

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/276271178>

A study on optical, dielectric and NLO properties of L-Alanine added ammonium dihydrogen phosphate single crystal

Article in *Journal of Optoelectronics and Advanced Materials* · September 2014

CITATIONS

3

READS

222

4 authors, including:



R.N. Shaikh

Milliya Arts, Science and Management Science College, Beed-43112...

23 PUBLICATIONS **94** CITATIONS

[SEE PROFILE](#)



Mohd Anis

Sant Gadge Baba Amravati University

103 PUBLICATIONS **491** CITATIONS

[SEE PROFILE](#)



Hussaini Shuakat

Milliya Arts Science & Management Science College

93 PUBLICATIONS **661** CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Development of organometallic nonlinear optical crystals [View project](#)

A study on optical, dielectric and NLO properties of L-Alanine added ammonium dihydrogen phosphate single crystal

R. N. SHAIKH, MOHD ANIS, M. D. SHIRSAT^a, S. S. HUSSAINI*

Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science and Management Science College, Beed-431122, Maharashtra, India

^aIntelligent Materials Research Laboratory, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004, Maharashtra, India

In the present investigation the effects of amino acid L-Alanine on the, optical, dielectric and NLO properties of ammonium dihydrogen phosphate (ADP) crystal is reported. The crystal is grown by slow evaporation solution growth method at room temperature. The crystal structure was studied by powder X-ray diffraction. The chemical composition of the grown crystal was determined by fourier transform infrared spectroscopy (FT-IR). The optical transmission study reveals the improved transparency of doped crystal in the entire visible region, which is an essential requirement for NLO applications. The cutoff wavelength has been found to be 340 nm and the optical band gap is found to be 5.4eV. The dependence of extinction coefficient (K) and refractive index (n) on wavelength has also been reported. The dielectric studies show that the dielectric constant and dielectric loss decreases exponentially with frequency at room temperature. The nonlinear optical behavior of grown crystal was tested by Kurtz-powder technique.

(Received December 08, 2013; accepted September 11, 2014)

Keywords: Nonlinear optical materials, SHG efficiency, Optical transparency, Dielectric constant

1. Introduction

An optically non linear material shows its applications in optoelectronics, telecommunication industries, laser technology and optical storage devices. Ammonium dihydrogen phosphate (ADP) ($(\text{NH}_4)_2\text{H}_2\text{PO}_4$) is an interesting material with varied application as a piezoelectric material in transducer devices, nonlinear optics (NLO), electro-optics [1-6].

Amino acid family crystals exhibit excellent nonlinear optical and electro-optical properties. Reports are available in literature on the doping of amino acids in ADP crystal. Many researchers have carried out studies on pure and doped ADP [7-9]. N.Pattanaboonmee et al has reported Glycine and L-Arginine doped ADP crystal [10]. Growth and Characterizations of DL-malic acid doped with ADP was reported by P. Rajesh et al [11]. Ferdousi et al has reported growth and charcerzations of L-Alanine doped ADP, however the optical parameters were not discussed [12]. This present study reports detailed evaluation of optical properties (optical band gap, extinction coefficient, refractive index, optical conductivity), dielectric properties (dielectric constant, dielectric loss, ac resistivity, ac Conductivity) and SHG efficiency of L-Alanine doped ADP, All these optical parameters are appilcable for its possible NLO applications.

In present investigation 1, 2, and 3 mole % L-Alanine was doped in pure ADP and the SHG efficiency of pure

and 1, 2 and 3 mole % L-Alanine doped ADP were carried out. It was observed that 1mole% L-Alanine doped ADP has highest efficiency; therefore 1 mole % L-Alanine doped ADP crystals were grown by slow evaporation technique at room temperature (40°C). The grown crystals were characterized by FT-IR, powder XRD, UV-visible transmission spectroscopy, dielectric study and SHG efficiency test.

