Growth and studies of picric acid doped potassium iodate crystals

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ABSTRACT *Picric acid doped potassium iodate (PAPI) crystals were synthesized and grown in the form of single crystals by solution method. Solubility of the sample in water has been measured by gravimetric method. The functional groups of picric acid doped potassium iodate crystal were found by FTIR spectral method. The various elements in the grown crystal were identified by EDAX technique. Second order NLO studies were carried out by Kurtz-Perry powder technique. Linear optical studies were performed by recording the transmittance and absorption spectra of PAPI crystal and optical band gap was evaluated. Thermal stability, endothermic and exothermic analysis was done by carrying out TG/DTA studies of the grown crystal.*

Keywords: *Single crystal; solution method; doping; XRD; FTIR; TG/DTA; band gap; transmittance; SHG; NLO*

1.Introduction

It is well known that the nonlinear optical (NLO) crystals are useful in the fields of optical communication, fibre optics, optical computing, optical data processing and optical storage etc because these crystals can generate UV and visible laser light. Among NLO crystals, most of organic NLO crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency. But the inorganic NLO materials have excellent mechanical and thermal properties, but have relatively moderate optical nonlinear property because of the lack of extended π-electron delocalization [1-3]. Some of the interesting inorganic NLO crystals are $LiNbO_3$, $KNbO_3$, Potassium Dihydrogen Phosphate (KDP), Potassium Titanyl Phosphate (KTP), and many of 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 [4-6]. Metal iodates like potassium iodate, sodium iodate, lithium iodate etc are the useful inorganic NLO materials[7-9]. It is reported that potassium iodate crystal shows the significant nonlinear optical effects and it is a ferroelectric compound undergoing four temperature dependent phase transitions between 110 K - 540 K [10, 11]. The crystal structure of potassium iodate crystal has been solved as triclinic structure in a distorted perovskite-type structure [12]. From the literature survey, it is observed that many dopants like organic and metal dopants have been added into many NLO crystals to modify their properties [13-15]. Keeping this in mind, an organic dopant like picric acid has been added into the lattice of potassium iodate to alter its properties. Picric acid is an yellow crystalline solid with bitter taste, soluble in water, alcohol, chloroform and the presence of three electron withdrawing nitro groups in the picric acid makes it as a good acceptor for neutral carrier donor molecule [16,17]. The aim of this investigation is to grow picric acid doped potassium iodate (PAPI) crystals and the results obtained from the various studies of the grown crystals are discussed in this paper.

2. Synthesis, growth and solubility

AR grade chemicals such as potassium chloride, iodic acid and picric acid were procured from Merck India. To synthesize the undoped and picric acid doped potassium iodate salts, two different borosil beakers were used. To obtain the undoped potassium iodate salt, potassium chloride and iodic acid were taken in 1:1 molar ratio. For the doped sample, 2 mole% of picric acid was added into the solution of potassium iodate. In the synthesis and growth process, double distilled water was used as the solvent. Saturated solutions of undoped and doped samples were prepared and using a hot plate magnetic stirrer, the solutions were stirred well separately for two hours and the solutions were heated at 50 ^{o}C for synthesis of the samples. Using the synthesized samples and water, the saturated solutions were again prepared and these solutions were taken in two different growth vessels covered with the perforated sheets for slow evaporation. Re-crystallization was carried out for further purification of the samples. Single crystals of undoped and picric acid doped potassium iodate were grown by slow evaporation technique after a growth period of 30 days. The photograph of the harvested picric acid doped potassium iodate (PAPI) crystal is displayed in the figure 1. The obtained crystal is observed to be yellow in colour and transparent. For measurement of solubility, the saturated aqueous solutions of the samples were prepared and the solubility of unodped and picric acid doped potassium iodate was measured gravimetrically at different temperatures. The solubility curves for both the samples are shown in Fig 2. From the graph it is observed that the solubility of both the samples in water increases with temperature, showing positive temperature coefficient of solubility. It is noticed that the solubility is more for PAPI crystal than that of undoped potassium iodate crystal.

