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CRYSTAL NUCLEATION, CRYSTAL GROWTH, SPECTRAL AND SHG STUDIES OF POTASSIUM IODATE CRYSTAL

P. Geneva Sequirea Roche*, A. Lesly Fathima & P. Selvarajan*****
* Department of Physics, Science and Humanities, Jayaraj Annapackiam CSI College of engineering, Nazareth, Tamilnadu
** Department of Physics, Holy Cross College, Nagercoil, Tamilnadu
*** Department of Physics, Aditanar College of Arts and Science, Tiruchendur, Tamilnadu

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Abstract:

Solution growth was adopted to grow crystals of potassium iodate and here AR grade chemicals of potassium chloride and iodic acid were used in the crystal growth experiment. The grown crystals were observed to be transparent and slightly hygroscopic. The solubility study has been carried out in the temperature range 30° C-60° C in water and it is found that the sample has positive temperature coefficient of solubility. The critical nucleation parameters were evaluated by nucleation kinetic studies. The lattice constants of the grown crystal of potassium iodate were found by XRD method and the crystallizes in triclinic system. The presence of the functional groups in the sample was confirmed by FTIR and FT-Raman methods. The nonlinear optical property of the grown crystal was confirmed by Kurtz-Perry powder technique and a study of its Second Harmonic Generation (SHG) efficiency in comparison with potassium dihydrogen phosphate (KDP) has been made.

Key Words: Crystal Growth, Solution Method, Nucleation Kinetics, Characterization, NLO, XRD, SHG & Spectroscopy

1. Introduction:

Light is important in nature and the study of light is known as optics. There are mainly two branches of optics viz., linear optics and nonlinear optics. The nonlinear optics has been recognized as the promising field which has significant applications in the fields of laser technology, communication technology, optical computing technology and opto-electronic technology [1-3]. There has been a lot of interest in growing varieties of nonlinear optical (NLO) crystals such as organic, inorganic and semiorganic crystals. The important factors for selecting materials depend not only on laser conditions but also on the physical properties of the crystals such as transparency, damage threshold, conversion efficiency, temperature and mechanical stability [4-8]. Organic materials has some drawbacks like low hardness, low thermal and mechanical stability but inorganic NLO crystals have high melting point and high degree of chemical inertness. Some of the useful inorganic NLO crystals discovered are $LiNbO_3$, $KNbO_3$, Potassium Dihydrogen Phosphate (KDP), Potassium Titanyl Phosphate (KTP), Barium Borate etc and many these crystals are the successful frequency doublers, mixers and parametric generators to provide coherent laser radiation at high efficiency. Considerable theoretical and experimental investigations have been done in order to understand the microscopic origin of nonlinear behavior of inorganic NLO materials [9-12]. The phenomenon of Second Harmonic Generation (SHG) in an inorganic material was first reported [13] in 1961, which led to the development of recent NLO materials such as inorganic systems, semiconductors and inorganic photorefractive crystals and these are covalent and ionic bonded in which the optical nonlinearity is considered as the bulk effect. Inorganic NLO crystals are being grown by many crystal growth methods such as solution growth, melt growth and vapour growth. Metal iodates are known to be interesting second order and third order NLO materials and some research works on iodate type crystals have been reported literature [14-16]. It is reported that potassium iodate crystal shows the significant nonlinear optical effects [17, 18] and it is a ferroelectric compound undergoing four temperature dependent phase transitions between 110 K - 540 K [19]. The crystal structure of potassium iodate crystal has been solved as triclinic structure in a distorted perovskite-type structure [20]. Since detailed studies on spectral, NLO and other properties of potassium iodate crystals are not found in literature, the inorganic potassium iodate crystal was considered in this work for the growth and different characterization studies.

2. Experimental Methodology:

AR grade potassium chloride and iodic acid chemicals were purchased commercially and they were taken in 1:1 molar ratio. The reactants were dissolved in double distilled water to prepare the saturated solution. Using a hot plate magnetic stirrer, the solution was stirred well for two hours for uniform mixing and at the same time the solution was heated at 50 °C. The synthiesized salt of potassium iodate was obtained in accordance with the following chemical equation

$$KCl + HIO_3 \rightarrow KIO_3 + HCl$$

The saturated solution was prepared using the synthesized salt and double distilled water and it was taken in a growth vessel covered with a perforated paper for slow evaporation. Re-crystallization was carried out

