Journal of Engineering and Technology Management 80 (2026)

GROWTH AND CHARACTERISATION OF A PIEZOELECTRIC AMMONIUM DIHYDROGEN PHOSPHATE WITH POTASSIUMTHIOCYANATE (KSCN) CRYSTAL FOR OPTOELECTRONIC APPLICATIONS

Dr.P.GIRIJA, Assistant Professor, Department of chemistry, Annamalai University, Chidambaram, Tamilnadu, India.

Abstract

Ammonium Dihydrogen Phosphate (ADP) doped Potassium thiocyanate (KSCN) crystal has been synthesized by slow evaporation solution growth process using distilled water as solvent. A close observation of FTIR, Single crystal and Powder XRD profiles of ADP doped Potassium thiocyanate sample reveals some minor structural variations, for Single crystal XRD there is change in system or space group as Monoclinic with angles $\alpha=\gamma=90^\circ$, $\beta=93.21^\circ$ differing from ADP parameter values forming a new mixed crystal. TG/DTA studies reports the purity and hardness of ADP doped Potassium thiocyanate samples and no decomposition is observed below the melting point. UV-Visible NIR spectroscopy reveals that Potassium thiocyanate doped ADP crystal have good transmittance with higher band gap energy than undoped ADP crystals and high optical quality and could be used for Optoelectronic applications in Industries and Laser Technology.

Key words – Slow Evaporation Solution growth Technique, UV-Visible spectroscopy, Potassium thiocyanate and Optoelectronics.

Corresponding author

Dr.P.Girija, Professor, Department of Chemistry, Annamalai University, Annamalainagar - 608002, India.

Introduction

Ammonium Dihydrogen Phosphate (ADP) a nonlinear optical crystals is applied for laser radiation conversion in laser fusion system[1]. Powder X-Ray Diffraction studies on the ADP crystals attracts the interest because of their unique nonlinear optical, dielectric and anti-ferroelectric properties and their applications as electro-optic modulator, harmonic generators and paramagnetic generator[2-13]. ADP an inorganic nonlinear optical material has made the researchers to know about its good susceptibility and optical transparency, low thermal and mechanical stability[14]. The enhancement of optical transmission[15], effect of complexing agent[16], dopant effect of KCl and Oxalic acid[17]. The effect of mixing of divalent and trivalent impurities on the growth, habit modification and structure of ADP[18-24] is also studied. A good number of investigations are reported on manganese as dopants. The unusual ferromagnetic properties of manganeseorthovanadate are studied[25].

The magnetic properties of nano crystals of Mn doped ZnO is recently reported[26]. The concentration effects of Mn (II) doping on ZTS is studied[27]. Effect of structural and optical properties of thiourea doped ADP crystal on second order nonlinearity[28]. Spectral and optical properties of l-tartaric acid[29] and benzoic acid[30] doping effects on ADP crystals are recently studied. Also studies on crystalline perfection and Manganese(II)[31] and (IV)[32] on ADP. In order to find new useful materials for academic and optical industrial use, an attempt has been made to modify the ADP crystal by doping with Potassium thiocyanate taking equimolar concentration each. The effect of doping is studied using FT-IR, UV-Visible spectra, Thermal, Single crystal XRD and Powder-XR Diffraction.

Materials and Methods

Synthesis and Crystal growth

Analytical grade ADP (SD fine chem.) is used as such. Spongy Crystal of ADP doped Potassium thiocyanate (KSCN) is grown by mixing equimolar composition of ADP AND KSCN in 1:1 ratio by slow evaporation solution growth technique at room temperature using triply distilled water as solvent. Here the mixture of ADP and Potassium thiocyanate taken at equimolar ratio dissolved in distilled water in a conical flask and the contents is stirred for 3-4 hrs in a magnetic stirrer, then the contents in conical flask is filtered in a beaker for removing impurities, the neck of the beaker with the filtrate is covered with polythene sheet provided with holes on the top, then labelled for identification. The filtrate in the beaker is maintained at room temperature condition for 15 days, at 9th day glittering small balls of seed crystals were found in the bottom of the beaker which is then grown into a bulky spongy crystal on 13th day and it was filtered and packed on 15th day. The images of ADP doped Potassium thiocyanate crystal is shown in Figure 1

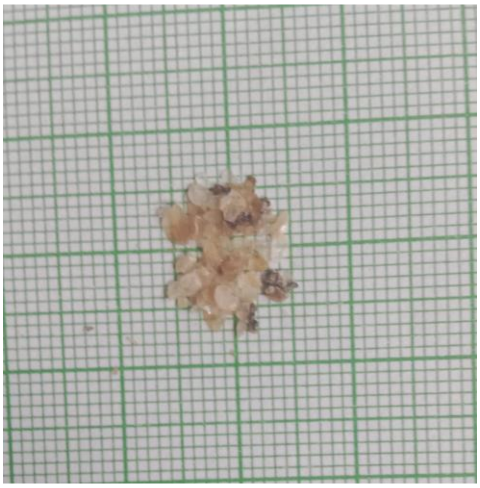

Figure.1 Images of ADP doped Potassiumthiocyanate crystals.

