International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056
Volume: 09 Issue: 08 | Aug 2022 www.irjet.net p-ISSN: 2395-0072

Synthesis, Growth and Characterization of Nonlinear Optical Semi Organic Potassium Sulphate Formate Single Crystal by Slow Evaporation Method

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Abstract - *Potassium Sulphate Formate (PSF) was prepared for equal molar ratio of Potassium Sulphate and Formic acid slow evaporation technique using water as solvent. The unit cell proportions were gained by both single crystal and powder X - ray diffraction analysis. The structural refinement of PSF shows that it crystallizes in the orthorhombic system with non – centro symmetric space group $Pna2_1$. The single crystal XRD analysis reveals the extended framework architecture of PSF through self - assembly process, involving short range and directional bonds among many other different interactions. Presence of functional groups and modes of vibrations for PSF was interpreted using Fourier transform infrared spectrum. The UV- visible and fluorescence spectral calculate were carried out and to find the optical quality and transmission range of grown crystal. The TG – DTA studies were performed in order to evaluate the thermal stability. The emission of green light on passing the Nd: YAG laser light confirmed the second harmonic generation property of the crystals and the SHG efficiency of the crystals was found to be higher than that of KDP.*

Keywords: **Semi organic, Slow evaporation, Powder XRD, FTIR Spectrum, TGA, SHG**

1. INTRODUCTION

Nonlinear optical (NLO) applications demand good quality single crystals, which inherit large NLO coefficient [1], coupled with improved physical parameters one potentially attractive system, where there is a potential for realizing very large second order nonlinear coefficient based on organic crystals. Organic materials have been of particular interest because the nonlinear optical responses in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials. In parallel to discover the new NLO materials [2], it is also very important to modify the physical, optical, and electrical, mechanical properties of these materials either by adding functional groups or by incorporation of dopants for tailor made applications. The Semi organic crystal could be developed from the aqueous solution with improved thermal stability and the hardness enable the crystal for easy cutting and polishing respectively. [2] Efficient molecules need to be selected for the process, which should possess the following features, the electronic organization of the molecule efficiently paired with electric field and better resonance must be utilized for response magnification and the chosen molecule must be concentric and symmetrically effective. Assessing the growth of the crystal, it possesses knowledge in the field of mathematics, chemistry, physics and crystallography. Crystal growth comprises mass and heat transfer phenomenon along with the conventional properties [2]. The concentration field and the concerned temperature possess a predominant impact on crystal quality. The grown crystals and powder X-ray analysis and UV spectral analysis, thermal analysis, SHG measurements results of these studies have been discussed in this paper detail. [3]

2. EXPERIMENTAL

2.1. Materials and methods

Potassium Sulphate Formate (PSF) were synthesised using slow evaporation solution technique at a room temperature and the short procedure is presented table1. The estimated amounts of Potassium Sulphate, Formic acid were taken in equimolar ratio and stirred by a constant magnetic stirrer to ensure homogeneous mixing of solutions. The stirred reaction mixture is heated up to 40^0C for 3 hrs. after which the temperature is slowly reduced to room temperature. The prepared clear solution was poured in to a beaker and covered. After 15 days, the solvent was evaporated and good quality transparent crystals are obtained. The PSF grown crystal is shown in Fig. 1.

Fig – 1: Photograph of as grown PSF

Table 1. Growth of PSF crystal

S. No.	Techniques	Slow evaporation
1	Solvent	Distilled water
2	Potassium Sulphate and Formic Acid	1:1 molar ratio
3	Temperature	40^0C and room temperature
4	Period of growth	15 days
5	Colour of crystal	Colourless

3. RESULTS AND DISCUSSION

3.1. Single Crystal X – Ray Diffraction Analysis

Single crystal X – ray diffraction analysis was performed on the as grown PSF crystal using ENRAF - NONIUS CAD – 4. X – ray diffraction analysis was carried using the good quality single crystal of PSF in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the PSF 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 Å, b = 7.05 Å, c = 6.28 Å, V = 904 $Å^3$ and is found to be in good agreement with the reported data.