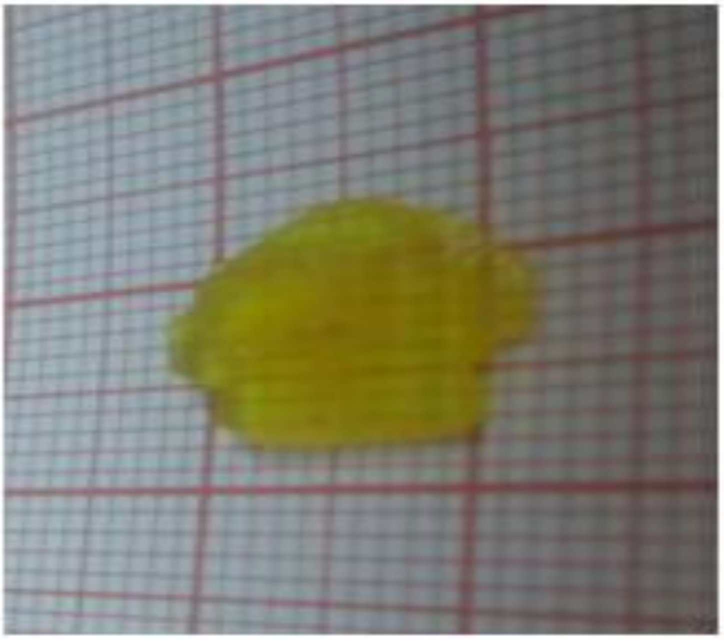

Fig.1. The harvested crystal of picric acid doped of potassium iodate

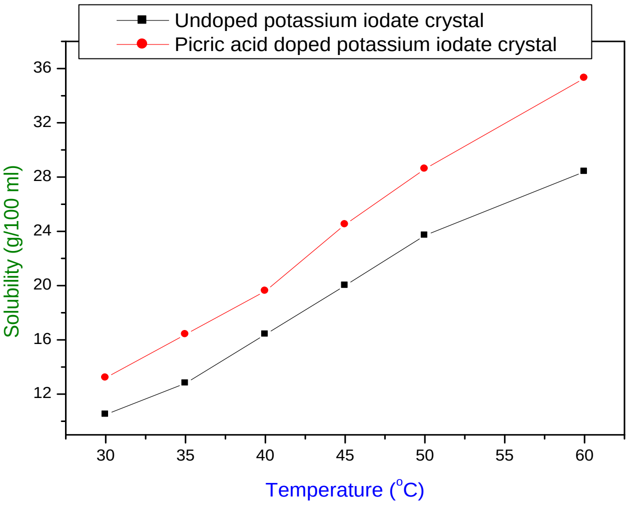

Fig.2. Solubility curves for undoped potassium iodate and picric acid doped

potassium iodate crystals

3.Resutls and discussion

3.1 Identification of functional groups

Infrared spectroscopy can be used to identify the functional groups of the samples and it deals with the study of virbrational spectra of molecules. The vibrational frequencies, their relative intensities and shapes of the infrared bands are used for the qualitative characterization of the samples. Fourier transform infrared (FTIR) method is based on the blending of a Michaelson interferometer with a sensitive infrared detector and a digital computer and an FTIR spectrometer has higher resolution, total wavelength coverage, higher accuracy in frequency and intensity measurements. FTIR spectrum of picric acid doped potassium iodate (PAPI) crystal was recorded using a Perkin Elmer FTIR spectrometer (Model: Spectrum RXI) in the wave number range 400 to 4000 cm^{-1} by KBr pellet technique and it is presented in the figure 3. The absorption peaks at 3445 cm^{-1} and 3084 $cm^{-1}$are corresponding to OH stretching and this indicates that there is water of crystallization in the lattice of the crystalline sample of picric acid doped potassium iodate. The peaks at 2923 cm^{-1} and 2853 cm^{-1} are due to CH stretching. The band at 1630 cm^{-1} is due to stretching of COO^- group of picric acid. The absorption peak at 747 cm^{-1} is corresponding to I=O stretching vibration. The various fundamental frequencies of metal and iodate vibrations are observed in the range 700 – 500 cm^{-1}. The FTIR spectral assignments to various absorption peaks/bands of spectrum of picric acid doped potassium iodate crystal are given in the table 1.