2. Experimental procedure

2.1. Crystal growth

As the SHG efficiency is found high in 1 mole% L-Alanine doped ADP, the seed crystals of the same were grown by slow evaporation solution growth method. A super saturated solution of L-Alanine doped ADP is obtained with deionised water at room temperature 40°C. The same solution is loaded at the same temperature in a constant temperature bath of accuracy $\pm 0.01^\circ\text{C}$ for nearly 24 h and then a good quality transparent seed is suspended in the solution, which is kept for slow evaporation. A transparent and well phased L-Alanine doped ADP crystal with dimension $1.8 \times 0.8 \times 0.7$ cm was harvested in 24 days.

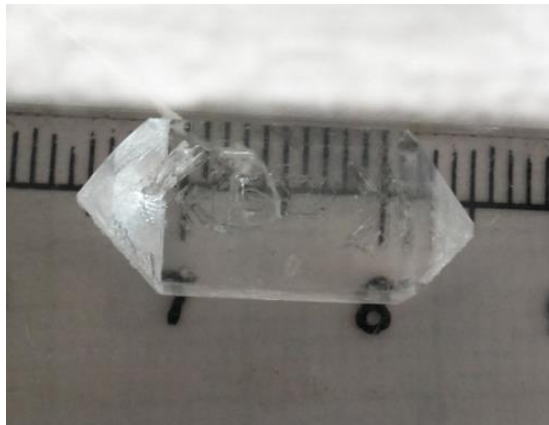


Fig. 1. Photograph of L-Alanine doped ADP.

3. Results and discussion

3.1 NLO studies

The study of NLO conversion efficiency of grown crystal has been carried out in accordance with the classical powder method developed by Kurtz and Perry [13]. It is an important and popular tool to evaluate the conversion efficiency of NLO materials. A Q-switched Nd:YAG laser beam of wavelength 1064 nm, with an input power of 2.8mJ/pulse, and a pulse width of 8 ns with a repetition rate of 10 Hz were used. The crystals of 1, 2 and 3mole% L-Alanine doped ADP was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser. The output from the sample was monochromated to collect the intensity of 532 nm component, and to eliminate the fundamental wavelength. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. The generation of second harmonic was confirmed by the emission of green light. A sample of pure KDP salt was used as a reference material for the present measurements. The SHG conversion efficiency of L-Alanine doped ADP was found to be 1.8 times that of pure KDP. The enhancement in SHG efficiency of L-Alanine doped ADP is due to the optically active amino group which may get added in the structure and hence increasing its SHG efficiency.

3.2. X-ray diffraction analysis

The grown crystal was subjected to powder XRD, the unit cell parameters obtained are $a=b=7.459\text{\AA}$ and $c=7.458\text{\AA}$ $\alpha=\beta=\gamma=90^\circ$. The XRD pattern is shown in Fig. 2. The obtained lattice parameter values confirmed that the addition of L-Alanine did not changed the tetragonal structure of ADP [14].

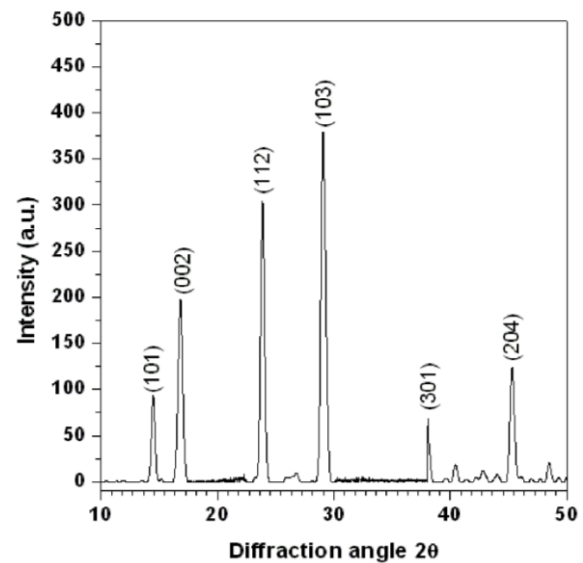


Fig. 2. Powder XRD pattern of grown L-Alanine doped ADP.