3.2. Powder X – Ray diffraction

The powder X – Ray diffraction analysis were carried out to confirm the crystallinity and also the purity of the grown crystal using a Bruker D8 Advance diffractometer with CuKα (1.5406 Å) radiation. From the powder X-ray data, the various planes of reflections were indexed using POWDERX program. The indexed powder X-ray diffraction pattern for PSF crystal is shown in Fig. 2. The appearance of sharp and strong peaks good crystallinity of the grown PSF crystal. Powder XRD pattern was recorded by scanning the sample over the range 0 - 90^0 at scan speed of 1^0/min. The good crystalline nature was confirmed from the sharp peaks. The slight shift in the sharp peak positions towards to lower angle side may be due to the addition of PSF crystal and it is also confirmed by a slight variation observed in the lattice parameters of the grown crystal. [5,6]

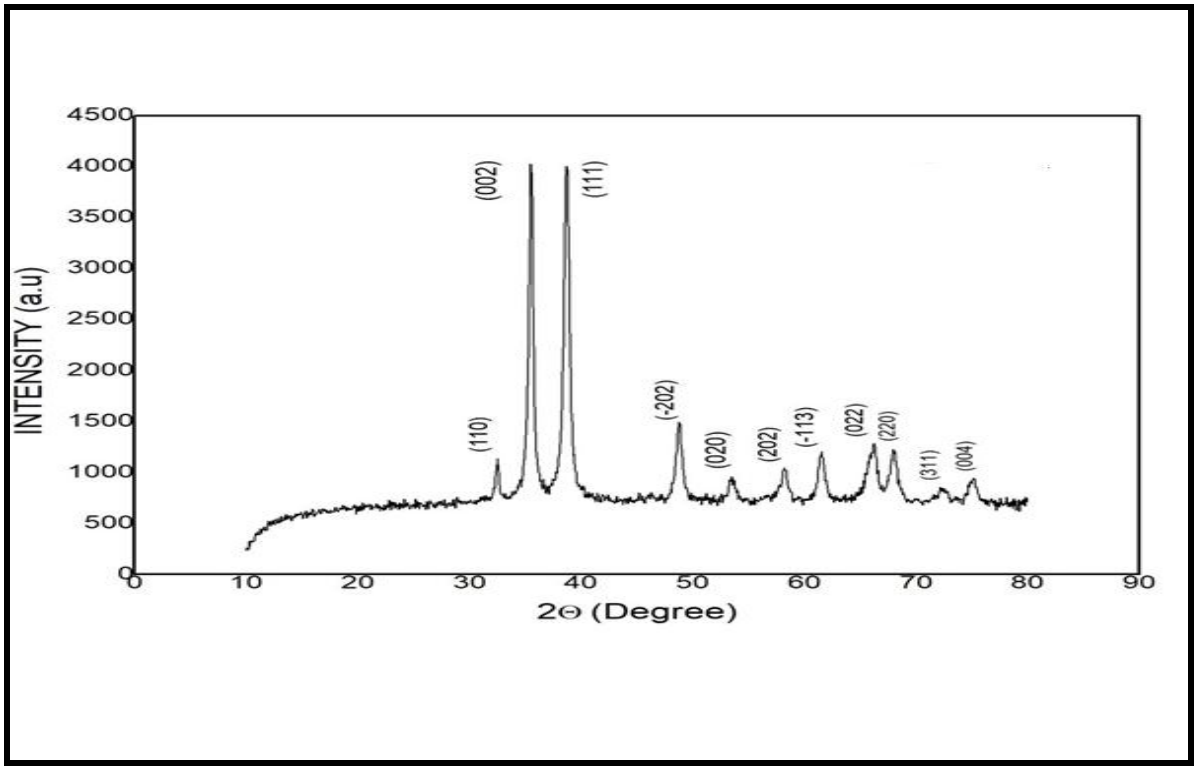

Fig – 2: The XRD data of the grown PSF crystal

3.3. Fourier Transform Infrared (FTIR) Spectral Analysis