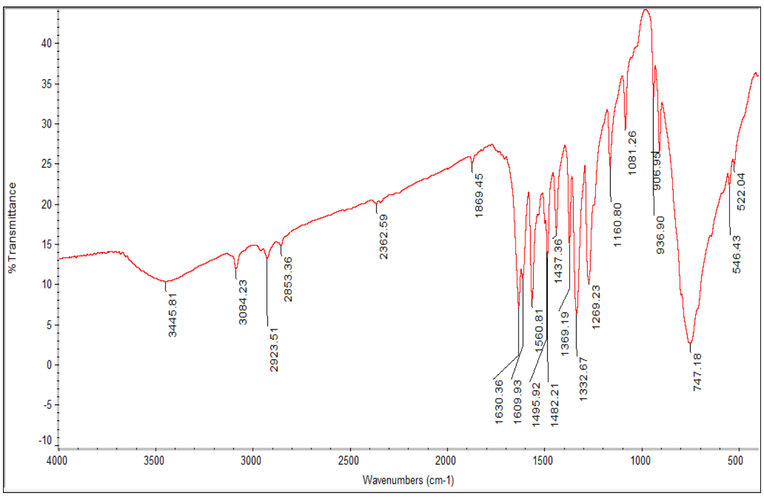

Fig.3. FTIR spectrum of picric acid doped potassium iodate crystal

Table 1: FTIR spectral assignments for picric acid doped potassium iodate crystal

Sl.No.	FTIR peaks/bands (cm^{-1})	Assignments
1.	3445	OH stretching
1	3084	OH stretching
2	2923	CH stretching
3	2853	CH stretching
4	1630	COO^- stretching
5	1482	K-I vibarational mode
6	1332	K-I vibrational mode
7	1269	K-I vibrational mode
8	747	I= O stretching vibration
9	546	I = O bending mode
10	522	I= O bending mode

3.2 UV-visible spectral studies

UV-visible spectroscopy is used to find the transmittance, absorbance, optical band gap and other linear optical parameters. The UV-visible spectrum of PAPI crystal was recorded using a UV-vsible spectrophotometer (Shimadzu UV-1061 make) in the wavelength range 190-1100 nm covering the near, visible, near infrared region to find the transmission range and to find the suitability of the sample for optical applications. Optically polished crystal PAPI with the thickness of about 1.2 mm was used for recording the transmittance and absorbance spectra of the sample and the recorded spectra are shown in the figures 4 and 5. From the both the spectra, the lower cut-off wavelength of picric acid doped potassium iodate crystal is approximately 485 nm. The absorbance in the wavelength range 300-370 nm is due to $\pi-\pi^*$ transitions of carboxylic group. Absorbance is a measure of the capacity of a crystal to absorb light and it is equal to the logarithm of the reciprocal of the transmittance. To find the optical band gap of the sample, Tauc's plot is drawn using the Tauc's equation as given by $(\alpha h\nu)^n = A\,(h\nu - E_g)$ where E_g is optical band gap of the crystal, ν is the frequency of light, h is the Planck's constant, α is the absorption coefficient (α) and A is a constant depending on the material. Here is n = 2 for a direct band gap material and n=1/2 for an indirect band gap material [18]. Since the Tauc's equation satisfies for n=1/2, picric acid doped potassium iodate crystal belongs to the indirect band gap material. Hence the Tauc's plot is drawn between $(\alpha h\nu)^{1/2}$ and hνand it is shown in the figure 6. From the graph, it is found that the value of optical band gap of picric acid doped potassium iodate (PAPI) crystal is 2.56 eV.

