Research Article

Influence of K_2CO_3 on the Growth and Properties of Sulphanilic acid Crystal

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Abstract

Single crystal of Potassium carbonate (PC) added Sulphanilic acid (SA) has been grown from deionized water as solvent by slow evaporation technique with the vision to improve the properties of the crystal. The objective of this study is to show how inorganic material influence the growth and properties of sulphanilic acid crystals. The crystal system was identified, the difference in the lattice constant between pure and PC added SA crystals have been studied and compared by means of single XRD analysis. Intensity variation in the powder X-ray analysis confirms the inclusion of the PC in pure crystal. The FTIR spectral analysis has been carried out to confirm the presence of various functional groups. The UV transmission spectrum was recorded and its cutoff wavelength is around 269 nm. Addition of 1 mol % PC improves the quality and transmission efficiency. The optical band gap energy of the crystal has also been evaluated. In addition, the sharp PL emission peak at 546 nm in PLE spectrum revealed that, the grown crystal exhibits green shift emission. To study the thermal and mechanical properties, TGA/DTA and Vickers micro hardness test were carried out. The SHG efficiency of the crystal was confirmed using Kurtz and Perry technique

Keywords: *Organic compounds; Crystal growth; Thermal and Optical properties*.

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Introduction

Great efforts have been devoted to the research and design of highly efficient organic nonlinear optical (NLO) materials due to their widespread applications such as high-speed information processing, optical communications and optical data storage [1]. Sulfanillic acid ($NH^{3+}C_6H_4SO_3^-$) exists as zwitterions and find a number of application including non linear optics [2]. The SA crystal displays an anionic part and a cationic part, indicative of the Zwitterionic structure and these units are linked into three-dimensional framework by two distinct two-centre N-H….O hydrogen bonds and a planar three centre N-H…..$(O)_2$ hydrogen bond [3]. In the present investigation Potassium carbonate (PC) added Sulfanilic acid (SA) crystal was grown from slow evaporation technique and subjected to various characterization studies. The crystal system, lattice parameters were identified by X-ray diffraction technique. The presence of various functional groups was confirmed by recording FT-IR spectrum. The transmission range of the grown crystal was determined by UV-Visible analysis. TGA/DTA and Mechanical hardness test were carried out to study thermal and mechanical stability of the grown crystals. The nonlinear optical property of the grown crystal was confirmed by second harmonic generation (SHG) using Q-Switched Nd:YAG laser.

Crystal growth

Crystals of pure and Potassium carbonate (PC) added Sulphanilic acids (SA) were grown by slow evaporation method at room temperature using deionised water as solvent. For the growth of PC added SA crystals 1 mol% of potassium carbonate was added to the homogeneous saturated solution of SA and maintained with continuous stirring for about 3 hours. The solution was filtered to remove any impurities if present and was kept undisturbed. Consecutively, to ensure the slow evaporation the beaker was covered with perforated polythene paper. The transparent colorless single crystals were grown in a span of 15 days. The pure SA crystals were grown from its saturated solution within a period of 11 days. The pure and PC added SA crystals are shown in **Figure 1a** and **1b**.

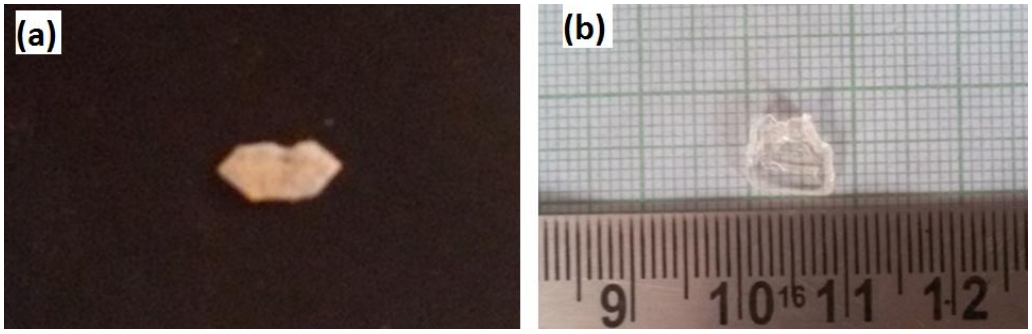

Figure 1 shows (a) pure SA crystal (b) PC added SA crystal.