3.3. FT-IR analysis

The FT-IR spectra of pure and L-Alanine doped ADP crystals were recorded using Bruker FTIR spectrometer in the region 600-4000 cm^{-1} . Fig. 3 shows the FT-IR spectra of pure ADP and L-Alanine doped ADP. In the FT-IR the O-H stretching vibration of water happened at 3075 cm^{-1} , P-O-H stretching at 1090 cm^{-1} , N-H stretching of ammonia at 2866 cm^{-1} and the PO_4 vibrations give their peaks at 645.8 cm^{-1} . The P-O-H vibrations at 1125 and 952 cm^{-1} of the pure ADP are shifted to 1090 and 860 cm^{-1} . Such a shift establishes the presence of L-Alanine in the lattice of ADP [12].

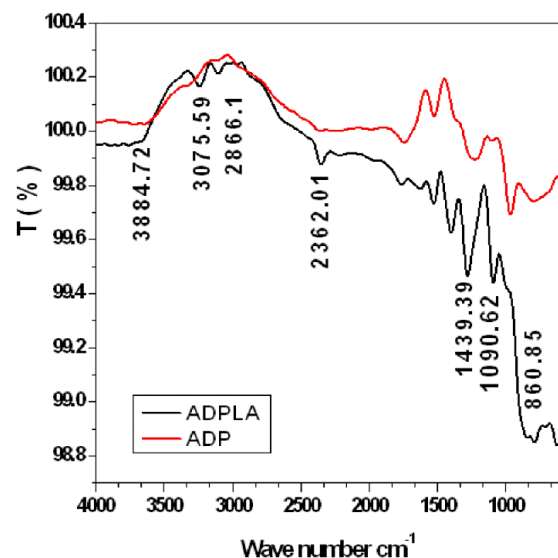


Fig. 3. FT-IR spectrum.

3.4. Optical studies

Optical parameters of material are important as they provide information on the electronic band structures, localized states and types of optical transitions. The optical transmission spectrum of grown solid crystals was recorded in the wavelength region 200-900 nm using Shimadzu UV-2450 Spectrophotometer and is shown in Fig. 4. The UV cut off wavelength for the grown crystal was found to be 340nm. The high transmission in the entire visible region suggests it's suitability for second harmonic generation [15-16].

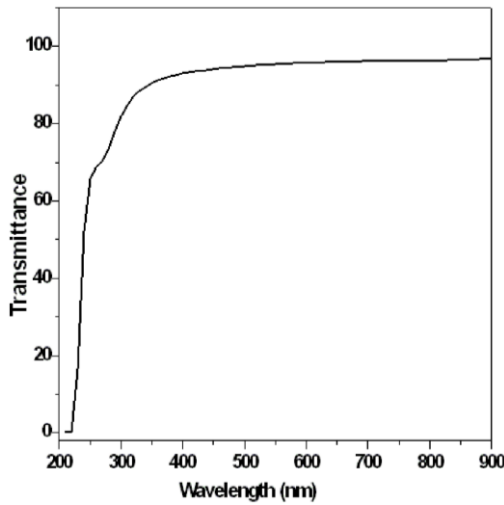


Fig. 4. UV-Vis. Spectrum of grown L-Alanine doped ADP.

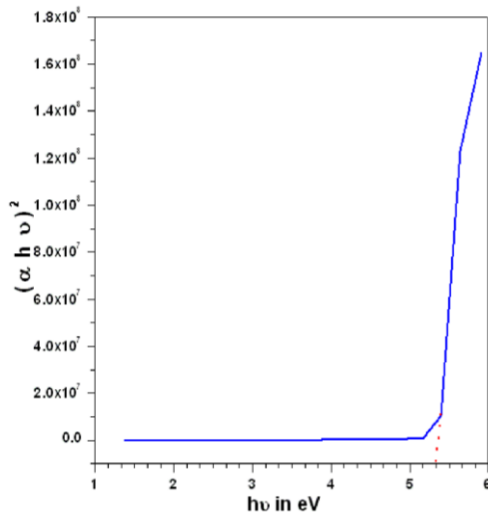


Fig. 5. $(\alpha h\nu)^2$ vs. photon energy $(h\nu)$.