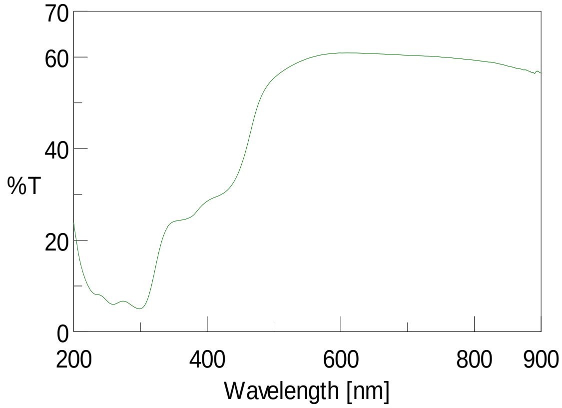

Fig.4.Transmittance spectrum of picric acid doped potassium iodate crystal

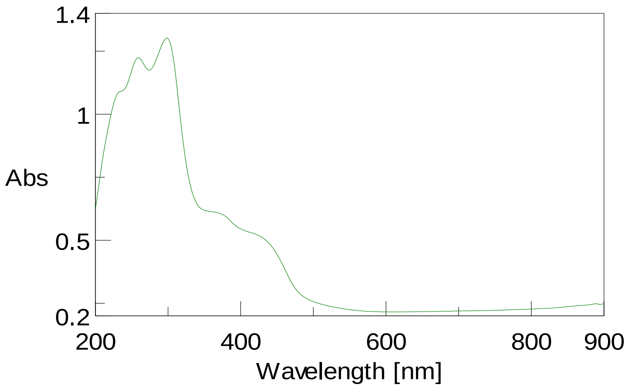

Fig.5. Absorbanc spectrum of picric acid doped potassium iodate crystal

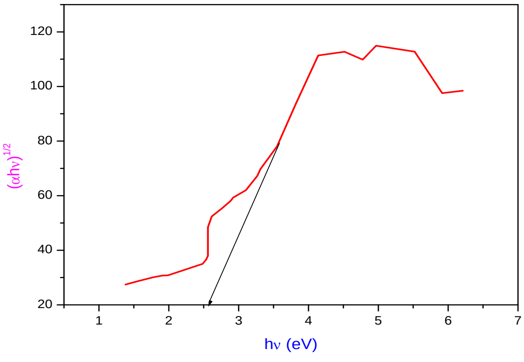

Fig.6. Tauc's plot for PAPI crystal

3.3 Thermal analysis

The thermal analysis of the grown picric acid doped potassium iodate crystal was carried out by recording TG/DTA curves in the temperature range 40-800 °C and these thermal curves were recorded simultaneously using a TG/DTA analyser in the nitrogen atmosphere at the heating rate of 10 °C/min and the curves are presented in the figure 7. From the results, it is observed that the sample has thermal stability upto 120 °C. There is a weight loss of about 20% noticed at 170 °C and this is due to liberation of water molecules from the lattice of host crystal. After liberation of water molecules, the sample is thermally stable in the temperature range 200-520 °C. The endothermic peak at 550 °C is corresponding to the decomposition point of the sample. Further decomposition of the sample takes place in the temperature range 600- 800 °C.

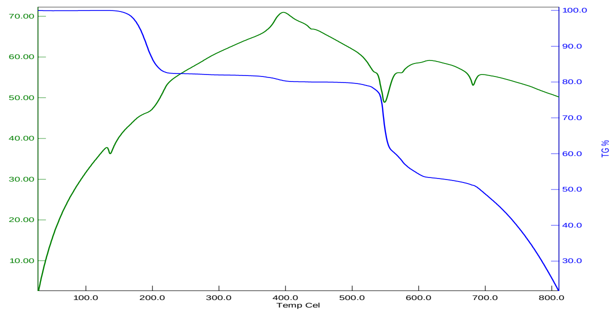

Fig.7. TG/DTA curves for picric acid doped potassium iodate crystal

3.4 EDAX studies

Energy dispersive X-ray spectroscopy (EDS or EDAX) is a spectral technique used to identify the different elements in the sample. In this technique, the EDS detector is a solid state device designed to detect X-rays and convert their energy into electrical charge and this charge becomes the signal which can be identified to find the X-ray energy and hence the corresponding element present in the sample. An EDAX analyser was used to record the EDAX spectrum of picric acid doped potassium iodate crystal and it is given in the figure 8. One or more peaks may be corresponding to a particular element and hence it is identified. From the spectrum, the elements such as K, I, O, C, N are identified and this leads to confirmation of the dopant (picric acid) present in the interstitial positions of the lattice of the crystal.

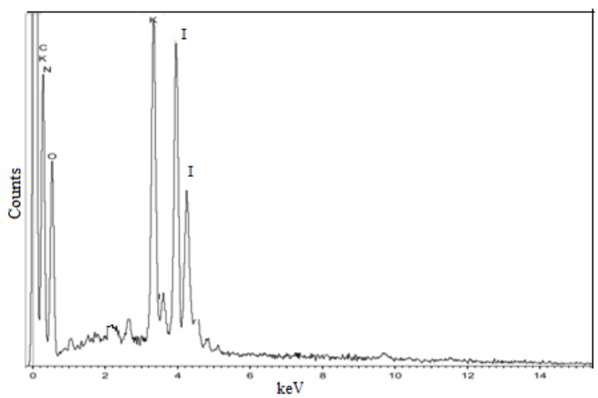

Fig.8. EDAX spectrum of picric acid doped potassium iodate crystal

3.5 Finding crystal structure

X-ray diffraction (XRD) method was adopted to find the crystal structure of the sample and it is based on the principle of Bragg's law. There are two XRD methods to identify the crystal structure and to find the lattice constants. If the sample is a single crystal, single crystal XRD method can be used for the crystal structural analysis. The lattice constants and hence the crystal structure of picric acid doped potassium iodate (PAPI) crystal were found by using a single crystal X-ray diffractometer (ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_α (λ=0.71069 Å). The obtained crystallographic data of PAPI crystal are a = 7.692 (2) Å, b = 7.719 (4) Å, c = 7.817(3) Å, α = 109.83 (4)°, β = 108.61 (3)° and γ =110.33 (1)°. From the data, it is confirmed that PAPI crystal crystallizes in triclinic structure. In the literature, it is reported that undoped potassium iodate crystal also crystallizes in triclinic crystal system [19] and hence the crystal structure of potassium iodate crystal is not changed when it is doped with picric acid.