The FT – IR spectroscopy was used to identify the presence of functional groups in the grown crystal using PERKIN ELMER Fourier transform infra – red Spectrometer. Using KBr pellet technique in the wavelength range between 500 – 4000 cm^{-1} carried out the FTIR analysis of PSF. The recorded FTIR spectrum of PSF is shown in Fig. 3. The broad band at 3398 cm^{-1} and the band at 1624 cm^{-1} are due to C=O stretching vibrations. S=O stretching vibrations are found at 1384 cm^{-1}. The band at 1285 cm^{-1} is due to S-O plane bending. The asymmetric stretching vibration of SO_4 give rise to a band in the region of 1107 cm^{-1} [7].

Table 2. Vibrational band assignments of PSF Crystal

Wave number (cm^{-1})	Bond Assignments
3398	O - H stretching of HSO_4 group
1624	C=O stretching
1384	S=O stretch
1285	S – O plane of bending of HSO_4
1107	SO_4 asymmetric stretching
611	C – H stretch

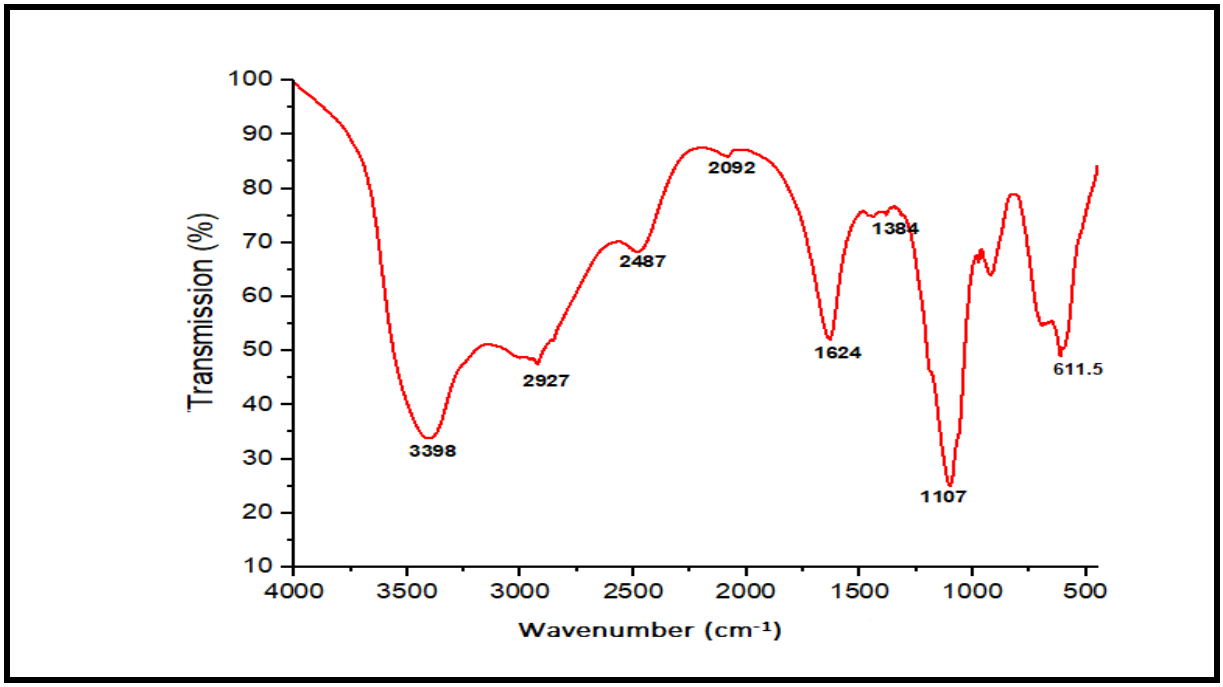

Fig – 3: FT – IR spectrum of the grown PSF crystal

3.4. UV – Visible Spectral Analysis

An optically polished crystal of 1 mm thickness was used for recording the optical absorption and transmission spectrum of Potassium Sulphate Formate (PSF) single crystal in the range of 100 nm to 1200 nm, is shown in Fig.5 and Fig. 6. The optical absorption coefficient (α) was used to find,