for further purification and to get good quality crystals. It took about 25-30 days to harvest the crystals of potassium iodate and it is to be mentioned here that the solubility of the solution was altered by adding some amount of ethanol (10 ml) into 100 ml of the aqueous solution of the reactants during the stirring of the solution. The harvested crystal of potassium iodate is shown in the figure 1 and the grown crystal is found to be colourless and transparent. The solubility of the grown crystal of potassium iodate was measured at different temperatures by gravimetrical method [21]. The grown crystal was crushed into powder and it was added in 50 ml of double distilled water taken in a beaker kept on the hot plate of magnetic stirrer and saturated solution was prepared. Then, 10 ml of the solution was pipetted out in a petri dish and it was warmed up till the solvent was evaporated out. By measuring the amount of salt present in the petri dish, the solubility of potassium iodate in double distilled water was determined. The solubility curve for potassium iodate crystal is shown in Fig 2. From the graph it is observed that the solubility of potassium iodate in water increases with temperature, showing positive temperature coefficient of solubility. The solubility diagram is divided into three regions viz. (i) saturation region is along the curve; (ii) supersaturation region is above the curve and (iii) under saturation is below the curve. The solubility diagram is used to prepare saturated and supersaturated solutions at a particular temperature and these data could be used to carry out nucleation kinetic studies of the sample.