3.6 Finding SHG efficiency

Second harmonic generation (SHG) is also called as the frequency doubling and it is one of the nonlinear optical (NLO) phenomena. Usually, from a non-centrosymmetric crystal, SHG is created when it is irradiated with high energetic laser light. The SHG efficiency of PAPI crystal was found by the Kurtz-Perry technique using a Nd: YAG laser with fundamental wavelength of 1064 nm. Here the grown crystal of PAPI was powdered to a size of about 150-200 micron and it was subjected to the SHG study. The emission of green laser of wavelength 532 nm from the sample indicates that the sample is a second harmonic generator. The SHG radiation of 532 nm detected by a photomultiplier tube and the optical signal incident on the PMT was converted into voltage output at the CRO. The input energy used in the experiment is 0.70 J/pulse and the output laser energy obtained from the sample is 9.26 mJ/pulse. The reference sample used in this experiment was KDP and the output laser energy obtained from KDP was 8.91 mJ/pulse. Hence, the relative SHG efficiency for PAPI crystal is found to be 1.03 times that of KDP sample.

3.7 Microhardness analysis

Mechanical properties like hardness, stiffness constant, yield strength etc of a crystalline sample can be determined by microhardness analysis. Microhardness testing involves the production of indentations in small areas on the surface of the sample by pressing a hard indenter of specified geometry. The microhardness characterization is extremely important as far as the device fabrication is concerned and it provides information about the directional strength, slip systems and molecular binding. The microhardness indentation techniques are used to study anisotropy, deformation, glide, state of dispersions of impurity, quench hardening, effect of irradiation and environment of dislocation mobility. A Vickers microhardness tester fitted with a diamond indenter was used to find the microhardness and it is determined using the formula $H_v = 1.8544\ P / d^2$ where H_v is Vickers hardness number, P is the applied load and d is the length of indentation impression. The plots of microhardness versus applied load for undoped and picric acid doped potassium iodate (PAPI) crystals are shown in the figure 9. From the results, it is observed that the microhardness increases with increase of the applied load for both the samples upto 125 g and then the cracks are formed when the load applied on the samples is beyond 125 g. The increasing behaviour of the plots is due to the reverse indentation size effect. Other mechanical properties of the samples like yield strength and stiffness constant were determined using the values of microhardness. Yield strength is determined using the relation $\sigma_y = (H_v/3)$ and stiffness constant is determined using the relation $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material. The calculated values of yield strength and stiffness constant of undoped and picric acid doped potassium iodate crystals are presented in the table 2. From the results, it is observed that both yield strength and stiffness constant increase with increase of the applied load for both the samples. When low load is applied on the sample, it seems that the sample is tightened due to increase of bond strength and the hence the mechanical properties like hardness, yield strength and stiffness constant increase with further increase of applied load upto 125 g. The obtained values of mechanical properties of both undoped and picric acid doped potassium iodate (PAPI) crystals are observed to be high and hence these samples can be used for device fabrication. When potassium iodate crystals are doped with picric acid, it is likely that the bond strength in the doped crystal increases due to incorporation of picric acid into the sample and hence the mechanical properties of PAPI crystal is more compared to the undoped potassium iodate crystal.