Extinction coefficient $K = \frac{\alpha}{4\pi}$ and Bandgap energy $E_g = \frac{1240}{\lambda}$ (eV)

Where λ is the lower cut – off wavelength of the sample and where h is Plank's constant. Bandgap energy was the difference in energy between the valence band and the conduction band of a solid material it is simply the energy of forbidden electrons movement in the material it is simply the energy was governed by the structural disorder, an imperfection in stoichiometric and passivation at the surface and the disorder of phonon states. It is inversely proportional to the bandgap energy. From the UV – VIS spectrum, lower cut - off wavelength was observed at 218 nm this is due to interbond electronic transitions. Using the lower cut – off wavelength bandgap energy value was calculated as 5.6 eV which is shown in Fig. 6. The high transmission of the grown crystal in the entire visible region with a wide bandgap indicates the low defect concentration in the grown material [8]. It is seen from the spectrum that the crystal is transparent in the entire range without any absorption peak, which is an essential parameter for the NLO crystals.

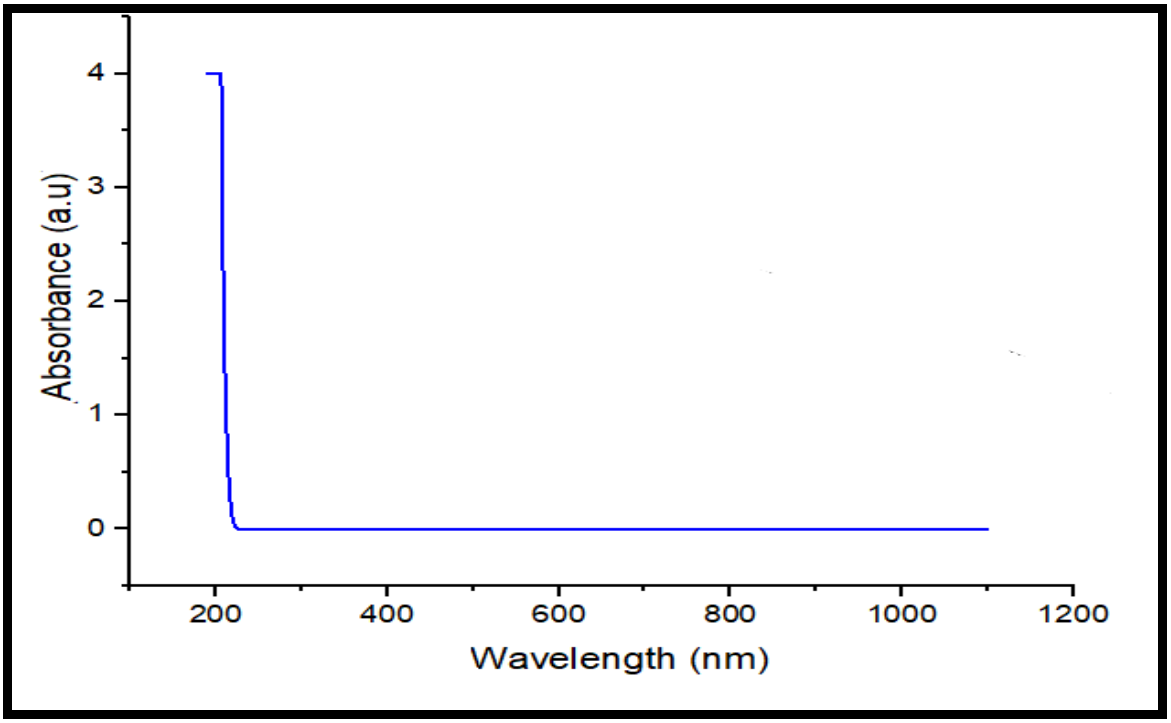

Fig – 4: UV – vis Absorbance of the grown PSF crystal

The PSF crystal is transparent in the entire UV – visible region. A better transmittance with lower cut – off wavelength in the visible region gives 4.98 eV. Optically polished single crystals of thickness 3 mm were used for this study Fig.5 shows that the absorption spectrum of the grown crystals and the presence of lower cut off wavelength range of the materials possessing NLO activity.