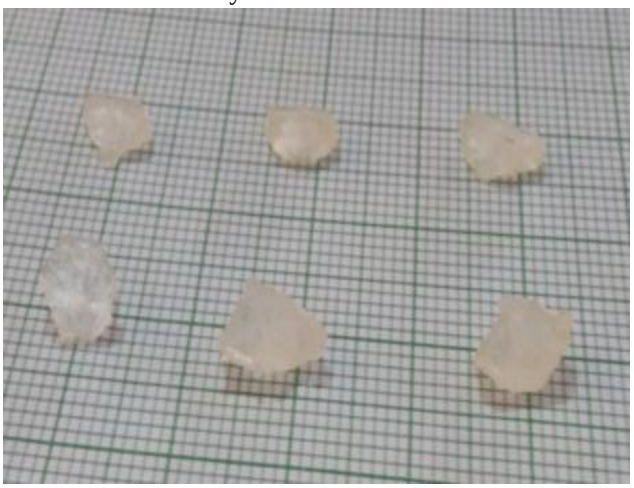

Figure 1: The grown crystals of potassium iodate

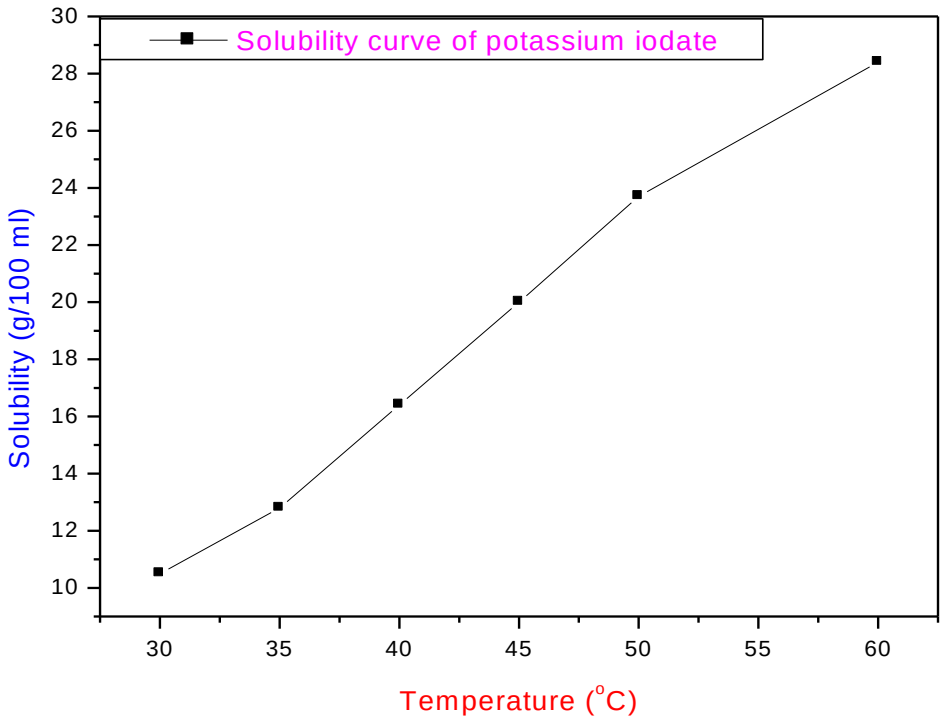

Figure 2: Variation of solubility of with temperature for potassium iodate

3. Results and Discussions:

3.1 Critical Nucleation Parameters of Potassium Iodate Crystal:

It is known that saturated solution is converted into supersaturated solution due to slow evaporation or slow cooling. After supersaturation of the solution is formed, few atoms, ions or molecules join together in the supersaturated solution and it is called a crystal nucleus or a cluster. The overall excess free energy change between the nucleus and solute in the supersaturated solution is called as Gibbs free energy change (ΔG) and it is sum of surface free energy change and volume free energy change. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The Gibbs free energy will be maximum for a certain value of radius (r^*) of nucleus, which is known as critical radius and the corresponding nucleus is called the critical nucleus. Nuclei formed with radius greater than critical radius are stable and its free energy decreases by growing. The time interval in which the observation of the first sparkling particle in the undisturbed supersaturated solution is called the induction period (τ). The induction period can be measured by isothermal method for different values of supersaturation ratio $S = C/C_o$ where C is the supersaturated concentration and C_o is the saturated concentration. For the measurement of induction period, isothermal method was used at the selected supersaturation ratios viz., 1.15, 1.18, 1.21, 1.24 and 1.27 at the constant temperature of 30 ^oC. Using these values, the critical nucleation parameters such as Gibbs free energy (ΔG^*), critical radius, interfacial tension (σ), the number of molecules in the critical nucleus (n) and the nucleation rate (J) were determined [22-24]. The nucleation rate (J) can be calculated using the equation $J = A \exp[-\Delta G^*/(kT)]$ where A is the pre-exponential factor. The variation of induction period with supersaturation ratio is shown in the figure 3. The results show that the induction period increases with increase of supersaturation ratio. The variations of the critical nucleation parameters with supersaturaiton ratio are presented in the figures 4-7. From the results it is noticed that the nucleation parameters such as radius of critical nucleus, Gibbs' free energy change, and number of molecules in the critical nucleus decrease with supersaturation ratio. The nucleation rate is observed to be increasing with the increase of supersaturation ratio. If the nucleation rate is low, the formation of multi-nuclei in the solution will be less and hence big-sized crystals could be grown. Interfacial energy at the solution crystal interface is a crucial parameter involved in theories of nucleation and crystal growth. The value of interfacial energy is found to be 1.758×10^{-3} J / m^2 for potassium iodate crystal. The interfacial energy plays a vital role in the nucleation mechanism. The stability and velocity of crystal growth depends on several crucial parameters such as temperature, the degree of supersaturation, concentration of impurities existing in the solution. The number of crystal nuclei produced per unit volume per unit time in the supersaturated solution is expressed as nucleation rate and the variables that affect the nucleation rate are pH, supersaturation, temperature and interfacial tension of the solution. Decrease in induction period is expected to increase the nucleation rate. The present study confirms that the evaluated nucleation parameters are feasible for the growth of bulk sized single crystals of potassium iodate.