Results and Discussion

Single X-ray diffraction analysis

Unit cell parameters of the PC added grown crystal was obtained employing Enraf Nonius MACH3-CAT4 single crystal diffractometer with MoKα (λ= 0.717Å) radiation. It was observed that the cell parameters of PC added SA crystal slightly differ (**Table 1**) from those of pure SA crystal reported values [2], which might be attributed to the presence of PC in SA crystals, but both the crystals belongs to orthorhombic crystal system with non-centro symmetric space group P_{21ac}. As non –centrosymmetric nature is one of the basic and essential requirements for the SHG activity [4], the grown crystal finds NLO application.

Table 1 Single crystal XRD result of reported and present study.

Parameter	Reported [5]	Present
a (Å)	7.51	7.43
b(Å)	7.27	6.99
c(Å)	13.89	13.44
V ($Å^3$)	783	756
System	orthorhombic	orthorhombic
Space group	P_{21ac}	P_{21ac}

Powder XRD analysis)

To confirm the crystalline nature of the crystal, powder X-ray diffraction analysis of the sample were carried out by subjecting fine powder of pure and PC added SA crystals to intense X-rays of λ =1.5418 A^0 at a scan speed of 1^0 per minutes in steps, over a 2θ range $4^0 - 80^0$ and are shown in **Figure 2a** and **2b**.The sharp and well defined Braggs peaks at specified 2 θ angles shows the good crystallinity of the crystals. A slight shift in the peak positions and variations in intensity may be due to the added PC, as confirmed by single crystal XRD analysis.

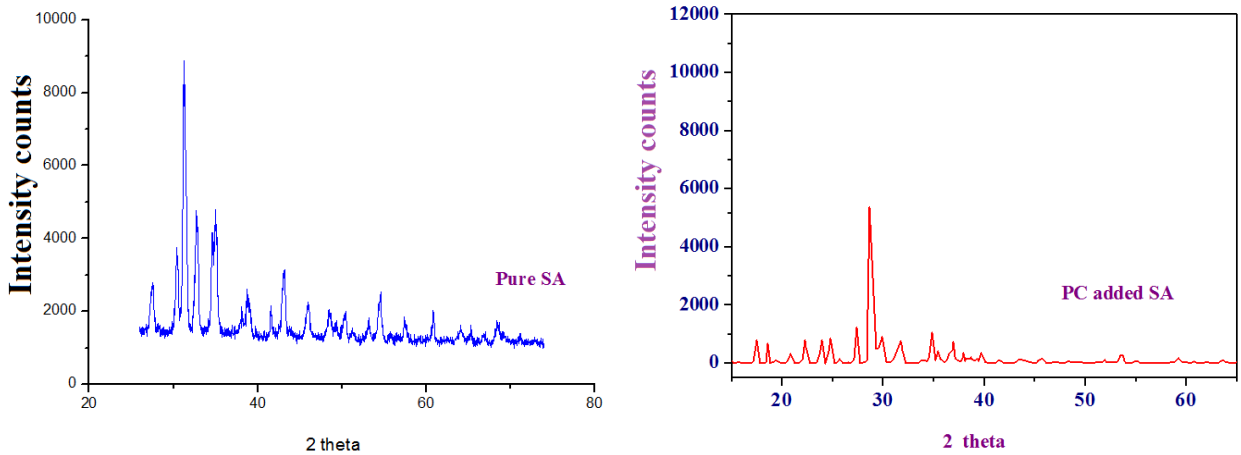

Figure 2 Powder XRD analysis (a) Pure (b) PC added SA crystal.

FT-IR spectral analysis

The FTIR spectrum of PC added SA crystal is shown in **Figure 3**. In the spectrum the band observed at 3488 cm^{-1} is due to N-H stretching vibrations as it occurs in its characteristics region 3522-3420 cm^{-1}. The peaks observed at 2894 cm^{-1}, 2632 cm^{-1} and 1079 cm^{-1}, 1049 cm^{-1} are assigned to C-H and S=O stretching vibrations respectively. The other characteristics vibrations establishing their identity peaks present in the compound are represented in **Table 2**. On comparison with reported SA spectrum [5], the slight shift in frequency is observed for PC added crystal, this may be due the incorporation of potassium carbonate. The appearance of peaks in the characteristics regions of C=O and C-O are also confirms the inclusion of K_2CO_3.