The transmittance (T) data was used to calculate absorption coefficient (α) from the following relation.

$$\alpha = (1/t)\ln(1/T) \tag{1}$$

where T is the Transmittance and t is the thickness of the crystal. Optical band gap was evaluated from the

absorption spectrum and optical absorption coefficient (α) near the absorption edge is given by,

$$\alpha = A\sqrt{h\nu - E_g} \tag{2}$$

where E_g is the optical band gap of the crystal and A is a constant.

The band gap of L-Alanine doped ADP crystal was estimated by plotting $(\alpha h\nu)^2$ vs. photon energy $(h\nu)$ at room temperature. As shown in Fig. 5, the value of band gap E_g is estimated by extrapolating the linear portion of the curve to the point $(\alpha h\nu)^2 = 0$. The band gap observed is 5.4eV. The wide band gap and high transmittance in the visible region makes it potential candidate for optoelectronic applications [17].

The extinction coefficient can be obtained in terms of the absorption coefficient,

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

Transmittance (T) in terms of (α) is given by the relation,

$$T = \frac{(1-R)^2}{1-R^2} \times \frac{\exp(-\alpha t)}{\exp(-2\alpha t)} \tag{4}$$

Reflectance in terms of absorption coefficient (α) & refractive index (n) is given by the relations respectively,

$$R = \frac{1 \pm \sqrt{\exp(-\alpha t) + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \tag{5}$$

$$R = (n-1)^2 / (n+1)^2 \tag{6}$$

The refractive index (n) is calculated using the relation as given by Nabeel et al [18].

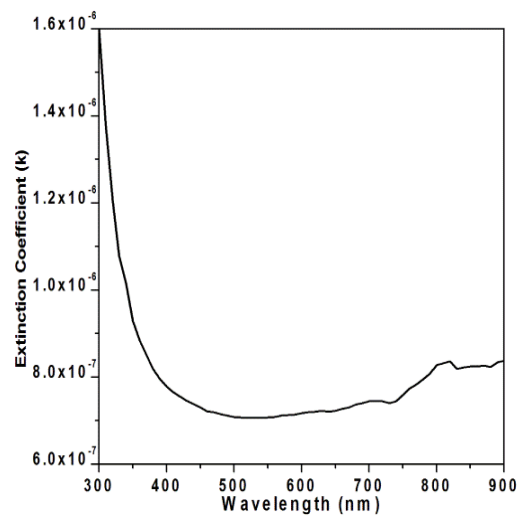


Fig. 6. Plot of Extinction coefficient vs. Wavelength.

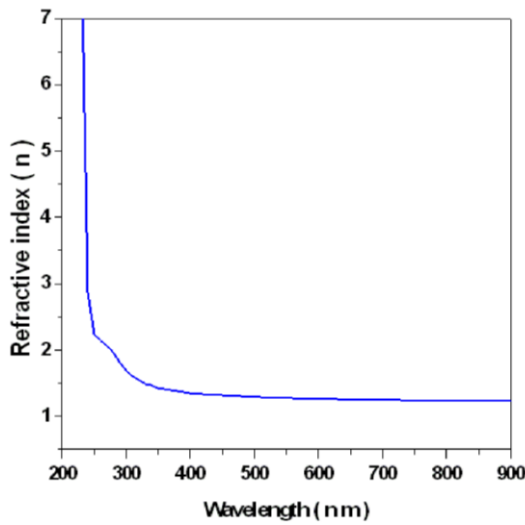


Fig. 7. Plot of refractive index vs. wavelength.