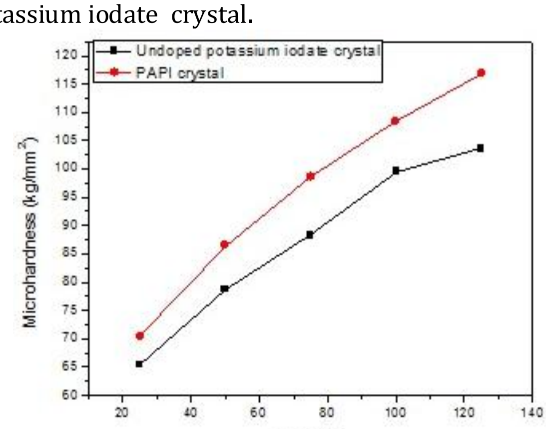

Fig.9. Plots of microhardness versus applied load for undoped and picric acid doped potassium iodate crystals

Table 2: Values of yield strength and stiffness constant for undoped and picric acid doped potassium iodate crystal

Sample	Applied load (g)	Yield strength x 10^6 (N/m^2)	Stiffness constant (N/m^2)
1)Undoped potassium iodate crystal	25 g 50 g 75 g 100 g 125 g	13.6401 257.0867 288.4467 325.0333 338.4267	2.5817E+15 3.5695E+15 4.3659E+15 5.3807E+15 5.7746E+15
2) PAPI crystal	25 g 50 g 75 g 100 g 125 g	229.9733 282.5667 322.0933 354.1067 381.5467	2.93696E+15 4.21137E+15 5.29578E+15 6.25096E+15 7.12313E+15

4.Conclusions

Picric acid was added as the dopant into the host potassium iodate crystal to modify its properties. Single crystals of undoped and picric acid doped potassium iodate (PAPI) were grown by solution growth method with slow evaporation technique. Solubility of PAPI crystal is observed to be more than that of undoped potassium iodate crystal. The functional groups and various elements present in the PAPI crystals were identified by spectral methods. The crystal structure and lattice parameters of PAPI crystal were found by single crystal XRD method. TG/DTA analysis was carried out to find thermal stability of the PAPI crystal and SHG efficiency of PAPI crystal was found to be 1.03 times that of KDP sample. Mechanical properties of both undoped and picric acid doped potassium iodate crystals like hardness, yield strength and stiffness constant were evaluated at various applied loads. Linear optical studies were carried out for PAPI crystal to find transmittance, absorbance and optical band gap.

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References

1. P.N. Prasad, D.J. Williams,Introduction to Nonlinear Effects in Molecules and Polymers, Wiley, New York (1991).
2. D.Xu, M. Jiang, and Z. Tan, Acta Chem. Sin, 41(1983) 570.
3. M. H, Aggarwal, J. Choi, W. S. S Wang, K. Bhat, R. B. Lal, A. D. Shields, B. G. Penn and D. V. Frazier, J. Cryst. Growth ,179 (1999) 2004.
4. Xiue Ren, Dongli Xu, Dongfeng Xue, J. Crystal Growth 310 (2008) 2005.
5. Dongfeng Xue, Henryk Ratajczak, J. Chem. Phys. Lett. 371 (2003) 601.
6. Dongfeng Xue, Siyuan Zhang, J.Chem. Phys. Lett. 301 (1999) 449.
7. 7.Xiaomin Liu, Guanghua Li, Yawei Hu, Yang Yu, Minghui Bi, Zhan Shi, Shouhua Feng, Inorganica Chimica Acta, 362 (2009) 65.
8. B. Van Troeye, Y. Gillet, S. Poncé, X. Gonze Optical Materials, 36 (2014) 1494.
9. C. Galez, Y. Mugnier, J. Bouillot, C. Rosso, Optical Materials 19 (2002) 33.
10. Y Xin, L Mengkai, Z Shaojun, and L Fuqi, Chinese Phys. Lett., 9, 77, 1978.
11. E Salje, Z. Kristallogr., 134:107–115, 1971.
12. V P Kalinin, V V Ilykhin, and N V Belov, Doklady Akademii Nauk *SSSR*, 239, 590–593, 1978.
13. Subbiah Meenakshisundaram, S. Parthiban, N. Sarathi, R. Kalavathy, G. Bhagavannarayana, J. Cryst. Growth 293 (2006) 376.
14. S. Ariponnammal, S. Radhika, N. Victorjaya, Cryst. Res. Technol. 40 (2005) 786.
15. C. Krishnan, P. Selvarajan, T.H. Freeda, Mat. Lett. 629 (2008) 4414.
16. M.A.F. Elmosallamy, Anal. Sci. 20 (2004) 285-290.
17. P.G. Farrell, F. Terrier, R. Schaal, Tetrahedron Lett. 26 (1985) 2435-2438.
18. J.Tauc, Amorphous and liquid semiconductors, Plenum Press, New York (1974).
19. V P Kalinin, V V Ilykhin, and N V Belov, Doklady Akademii Nauk *SSSR*, 239 (1978) 590–593.