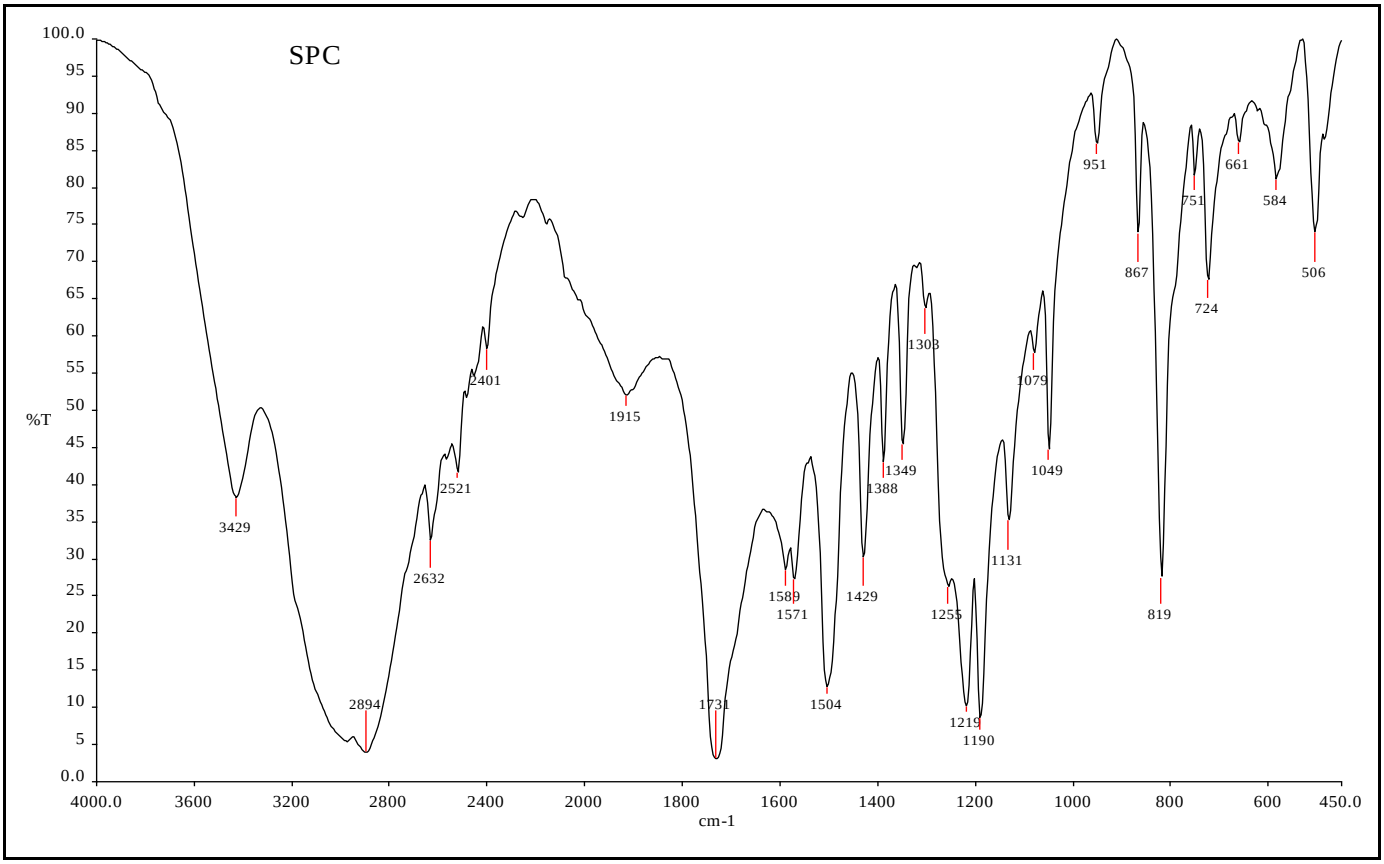

Figure 3 FTIR spectrum of PC added SA.

Table 2 Vibrational assignment.

PC added SA (Frequency cm^{-1})	Band assignment
3488	N-H stretch
2894	C-H stretch
2632	C-H stretch
1731	C=O
1190	C-O
1589, 1571	NH_3 Bending & Scissoring
1504,1429,1388,1349,1303	C=C ring, C-C str
1255, 1219	C-H in plane bending
1131,	NH_2 rocking
1079,1049	S=O str
867,819,751,724	C-H out of plane bending
661	NH_3 twisting

UV transmission analysis

The high transmission property of the crystal in the entire visible region suggests its suitability for SHG applications [6, 7]. The optical transmission spectra for PC added crystal was recorded in the wavelength region from 200 to 1100 nm. The UV absorption edge for the grown crystal is observed around 269 nm as shown in **Figure 4** and has 78% of transmission in the entire visible region where as, it was only 40% for the reported pure SA crystal [8]. So we can infer that the Potassium carbonate enhanced transmission efficiency as well as the quality of the crystal shows i.e. defect concentration in the grown crystal is very low and its suitability for NLO application. The band gap energy was estimated using the relation $E_g=1243\times10^3/\lambda_{max}$ and is found to be 4.6 ev, this wide band gap energy suggest its use for practical application as optical material [9].