Fig. 6 shows the variation of extinction coefficient as a function of wavelength, from graph it is clear that extinction coefficient depends on the wavelength. The doping of L-Alanine diminished the refractive index of ADP with increasing wavelength as shown in Fig. 7, it also decreases optical dispersion, which minimizes optical aberration and makes crystal suitable for optical fabrication [19].

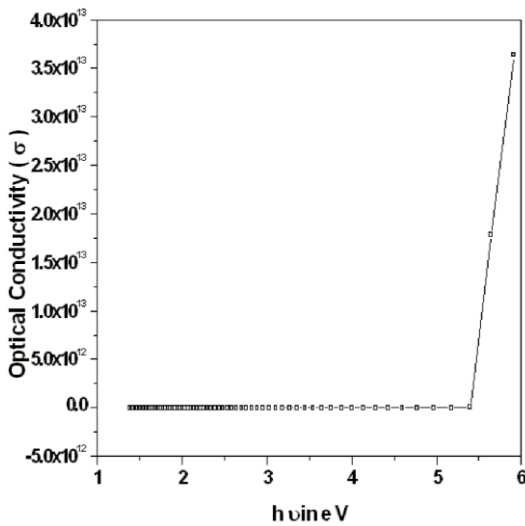


Fig. 8. Plot of optical conductivity vs. Photon Energy.

The optical conductivity is a measure of frequency response of the material when irradiated with light.

$$\sigma = \alpha n C / 4\pi \tag{7}$$

where C is the velocity of light. The plot between optical conductivity against photon energy was depicted in Fig. 8. Improved optical properties viz. wide band gap, high transparency, low extinction coefficient and high optical conductivity of the grown crystal causes to enhance the SHG efficiency which is found to be 1.8 times KDP [20].

3.5. Dielectric studies

The dielectric behavior of the grown crystal has been studied at room temperature using the Gwinstek LCR-819 cube meter having frequency range of 12Hz to100kHz. The dielectric constant and dielectric loss have been calculated using the formula,

$$\epsilon = cd / \epsilon_0 A \tag{8}$$

$$\text{Dielectric Loss} = \text{Tan } \delta = \epsilon / \epsilon_0 \tag{9}$$

Where, C is the capacitance, d is the thickness of the sample, A is the area of the sample.

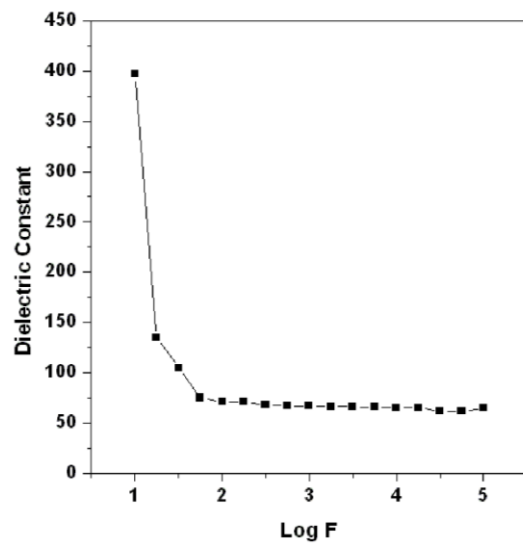


Fig. 9. Plot of Dielectric Constant vs. Log F.

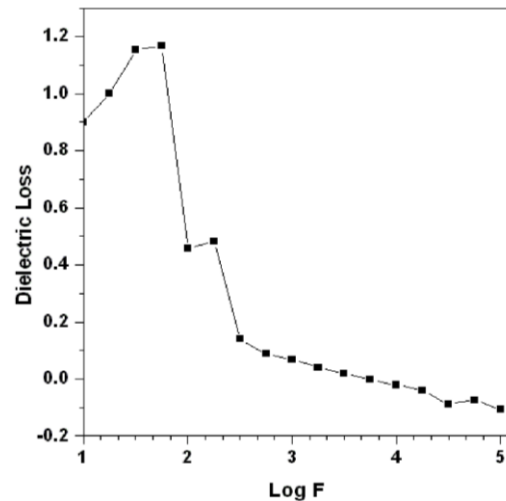


Fig. 10. Dielectric Loss vs. Log F.