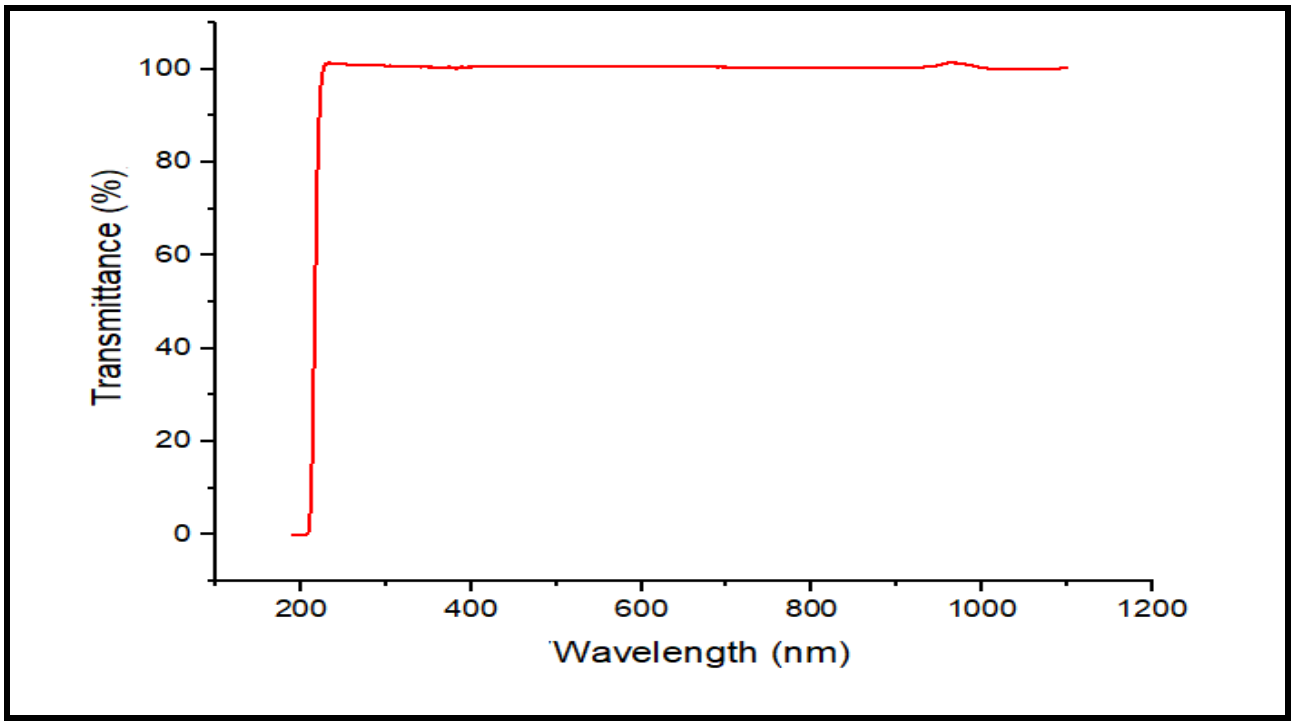

Fig – 5: UV – vis Transmission spectrum of the grown PSF crystal

3.5. Fluorescence Analysis

Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiations. The most striking examples of fluorescence occur when the absorbed radiation is in the UV region of the spectrum and thus invisible to the human eye and the emitted light is in the visible region. Fluorescence generally found in compounds containing aromatic functional groups with low energy π - π^* transition levels. Compounds containing aliphatic and alicyclic carbonyl structures or highly conjugated double – bond structure exhibit fluorescence. The emission spectrum of PSF in the range 200 – 800 nm. The spectrum is given in Fig. 7 Which shows a peak at about 513 nm indicates that PSF crystal has a blue fluorescence emission.