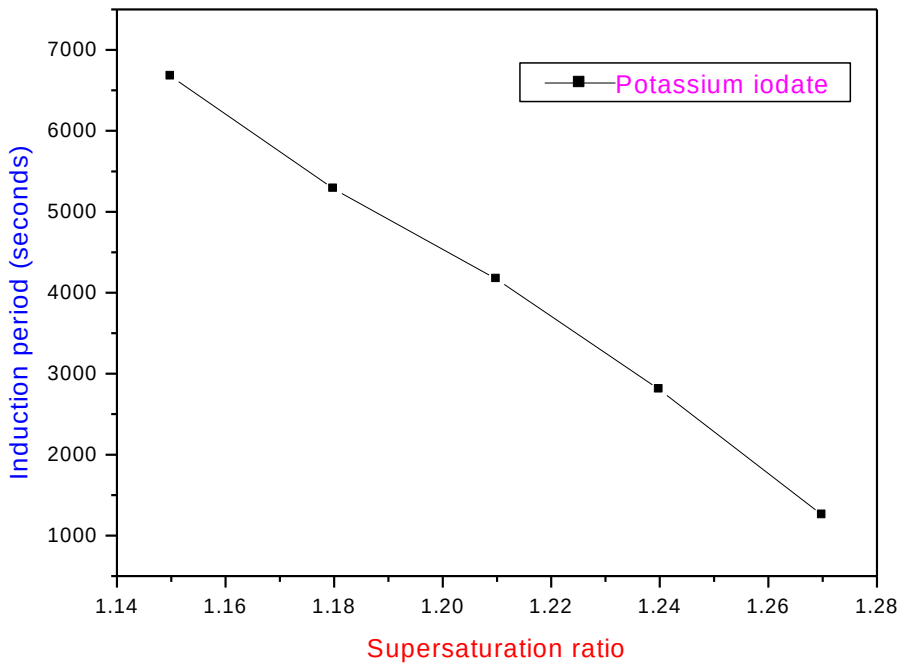

Figure 3: Variation of induction period with supersaturaion ratio for potassium iodate crystal

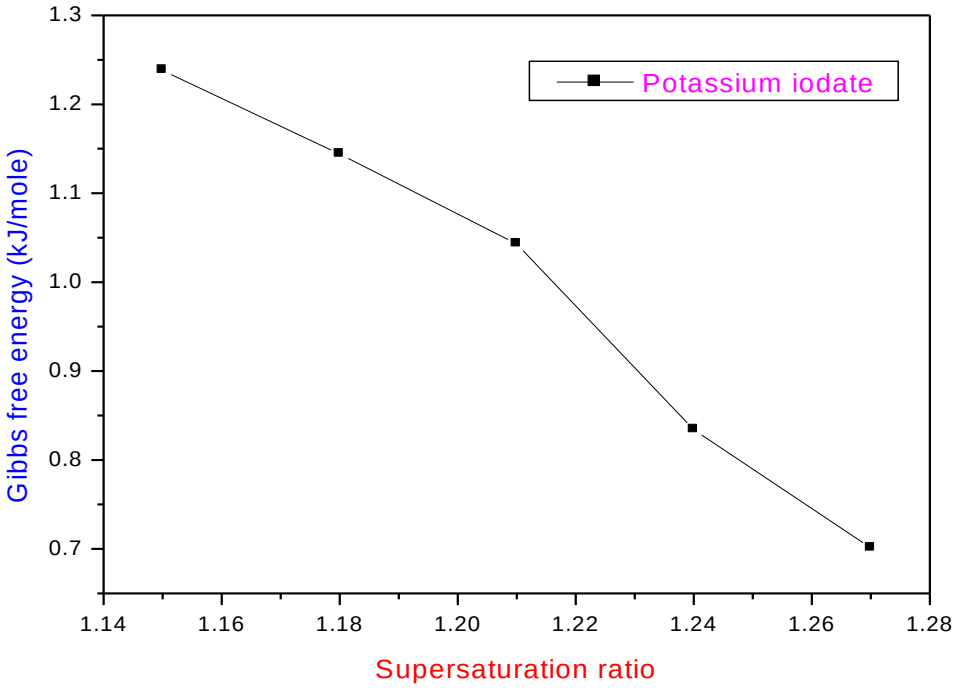

Figure 4: Variation of Gibbs free energy change with supersaturaion ratio for potassium iodate crystal