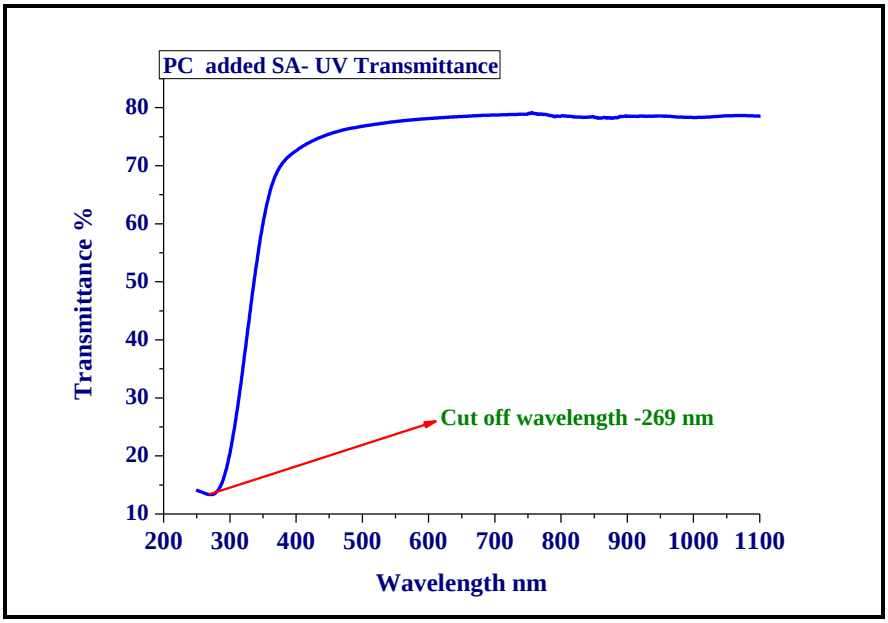

Figure 4 UV transmission spectrum of PC added SA crystal.

Photoluminescence (PL) Studies

Luminescent materials are substances which convert incident energy input into the emission of electromagnetic waves in the Ultra violet, visble or Infrared regions and above that due to black body emission. Photoluminescence, where the Luminescence is stimulated by UV or Visible light, is widely used technique to identify the impurities and finds applications in lighting technologies [10]. It the mechanism through which the excited specimen relaxes to the equilibrium state. Luminescence process is being excited using a beam of light that leads to the creation of an electron-hole(e-h) pair and it may recombine across the gap and emit a photon with energy equal to band gap [11]. The e-h recombination process can be occurred because, excited elcectron and hole cannot remain in their initial excited states for very long instead they can relax very rapidly (approximately 10 -13 ns) to the lowest energy states within their respective bands by emitting phonons [12]. The sample was excited at 269 nm and the emission spectrum was recorded between 400 nm to 650 nm as shown in **Figure 5**. In the present study, PL emission 546nm green emission is an indicative of the charge transfer process as well as tapping of electrons and it is due to the contribution of the shallow holes than the deep holes [13]. Due to such strong PL emission it may find potential application in optoelectronic devices [10] and lighting technologies [11].

