 200–800 nm using Varian Carry 5E model spectrometer. Polishing of crystal plays a major role in enhancing the transparency of optical materials, hence as grown crystal was subjected to polishing using alumina powder and polishing sheet. The cut and polished A4MBS crystal of thickness 1 mm was used for UV–Vis spectral study and the transmission spectrum is shown in Fig. 7. It is observed from Fig.7, that A4MBS single crystal has good transmittance of about 75% with lower cut-off wavelength 300 nm.The absence of significant absorption in the region between 300 nm and 800 nm shows that the A4MBS crystal may be exploited for nonlinear optical applications.

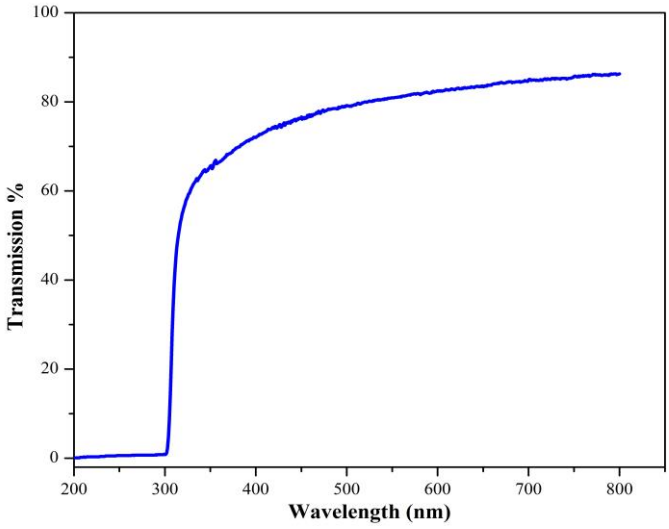

Fig – 7: UV transmission spectrum of A4MBS

3.5 Nonlinear Optical Study

The second harmonic generation efficiency was studied by employing the Kurtz and Perry powder technique [10] which remains a valuable tool for the initial screening materials for

SHG property. Q-switched Nd:YAG laser with the fundamental beam of 1064nm, repetition rate of 10 Hz and pulse width 10 ns was used to measure the SHG efficiency ofA4MBS.The standard reference material potassium dihydrogen phosphate (KDP) was used to compare the SHG efficiency. The optical signal incident on a photomultiplier tube was converted into voltage output.

The SHG output signal intensity of 69.7 mV was measured for A4MBS crystalline powder while that for standard KDP crystalline sample was 17.4 mV for an input energy of 5 mJ/pulse. Thus it is clear that the SHG efficiency of A4MBS was found to be 3.96 times greater than that of standard reference material KDP.

3.6 Laser Damage Threshold (LDT) study

In order to evaluate the laser damage stability of A4MBS crystal it was subjected to LDT with multiple shots experiment. Good optical quality, cut and polished sample was used for the study. A fundamental beam of 1064nm, repetition rate of 10 Hz and pulse width 10ns of Q-switched Nd:YAG laser was used to measure the LDT ofA4MBS. The input energy was raised from 5mJ/pulse until damage was observed. The spot size of the beam was measured to be 1 mm. The laser damage threshold of the crystal was calculated using the expression:

$$\text{Power density} = E / \tau\pi r^2 \qquad (GW/cm^2)$$

where, 'E' the input energy (mJ), 'τ' the pulse width (ns), 'r' the radius of the circular spot (mm).The Laser damage threshold value of A4MBS was found to be 3.23 GW/cm^2 which is found to be slightly greater than that of standard reference material KDP (0.20 GW/cm^2).

3.7 Thermal analyses

Thermo gravimetric and differential thermal analyses were carried out using NETZSCH STA 409 thermal analyzer instrument in nitrogen atmosphere at a heating rate of 10 ^{o}C/min in the temperature range 30–500 ^{o}C. The thermal stability of materials is a major requisite for device and other applications. The thermal character of A4MBS was studied using simultaneous Thermo-Gravimetric (TG) and Differential Thermal Analyses (DTA).