The dielectric properties are correlated with electro-optic properties of the crystals. Fig. 9 shows the plot of dielectric constant vs. log frequency (F). The higher value of dielectric constant at lower frequencies may be due to the presence of all the four polarizations namely; space

charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually [21].

For a material to be a potential candidate for NLO applications, the dielectric loss ($\tan \delta$) must also be kept as low as possible. The plot of dielectric loss with frequency (Fig. 10) revealed that the grown crystal exhibit very low dielectric loss at high frequencies and can be used for NLO applications [22].

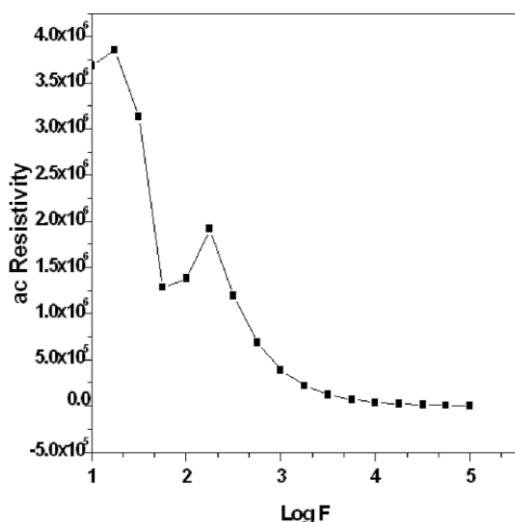


Fig. 11. Plot of ac resistivity vs. Log.

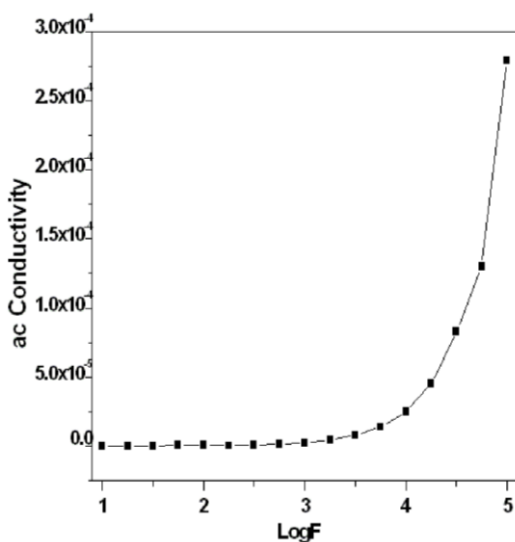


Fig. 12. Plot of ac Conductivity vs. Log F.

The Fig. 11 and 12 gives the variation in ac resistivity and conductivity with the frequency for the grown crystal. The ac resistivity and ac conductivity were calculated using the relation,

$$\rho_{ac} = A / \omega C d \quad (10)$$

$$\sigma_{ac} = 1 / \rho = \epsilon_0 \epsilon_r \text{Tan} \delta \quad (11)$$

where C is the capacitance, d is the thickness, A is the area of crystal, angular frequency ($\omega = 2\pi\nu$). As shown in Fig. 11 and 12 ac resistivity decreased rapidly as frequency increased and obviously reverse trend was observed for ac conductivity.

4. Conclusions

The ADP doped with L-Alanine crystal has been grown from aqueous solution by slow evaporation technique. The SHG studies revealed that grown crystals are a promising material for NLO applications. The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2θ angles shows the crystalline nature and purity of the crystal. The optical studies show that the crystal is transparent in the region of 360–900 nm. The UV-visible spectrum shows wide band gap of doped crystal as 5.4eV suggesting that it is optically active material. The grown crystal foreshow good optical parameters such as transmittance, reflectance, extinction coefficient and low refractive index in entire visible region, showing the suitability of grown crystal for optoelectronics applications. The dielectric studies reveal that the grown crystal posses low dielectric loss, low dielectric constant, high ac conductivity and low resistivity at high frequencies makes it potential candidate for fabrication of devices and microelectronics industry.