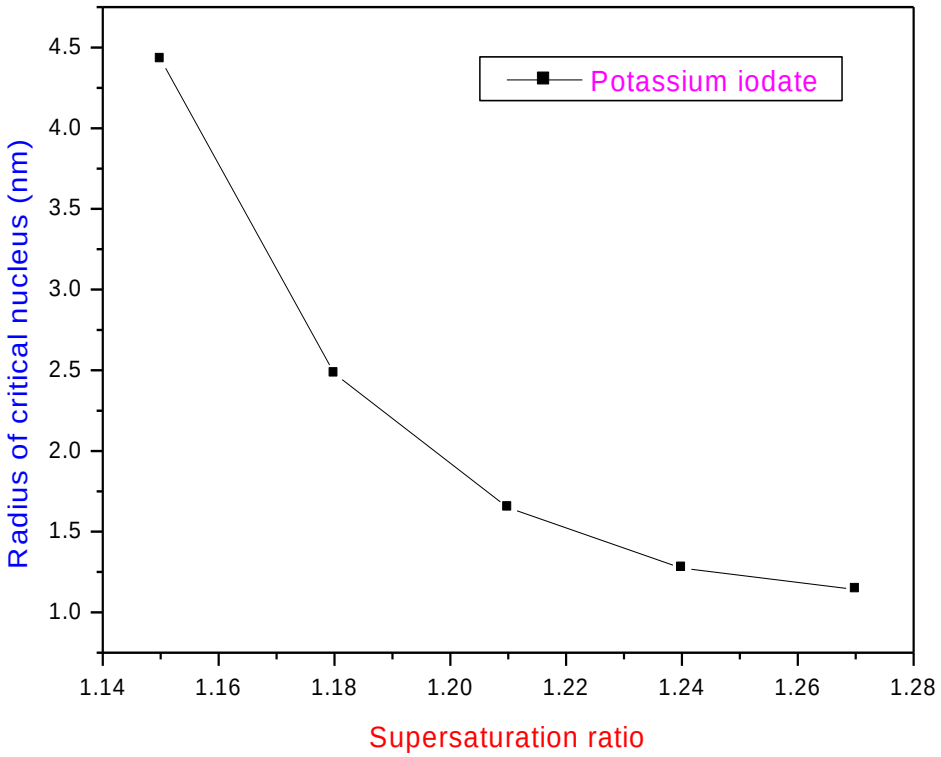

Figure 5: Variation of radius of critical nucleus with supersaturaion ratio for potassium iodate crystal

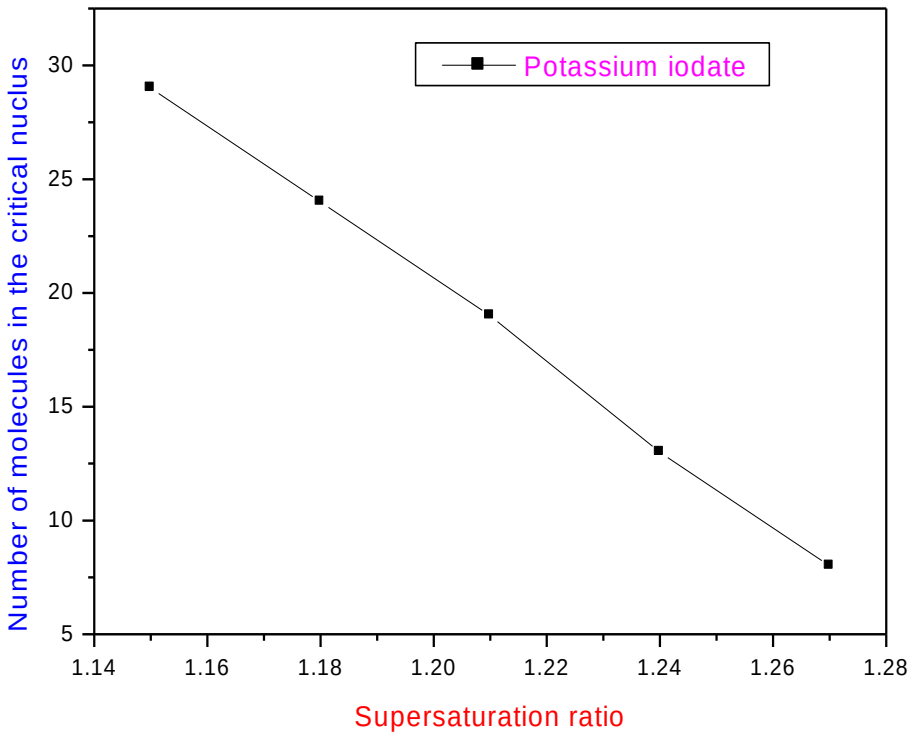

Figure 6: Variation of number of molecules in the critical nucleus with supersaturaion ratio for potassium iodate crystal