An A4MBS crystalline sample weighing 5.172 mg was used to evaluate the thermal parameters and the TG-DTA curve in shown in Fig.8. The TG curve shows the same changes as in the case of DTA curve. From the TG curve it is clear that the title material is stable up to 257^{o}C and it is free from moisture. The TG curve shows two stages of weight losses when the crystalline sample is heated from 35 ^{o}C – 500 ^{o}C. The first stage of weight loss occurs in the temperature range about 364 ^{o}C to 395 ^{o}C with the elimination of materials into gaseous product such as, CO, CO_2, NH_3 etc., [11] as seen in the low temperature region. Immediate, second stage of weight loss occurred from the temperature range around 395 ^{o}C till the decomposition of the end materials. The endothermic peak as 322 ^{o}C in DTA curve corresponds to the melting point of A4MBS. Thus it is evident from the TG-DTA curve that the material decomposes before melting and can be claimed that the title material is thermally stable and can be used for applications in the field NLO by considering their stability up to 322 ^{o}C.

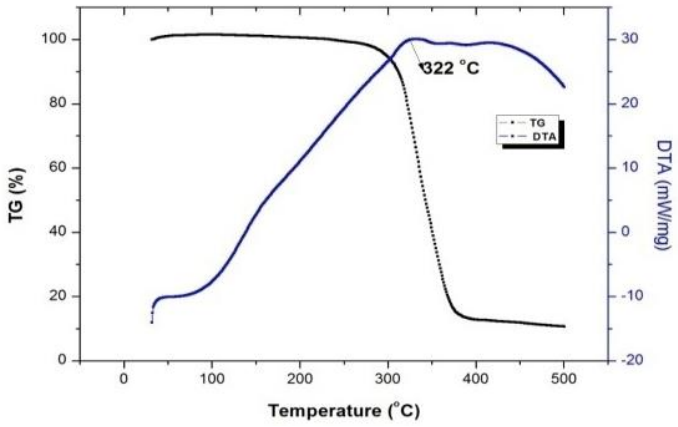

Fig – 8: TG-DTA curve of A4MBS

3.8 Chemical Etching analysis

Etching is an important tool for the identification of the crystal defects. Generally a crystal grown from solution suffers from the growth imperfections such as solvent inclusions, twins, grain boundaries and dislocations. The pattern observed on the surface like line pattern yields considerable information on the growth process and growth mechanism of the crystal.

The etching analysis was carried out on plane surface of the as grown single crystal of A4MBS using water as an etchant at room temperature for different etching times of 10 s (9(a)), and 20 s (9(b)) is shown in Fig.9 (a &b).It is clear from the Fig. 9 (a) and (b), the size of the etch pits increases with increase in etching time while the pit pattern remains the same. The observed etch pits are attributed to the layer growth and confirmed the two-dimensional nucleation (2D) mechanism [12]. A4MBS crystals for (a) 10 s and (b) 20 s are as shown in the fig. 9.