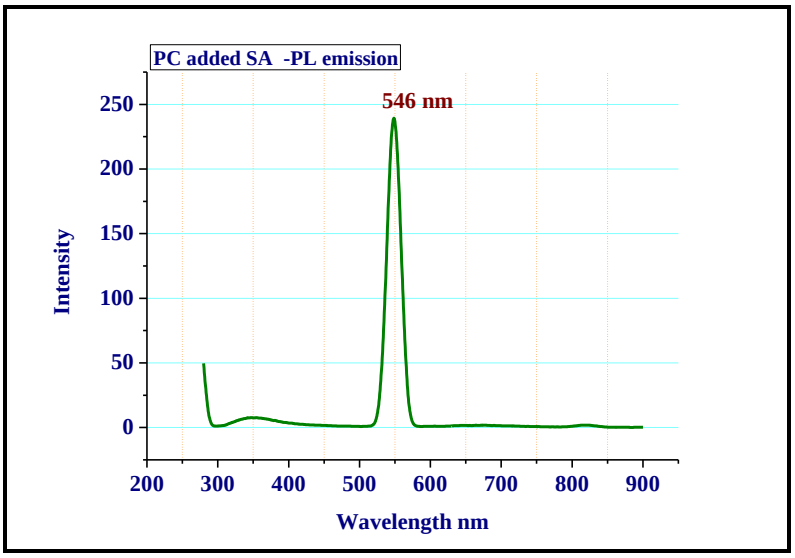

Figure 5 Photoluminescence spectrum of PC added SA crystal.

3.6. Microhardness studies

The good-quality crystals are needed for various applications not only with good optical performance but also with good mechanical behaviour. Hardness of a crystal is due to the resistance offered by a solid to the movement of dislocation, practically which is caused by scratching or indentation [14, 15]. The Vicker's micro hardness number of pure and PC added grown crystals were calculated using the relation $Hv=1.8544\ P/d^2\ kg/mm^2$,where Hv- is Vicker's hardness number, P-is the applied load in kg, d-is the average diagonal length in mm of the indentation mark. The load vs. hardness plot for pure and PC added SA crystals are shown in **Figure 6**. It is observed that for pure SA crystal, the hardness value fluctuate up and down with increase of load from 25 – 300 gm, thus exhibits both normal and reverse indentation effects and for loads above 300 gm, cracks started developing around the indentation marks. Whereas for PC added SA crystal the hardness (H_v) increases with load and saturates (H_v =108 kg/mm^2) for higher loads above 300 gm. When the indenter just touches the surface of the crystal, dislocations are generated in the indenter region, so micro hardness increases initially. Above a particular load i.e. 300gm, the micro hardness attains a constant value due to rearrangement of dislocations and mutual interaction of dislocations [16]. This may attributed to the addition of PC, the higher hardness value (H_v =108 kg/mm^2) indicates the crystalline perfection and the greater stress required to form dislocation.

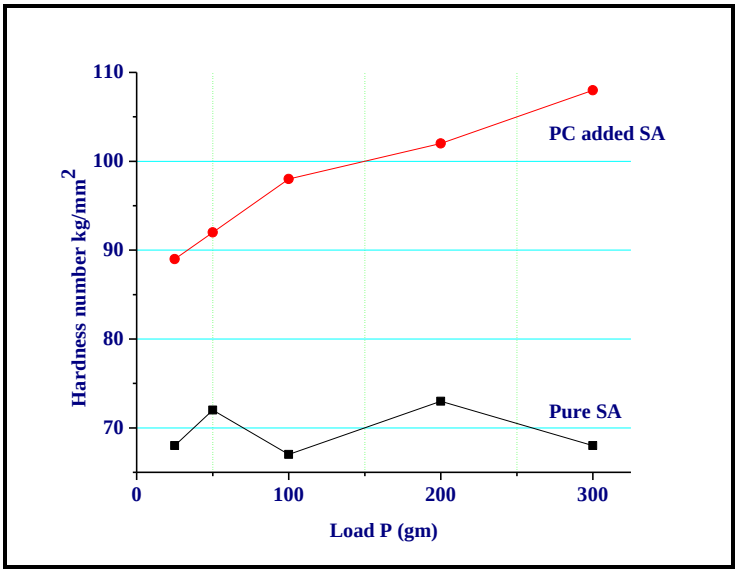

Figure 6 Plot of micro hardness study of pure and PC added crystal.

Thermal Analysis studies

Thermal analysis was used to find out the weight loss (TGA) and energy change (DTA) in the compound with respect to the temperature. In the present study thermal analyzers was carried out on the crushed specimen of PC added SA crystal by employing DTA/TGA analysis at 20 degree celcius/min heating rate in the nitrogen atmosphere shown in **Figure 7**. In the DTA analysis the two endothermic reactions are observed at 80 °C and 203 °C. The major weight loss of about 4.181 mg is observed in the temperature range 176 °C–349 °C, due to the fusion process or decomposition of the sample and is confirmed by its corresponding endothermic peak observed at 203 °C in DTA trace. The next major weight loss due to loss of water is occurred in the range 54 °C–96 °C, as confirmed by the endothermic peak at 79 °C. The sharp peak at 203 °C in DTA trace, shows the melting point of the crystal. The sharpness of the endothermic peak indicates the good crystallinity and purity of the crystal. At the same time the melting point of the PC added SA crystal is found to be greater than that of reported value 173 °C of the pure SA crystal [2]. The DSC analysis carried out in range 40 °C–730 °C in air atmosphere which also matches with above prediction.