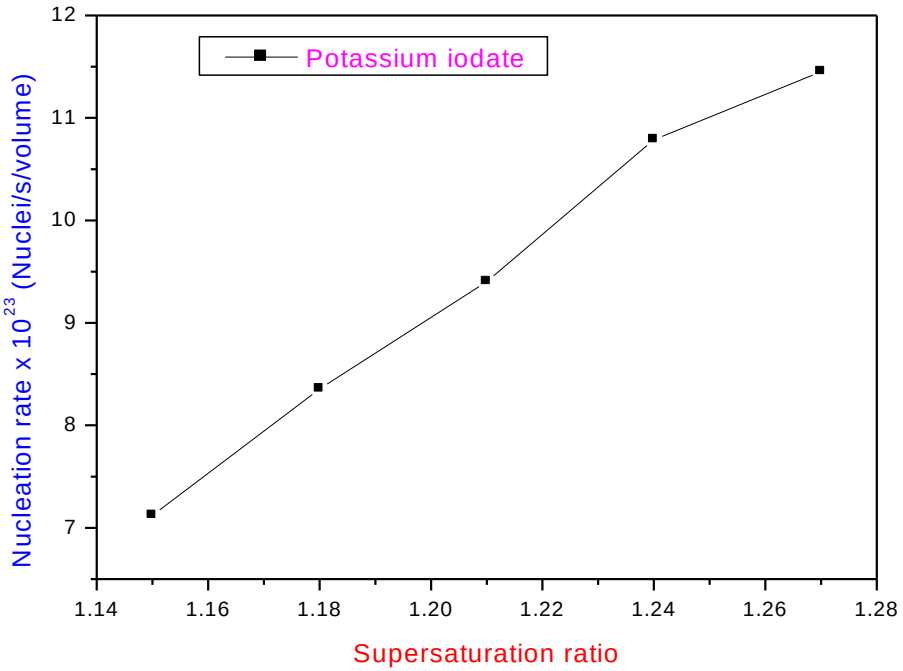

Figure 7: Variation of nucleation rate with supersaturaion ratio for potassium iodate crystal

3.2 X-Ray Diffraction Analysis:

The grown potassium iodate crystal was subjected to single crystal X-ray diffraction study using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_{α} (λ=0.71069 Å) radiation to evaluate the lattice parameters and the obtained data for the potassium iodate crystal are presented in Table 1. From the data, it is

ascertained that the grown potassium iodate crystal belongs to triclinic system [20]. It is to be mentioned here that this crystal crystallizes in the non-centrosymmetric space group P1.

Table 1: Single crystal XRD data of potassium iodate crystal

Molecular formula	KIO_3
Crystal Color	Colourless, transparent
Unit cell parameters	a = 7.685(4) Å
	b = 7.726(5) Å
	c = 7.791(2) Å
	$\alpha = 108.74\ (3)^o$
	$\beta = 107.94\ (4)^o$
	$\gamma = 109.82\ (2)^o$
Volume of the unit cell	439.93 (2)
Crystal system Space group	Triclinic P1
Diffractometer	Bruker-Nonius MACH3/CAD4
Radiation wavelength	Mo K_α , λ=0.71069 Å

The powder XRD pattern of potassium iodate crystal was recorded in the range 10^o-80^o at a rate of 10^o/min using a powder X-ray diffractometer with CuK_α radiation and it is shown in the figure 8. The various planes of reflections observed in XRD pattern were indexed by using INDEXING software package following the procedure of Lipson and Steeple [25]. Well-defined peaks at specific 2θ values indicate high crystallinity of the grown crystal. The lattice parameters of the potassium iodate crystal were also obtained from the XRD peaks using the UNIT CELL software package. The lattice parameters obtained from powder XRD method are a= 7.673 Å, b= 7.735 Å, c= 7.797 Å, $\alpha=108.42^o$, $\beta= 107.89^o$ and $\gamma=109.81^o$ and are found to agree well with those observed through single crystal XRD study. The crystallographic parameters such as 2θ, d-spacing, relative intensity and the (h k l) values are given in table 2.