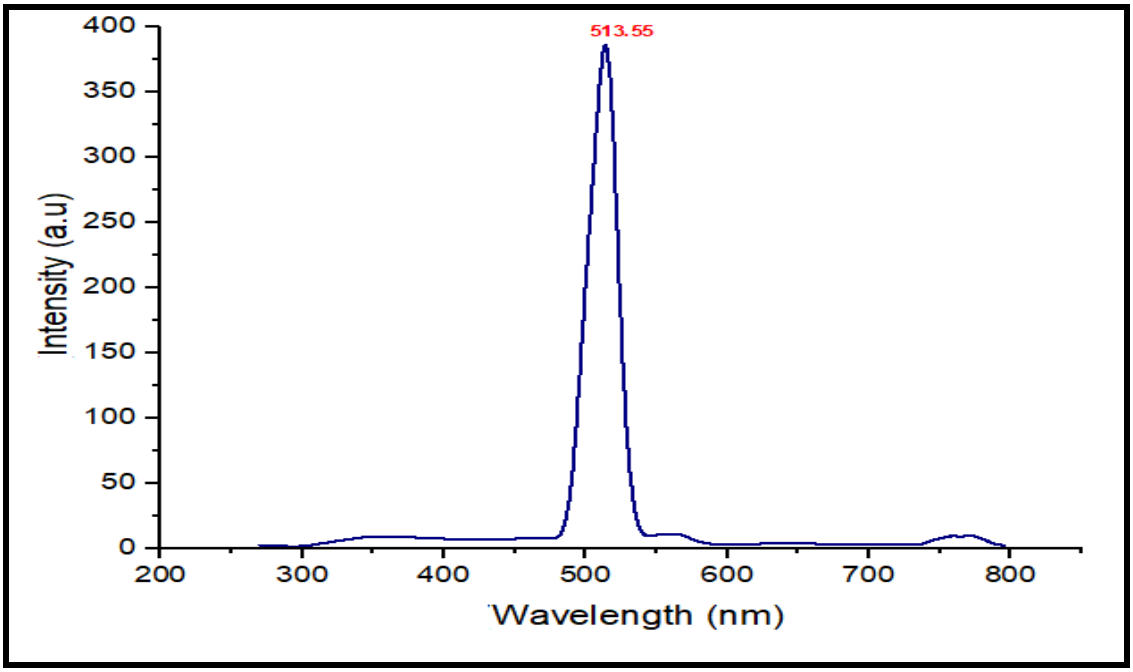

Fig – 6: Fluorescence spectrum of the grown PSF crystal

3.6. Thermal Analysis

The grown PSF crystal was subjected to Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) and the spectra are shown in Fig.8. They were carried out using Perkin Elmer Dia TG/DTA instrument in a nitrogen atmosphere for a temperature range from 40^{0}C to 680^{0}C at a heating rate of 20^{0}C/min. The decomposition switches nearly from 120^{0}C to 210^{0}C and a major weight loss of 99% obtained at 205^{0}C. The weight loss directed that the decomposition nature of the sample and NLO applications SPF was used below 120^{0}C [24]. However, there is no weight loss was detected below 100^{0}C which shows there is no water molecule in SPF. A sharp exothermic peak at 121^{0}C was obtained in the DTA spectrum of SPF which indicates the melting point of the grown sample. The weight loss was spotted at 121^{0}C from this the decomposition starts before melting. The acuity of the peaks indicates a good degree of crystallinity of the sample.