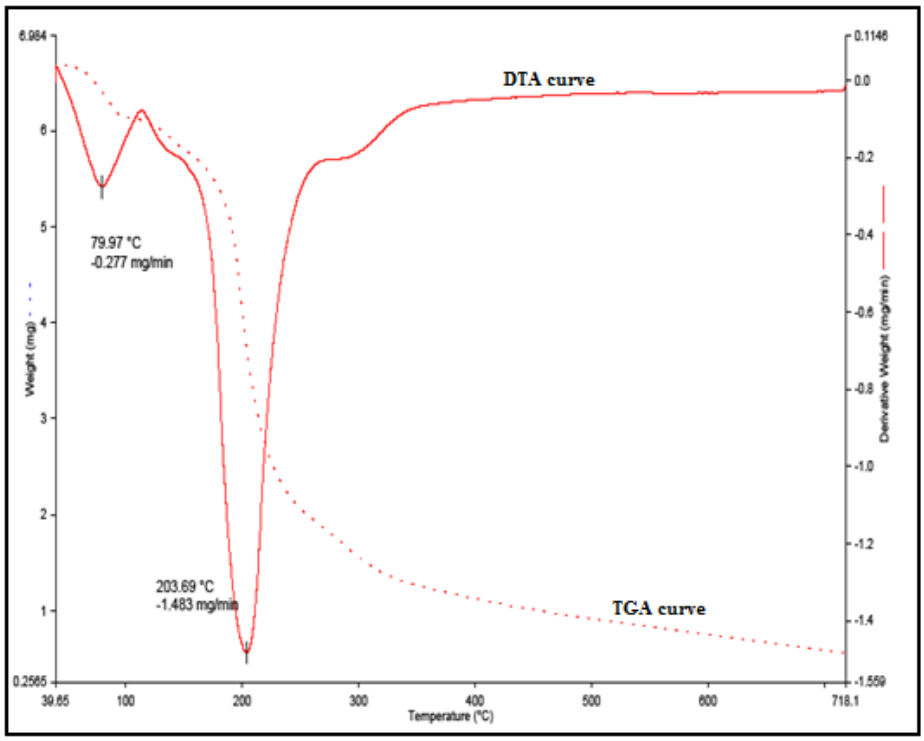

Figure 7 TG/ DTA curves of PC added crystal.

SHG conversion efficiency

The grown crystal was subjected to Kurtz and Perry technique to determine NLO efficiency of the crystal [17]. The crystalline powder was illuminated using Q –switched high energy Quanta ray Nd: YAG laser using first harmonic output of 1064 nm with a pulse width of 10 ns and repetition rate of 10 Hz. The second harmonic signal generated in the crystalline was sample confirmed from emission of green radiation of wavelength 532 nm. The SHG conversion efficiency value was calculated with KDP as a reference material **Table 3**, and is equal to 0.88 times as that of KDP.

Table 3 SHG measurement

Samples	Input Energy (Joules)	OutputEnergy(milli Joules)
PC added SA	0.7	4.46
KDP	0.7	5.03

Conclusion

Potassium carbonate added Sulphanilic single crystals were grown by solution growth technique. The inclusion of potassium carbonate into the crystal lattice was confirmed by powder and single crystal XRD analysis.UV transmission analysis reveals that the PC added SA crystal has wide band gap energy and enhanced transmission efficiency than that of SA crystal, this wide band gap energy suggest its suitability for NLO application. Microhardness study, confirm that the addition of PC increased the hardness value of the crystal. The decomposition stages of PC added SA crystal were analyzed using TGA/DTA curves and has a higher melting 203 0 C; hence, it suggests the application limit. From the characterization results, it is observed that the PC added SA crystal is a potential material for optical application.

Acknowledgement

The authors are thankful to Prof. P. K. Das, IISc, Bangalore, India for the SHG test. They also express their gratitude to the authorities of SAIF, IIT, Chennai, India, ACIC St. Joseph's College, Trichy, India and Cochin University, STIC, Kerala, India for providing thermal analysis facilities, to undertake this study.

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Publication History
Received 15th Jun 2016
Accepted 20th Jul 2016
Online 30th Sep 2016