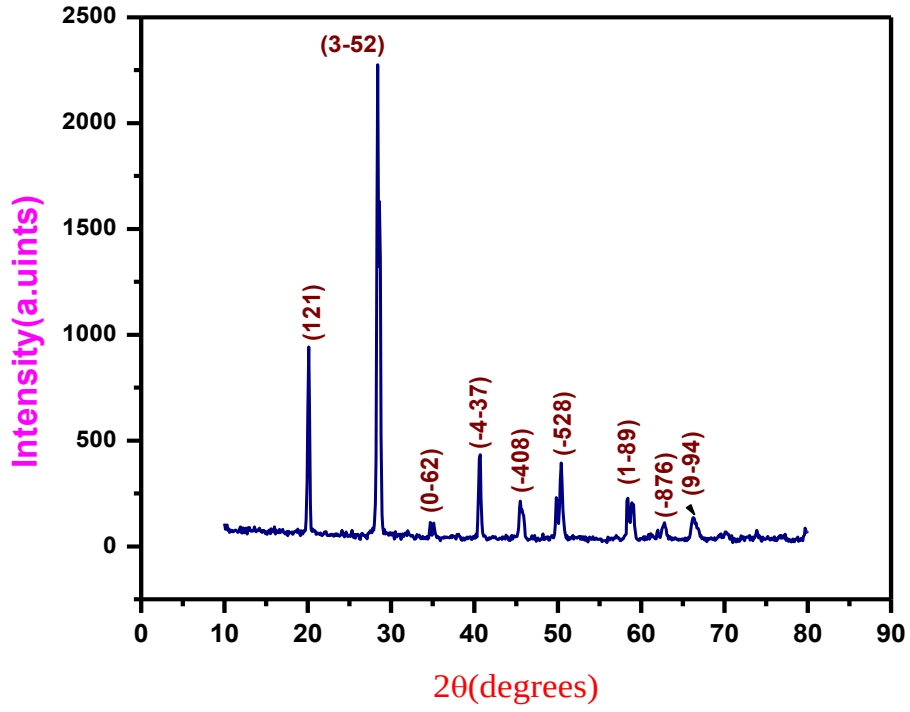

Figure 8: Powder XRD pattern of potassium iodate crystal

3.3 FTIR and FT-Raman Spectral Analyses:

FTIR spectrum of the sample was recorded in KBr matrix using Perkin Elmer Fourier Transform Infrared spectrometer (Model: Spectrum RXI) in the wave number range 400 to 4000 cm^{-1} and it is presented in the figure 9. The recorded FT-Raman spectrum of potassium iodate crystal is shown in the figure 10. It is observed from the spectrum that there is no water of crystallization in the lattice of the crystalline sample of potassium iodate. This study suggests a symmetrical pyramidal structure of the IO_3 anions. The band due to vibrations between metal, iodine and oxygen at 771 cm^{-1} is noticed. The various fundamental frequencies of

metal and iodate vibrations are observed in the range 700 – 800 cm^{-1}. The fundamental vibrational frequencies (ν_1, ν_2, ν_3 and ν_4) due to I = O vibrations are observed from the spectra [26, 27] and they are provided in the table 3.