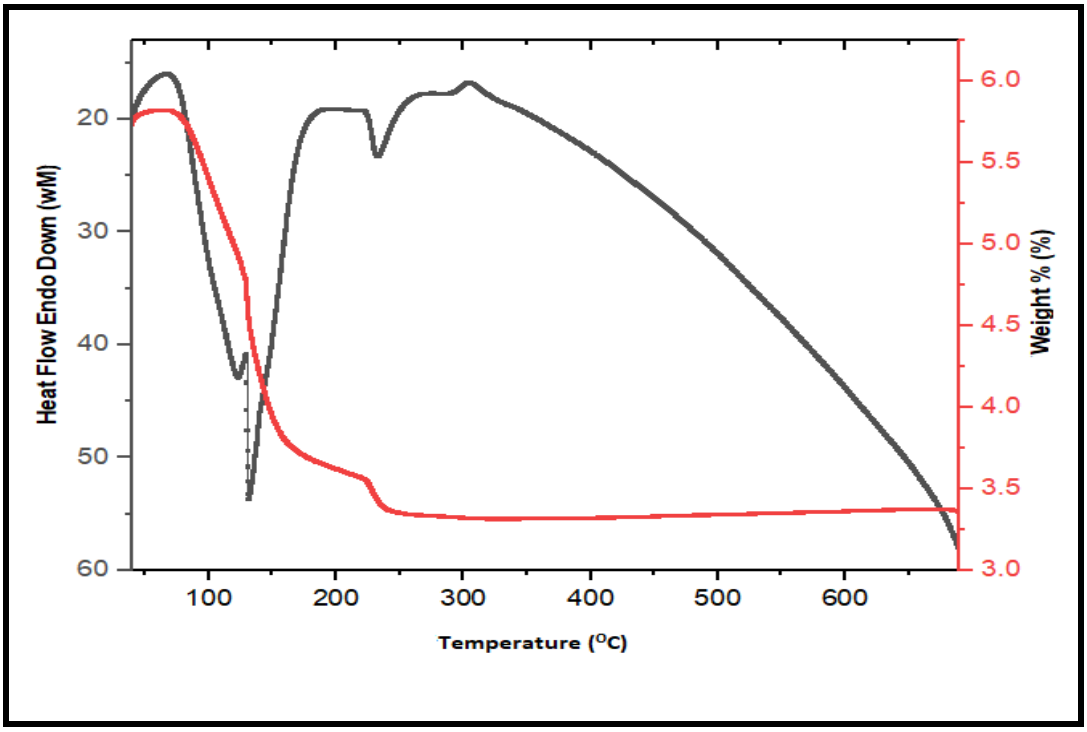

Fig – 7: TG - DTA curve for PSF crystal

3.7. Nonlinear Optical Test

The second harmonic generation was studied by analysing the efficiency in terms of sample output and KDP value with the help of common powder methodology as Kurtz – Perry powder technique [2]. Q – switched Nd: YAG laser with the fundamental beam 1064 nm, repetition rate of 10 Hz and pulse width 10 ns was used to measure the SHG efficiency of PSF. 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 is confirmed by the emission of green radiation at 518 nm and the SHG efficiency is found to be 2.76 times greater than that of standard reference material KDP.

4. Conclusion

Potassium Sulphate Formate (PSF) crystals are grown by slow evaporation technique. The crystalline nature and purity of grown crystal is confirmed by power XRD technique. We have obtained those crystals possess an orthorhombic arrangement structure. The recorded FTIR spectrum of the grown crystal PSF confirms the presence of functional groups in the compound. UV - VIS - NIR spectrum of PSF shows non-linear optical property which is the essential requirements for any non-linear optical material. The thermal studies of the samples suggest that the thermal stability is better for doped crystals. The fluorescence of the grown sample is confirmed by nonlinear optical property. The SHG efficiency of PSF crystal is nearly 2.76 times that of standard KDP material. From the overall analysis, it is clear that the synthesized PSF possess higher efficiency than KDP and can be effectively applied in the optoelectronic field.

Acknowledgements

One of the authors (LJ) thanks Sophisticated Instrumentation centre, Indian Institute of Technology, Chennai and Central Instrumentation centre MK University for the support in Powder XRD, Fluorescence, FT - IR, DSC and TG/DTA data collection. LJ also, thanks to Prof. P.K. Das, Institute of Science, Bangalore for having protracted laser facilities for SHG measurements.

References

[1] E. Vinoth, S. Vetrivel, S. Gopinath & J. Suresh, Journal of Taibah University for Science, Vol.13, Issue 1979 – 992, Sep. 2019.