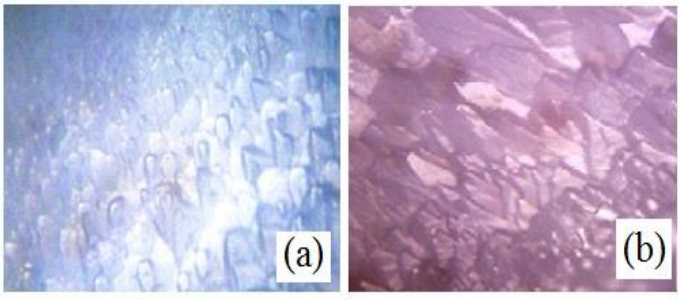

Fig – 9: Etching pattern of as grown A4MBS

4. CONCLUSION

Good quality single crystal of Ammonium 4-Methylbenzenesulfonate (A4MBS) was grown by slow evaporation technique using water as solvent. The solubility study was carried out to optimize growth parameters. The unit cell parameters and crystal system were found out by single crystal X-ray diffraction studies. Crystalline perfection was analyzed using HRXRD technique. The presence of functional groups and modes of vibrations for A4MBS was interpreted using FT-IR and Raman spectroscopy. UV–Vis transmission studies revealed that the A4MBS crystal is highly transparent in the entire visible region. The presence of second harmonic generation (SHG) in the title compound was confirmed by powder Kurtz-Perry technique. Laser Damage Threshold (LDT) of A4MBS was found to 3.23 GW/cm^2 by multiple shots experiment. The TG-DTA analysis was done in order to find the melting point and thermal stability of A4MBS. Etching study was carried out to reveal the growth mechanisms and it shows layer by layer growth mechanisms.

ACKNOWLEDGEMENT

Special thanks to the Management and Staff members of Aalim Muhammed Salegh Polytechnic College for supporting during my research work.

REFERENCES

[1] L. Dalton, Polymers for Photonics Applications 1, Adv .Polym. Sci., 158**,** 2002.

[2] G.R. Meredith, Nonlinear optical properties of organic and polymeric methods, ACS Symp Series-223, Washington, DC,1983.

[3] B.J.Coe, J.A. Harris , A. K. Clays, G. Olbrechts, A.Persoons, J.T.Hupp, "Quadratic Nonlinear Optical Properties of N - Aryl Stilbazolium Dyes**,"** Adv. Funct. Mater., Vol.12, Jan. 2002, pp. 110-116. doi: 10.1002/1616-3028(20020201)12:2<110::AID-AD FM110>3.0.CO;2-Y

[4] R.D. Rogers, A .H. Bond, R.F. Henry, "Structure of ammonium p-toluenesulfonate," Acta. Crystalogr., Vol. C47, Jan. 1991, pp. 168-170. https://doi.org/10.1107/S0108270190006497

[5] G. Socrates, Infrared and Raman Characteristic Group Frequencies, Tables and Charts, (3rd edn), Wiley: Chichester, 2001.

[6] Y.R. Sharma, Elementary Organic Spectroscopy Principles and Chemical Applications, S. Chand & Co, New Delhi, 2004.

[7] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1991.

[8]G. Bhagavannarayana, S. Parthiban, S. Meenakshi sundaram, "An Interesting Correlation between Crystalline Perfection and Second Harmonic Generation Efficiency on KCl- and Oxalic Acid Doped ADP Crystals," Cryst. Growth Des, Vol. 8, Aug. 2008, pp. 446-451. doi:10.1107/S0021889810033649.

[9] G. Bhagavannarayana, A. Choubey, V. Shubin, Krishan Lal, "Study of point defects in as-grown and annealed bismuth germanate single crystals," J. Appl. Cryst. Vol. 38, Feb. 2005, pp. 448-454. doi:10.1107/S002188980500590X.

[10]S.K Kurtz, T.T.Perry, "A Powder Technique for the Evaluation of Nonlinear Optical Materials," J.Appl.Phys., Vol. 39, Jul. 1968, pp. 3798-3813. https://doi.org/10.1063/1.1656857

[11] V. Chithambaram, S. Jerome Das , R. Arivudai Nambi , S. Krishnan, "Synthesis, growth and characterization of nonlinear optical urea-ammonium chloride crystals," Solid State Sciences, Vol. 14, Feb. 2012, pp. 216-218. doi:10.1016/j.solidstatesciences.2011.11.013.

[12] Mukerji S and Kar T, (1999), "Etch pit study of different crystallographic face of L-arginine hydrobromide monohydrate (LAHBr) in some organic acids," J. Cryst. Growth, Vol.204, pp.341-347. https://doi.org/10.1016/S0022-0248(99)00137-2