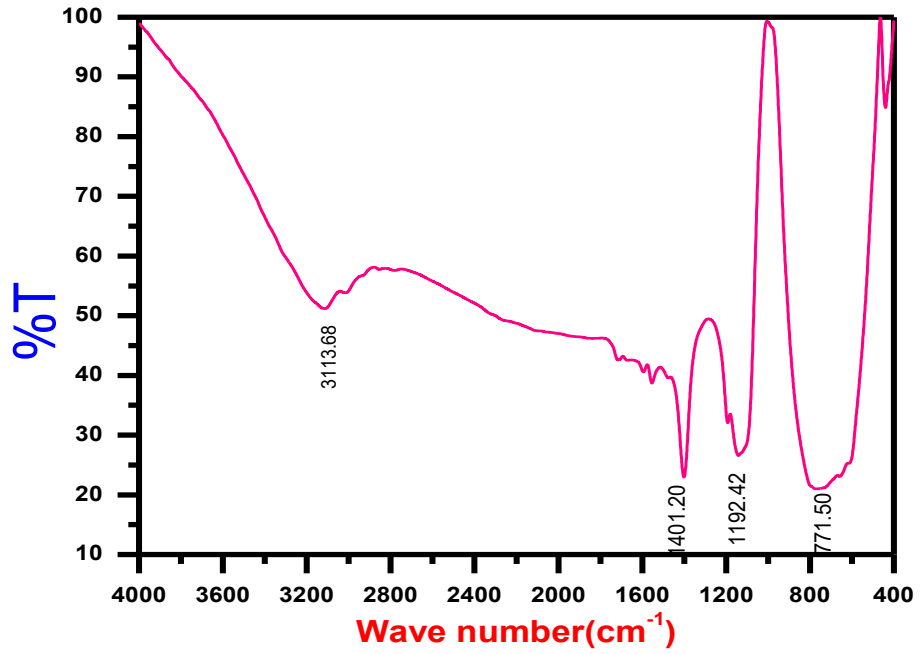

Figure 9: FTIR spectrum of potassium iodate crystal

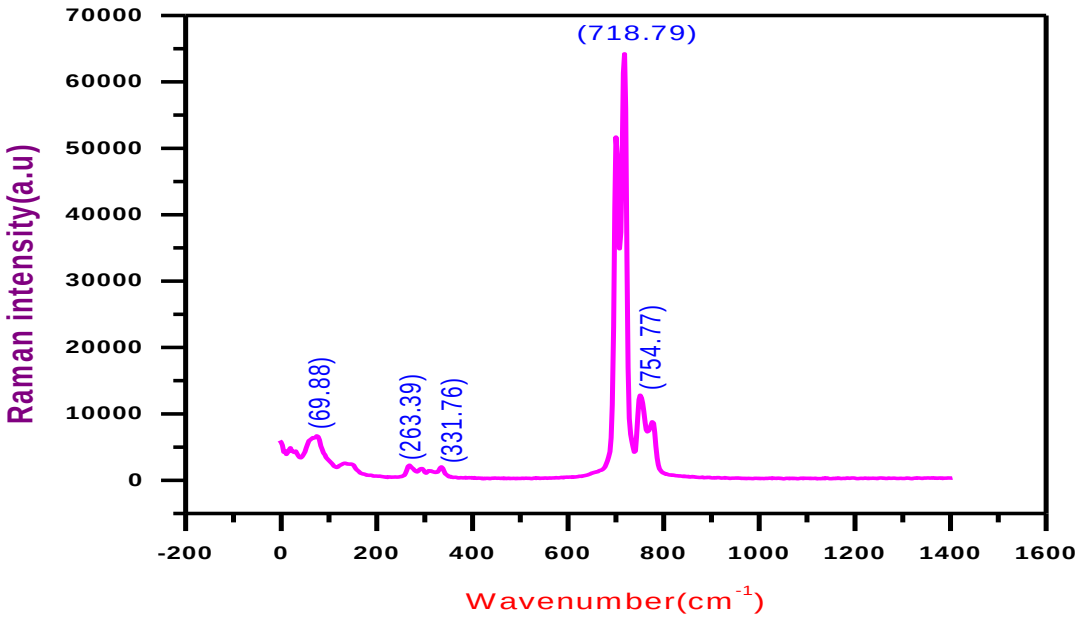

Figure 10: FT-Raman spectrum of potassium iodate crystal

Table 3: Important wave numbers observed and their assignments of FTIR and FT-Raman spectra for potassium iodate sample

S.No	FTIR(cm^{-1})	FT-Raman (cm^{-1})	Band Assignments
1	3113.68	-	OH stretching due to moisture
2	1401.20	-	K-I vibarational mode
3	1192.42	-	K-I vibrational mode
4	1141.20	-	K-I vibrational mode

5	771.50	754.77	I= O stretching vibration (ν_1)
6	-	718.79	I = O stretching mode (ν_3)
7	-	331.76	I= O bending mode (ν_4)
8	-	263.39	I = O bending mode (ν_2)

3.4 SHG Studies:

The second harmonic generation (SHG) test was performed to find the NLO property of potassium iodate crystal and it was carried out by powder Kurtz and Perry technique [28]. The powdered sample was illuminated using Spectra Physics Quanta Ray DHS2-Nd: YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repetition rate 10 Hz. The second harmonics signal, generated in the crystal was confirmed from the emission of green radiation by the crystal. The SHG radiations of 532 nm green light was collected by a photomultiplier tube and the optical signal incident on the PMT was converted into voltage output at the CRO. Second harmonic output of 7.26 mJ was obtained from the sample for an input energy of 0.70 J. The powdered potassium dihydrogen phosphate (KDP) was used as the reference material in the SHG measurement and the output was found to be 8.91 mJ. Thus, the relative SHG efficiency for potassium iodate crystal is found to be 0.815 times that of KDP sample. The obtained values of SHG for potassium iodate are provided in the table 4.

Table 4: Values of SHG data for potassium iodate

S.No	Name of the Sample	Output Energy (milli joule)	Input Energy (joule)
1	Potassium iodate	7.26	0.70
2	KDP (Reference)	8.91	0.70

4. Conclusions:

Single crystals of potassium iodate were grown by solution growth technique. Solubility of the sample was found at different temperatures. The unit cell parameters of potassium iodate were confirmed by X–ray diffraction analysis. The critical nucleation parameters such as Gibbs free energy, interfacial tension, critical radius, nucleation rate of potassium iodate have been determined The functional groups present in the crystal were confirmed by FTIR and FT-Raman studies. The SHG efficiency was confirmed and found to be 0.815 times that of KDP.

5. Acknowledgement:

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