[2] D. Prem Anand, S. Selvakumar, K. Ambujam, K. Rajarajan, Indian Journal of Pure & Applied Physics, Vol. 43, Issue 2, 863 – 868, November 2005.

[3] P. Saritha, S. Barathan, Elixir Crystal Research, Volume 6, Issue 3, 42503 – 42505, 2016

[4] Ezil Vizhi, Vijayan Narayanasamy, N. Sivakumar, Optik 123(5), 409 - 413, 2012.

[5] N. Indumathi, K. Deepa and S. Senthil, Int. J. Eng. Devel. Reser. Vol. 5, Issue 1, 2321- 9939, 2017

[6] S. Sivasakthi, M. Haridas, G. Pasupathi, Int. J. Innov. Reser. Mult. Fie. Vol.3, Issue 6, 2455 0620,2017.

[7] Albert Irudayaraj, A. Dhayal Raj, S. Karthick, R. Vinayagamoorthy, G. Jayakumar, Int. J. Rece. Sci.Reser. Vol. 6, Issue 2, 2732 – 2736, 2015.

[8] R. Sakunthaladevi, L. Jothi, J. Mol. Struc. Vol. 1233, 0022 – 2860, 2021.K. Uma, R. Manimekalai, G.

[9] Pasupathi, Int. J. Che. Mater.Reser.Vol.3, Issue 4, 91-99, 2015.

[10] S. Arulmani, K. Deepa, S. Senthil, Int. J. Sci. Reser. Sci. Tech. Vol. 4. Issue 5, 184 - 189,2018.

[11] T. Kalaiarasi, M. Senthilkumar, S. Shanmugam, Bull. Mater. Sci. Vol. 13, Issue 1, 12034 – 021- 02421– 6, 2021.

[12] N. Nithya, R. Mahalakshmi and S. Sagadevan, Int. J. Med. Sci. Edu. Vol. 13, Issue 1, 50 – 57, 2016

[13] Cynthia Sundararaj, Suresh Sagadevan, Mater. Reser. Vol. 21, Issue 1, 5373 - 5379, 2016.

[14] P. Sakthi, R. Rajasekaran, A.Arun, J. mate. Sci. poland DOI:10.2478/MSP -2019-0033.

[15] K. Suguna, G. Suhanya, Int. J. Adv. Reser. Sci. Eng. Tech. Vol. 5, Issue 12, 7690 - 7696, 2018.

[16] S. Alfred Devaprasad and J. Madhavan, Arch. AppL. Sci. Reser. 2010,2(4):26-32.

[17] R. Anitha, S. Athimoolam, M. Gunasekaran, K. Anitha, J.Mol. Struc. Vol. 1076, 115-125, 2014.

[18] Koteeswari, Pandurangan and Sagadevan Suresh, J. Mater. Vol. 6, Issue 1, 1453 - 1460, 2014.

[19] A. Sarbudeen, I. Md. Zahid, G. Foize Ahmad, M. Gulam Mohamed, Int. J. Eng. Reser. Tech. Vol. 5, Issue 3, 2395 – 0072, 2018.

[20] K. Selvaraju, K. Kirubavathi, S. Kumararaman, J. Mine. & Mate. Charac. Eng. Vol. 11, Issue 3, 303 310,2012

[21] C. Sudhakar, L. Jothi, Int. J. Reser. Rev. Vol. 6, Issue 1, 2349 – 5138, 2019

[22] L. Jothi, G. Vasuki, R. Ramesh Babu, K. Ramamurthi, Optik 125 (2013) 2017- 2021

[23] P. Yasotha, R. Thiyagarajan, P. Sagunthala, Journal of Non – Oxide Glasses, Vol. 8, Issue 1, 29 – 36, 2016

[24] P. Girija, S. Kumaravel, C. Vidya and P. M. Anbarasan, Int. J. Adv. Sci. Eng. Vol. 3 No.3 373 – 3378,2017

[25] P.V. Radhika, K. Jayakumari, C.K. Mahadevan, Int. J. Eng. Reser. and Appl. Vol. 3, Issue 6, 1841 – 1849, 2013.