Acknowledgment

The authors are thankful to the Department of Science and Technology (DST/SR/S2/LOP-22/2010), and University Grants Commission (UGC/41-591/2012/SR), New Delhi, for financial assistance. The authors are also thankful to Prof. P.K Das, Department of Physical Chemistry, Indian Institute of Science (IISc), Bangalore, India for SHG Test.

References

- [1] S. S. Hussaini, N. R. Dhumane, V. G. Dongre, P. Ghughare, M. D. Shirsat, *Optoelectron. Adv. Mater. - Rapid Comm.* **1**, 707 (2007).
- [2] S. S. Hussaini, N. R. Dhumane, V. G. Dongre, M. D. Shirsat, *Optoelectron. Adv. Mater. - Rapid Comm.* **2**, 108 (2008).
- [3] N. R. Dhumane, S. S. Hussaini, V. V. Navarkhale, M. D. Shirsat, *Cryst. Res. Technol.* **41**, 897 (2006).
- [4] M. D. Shirsat, S. S. Hussaini, N. R. Dhumane, V. G. Dongre, *Cryst. Res. Technol.* **43**, 756 (2008).
- [5] N. R. Dhumane, S. S. Hussaini, V. G. Dongre, Mahendra D. Shirsat, *J. Optical mater.* **31**, 328 (2008).
- [6] P. Rajesh, P. Ramasamy, C. K. Mahadevan, *J. Cryst. Growth* **311**, 1156 (2009).
- [7] P. Rajesh, P. Ramasamy, *Spectrochim. Acta A* **74**, 210 (2009).

- [8] P. Rajesh, P. Ramasamy, *cryst. Mater. Lett.* **63**, 2260 (2009).
- [9] M. Meena, C. K. Mahadevan, *Cryst. Res. Technol.* **43**, 166 (2008).
- [10] N. Pattanaboonmee, P. Ramaswamy, R. Yimmirun, P. Manyum, *J. Cryst. Growth* **314**, 196 (2011).
- [11] P. Rajesh, P. Ramasamy, *J. Cryst. Growth* **311**, 3491 (2009).
- [12] Ferdousi Akhtar, Jiban Podder, *J. Cryst. Process & Tech.* **1**, 18 (2011).
- [13] S. K. Kurtz, T. T. Perry, *J. Appl. Phys.* **39**, 3798 (1968).
- [14] H. J. Simpson Jr., R. E. Marsh, *Acta Crystallographica* **20**, 550 (1966).
- [15] Sagadevan Suresh. *British J. Appl. Sci. & Tech.* **3**, 340 (2013).
- [16] T. C. Sabari Girisun and S. Dhanuskodi, *Cryst. Res. Technol.* **44**, 1297 (2009).
- [17] Sagadevan Suresh. *J. Appl. Sci. & Techn.* **3**, 340 (2013).
- [18] Nabeel A Bakr, A. M. Funde, V. S. Waman, M. M. Kamble, R. R. Hawaldar, D. P. Amalnerkar, S. W. Gosavi, S. Jadkar, *J. Phys.* **76**, 519 (2011).
- [19] Fahrettin Yakuphanoglu, Hilmi Erten, *Optica Applicata*, **35**, 4 (2005).
- [20] J. Ramajothi, S. Dhanuskodi, K. Nagarajan, *Cryst. Res. Technol.* **39**, 414 (2004).
- [21] G. Prabakaran, S. Arulmozhi, M. Dinesh Raja, J. Madhavan, *J. Appl. Phys.* **2**, 51 (2013).
- [22] T. Arumanayagam, P. Murugakoothan. *J. Minerals & Mat. Charact. & Eng.* **10**, 1225 (2011).

*Corresponding author: Shuakionline@yahoo.co.in