RESULTS AND DISCUSSION

Fourier Transform InfraRed Spectroscopy

The Fourier transform infrared (FTIR) investigations are carried out on the powdered samples of ADP doped Potassiumthiocyanate crystals. Figure.2 shows the prominent peaks in the FTIR pattern of ADP doped Potassiumthiocyanate crystals. The growth frequency region is located below 4000 to 1300cm^{-1} and the fingerprint region 1300 to 700cm^{-1}.

In the spectrum of ADP doped Potassiumthiocyanate , there is a broad band in the higher energy region 3434.7cm^{-1} due to O-H (hydrogen bonding) stretching vibration within the crystal. Presence of water molecule is disturbed by the bending vibrations occurring at the band 1684cm^{-1} for O-C=O stretching vibration, this broadband is narrowed due to the doping effect. The intensity of the peaks for ADP doped Potassiumthiocyanate crystal is very sharp in the range 1405.2cm^{-1} which could be due to the incorporation of dopant Potassiumthiocyanate on the lone pair of ammonia of ADP and the absence of hydrogen bonding. A less intense weak absorption peak at 2378cm^{-1} indicates SH stretching vibration of Potassiumthiocyanate doped ADP crystal. A intense sharp peak at 1282.1cm^{-1} indicates the stretching vibration of carbon-Nitrogen(C-N) bonds of ADP doped

Potassiumthiocyanate crystal. A peak at 1069.7cm^{-1} confirms that P-O-H bond is disturbed due to influence of Potassiumthiocyanate on ADP crystal matrix. The peak at 907cm^{-1} is due to =C-H out of plane bending vibration and peak at 795.8cm^{-1} in the finger print region is assigned for phosphate part of ADP matrix.

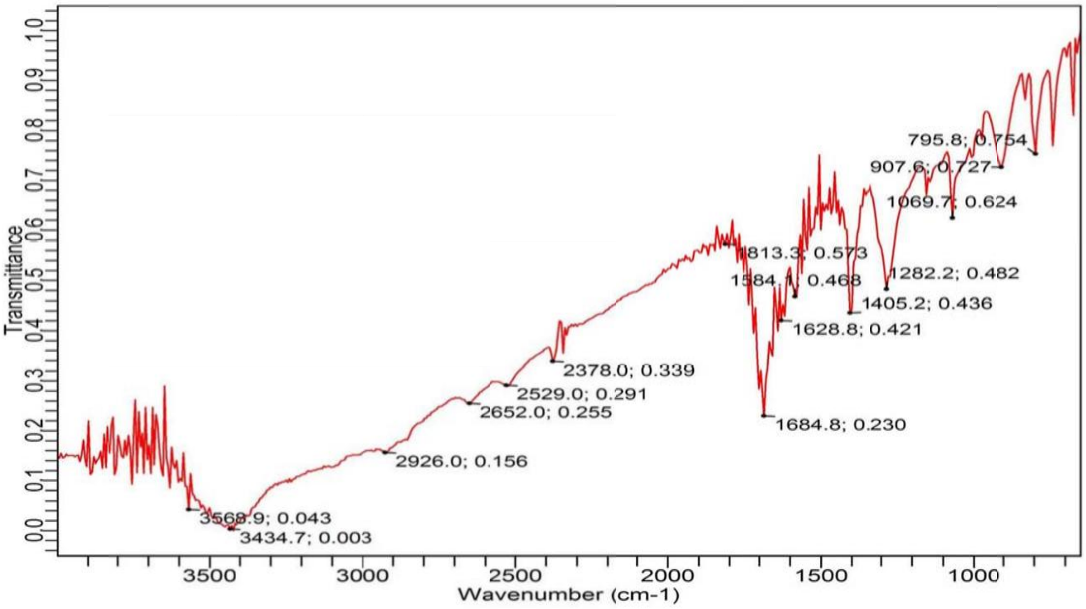

Figure.2 FTIR spectra of ADP doped Potassium thiocyanate

UV-Visible NIR Spectra

UV-Visible spectra in the spectral range of 200-2500nm for Ammonium Dihydrogen Phosphate doped Potassium thiocyanate crystal absorbance and reflectance graphs are shown in Figure.3.(a, b) . The higher transmittance in the visible region could lead to the applications of this crystal in optical windows. In absorbance spectrum of ADP doped Potassium thiocyanate crystal the absorption is maximum at 2400nm where as minimum at 202 and 300 nm indicating the synthesized crystals higher optical quality. In the reflectance spectrum the doping of Potassium thiocyanate to ADP drastically increases the reflectance at 230nm (lowering of absorbance) and hence we can conclude that Potassium metal is acting as useful dopant. The band gap energy for ADP doped Potassium thiocyanate crystal is calculated by using the formulae $E\ g = h\ c\ /\ \lambda\ max$ Where h–Plank constant, c – Velocity of light, λ_{max} = Maximum wavelength (nm) as 6.15 ev for ADP doped Potassium thiocyanate crystal and 4.14ev for ADP pure crystal inferring that higher the band gap energy higher will be its optical property of the crystal so from the Table.1 it is concluded that ADP doped Potassium thiocyanate crystal the optical property is too high making it vital role in Optoelectronic and Photonic industries.

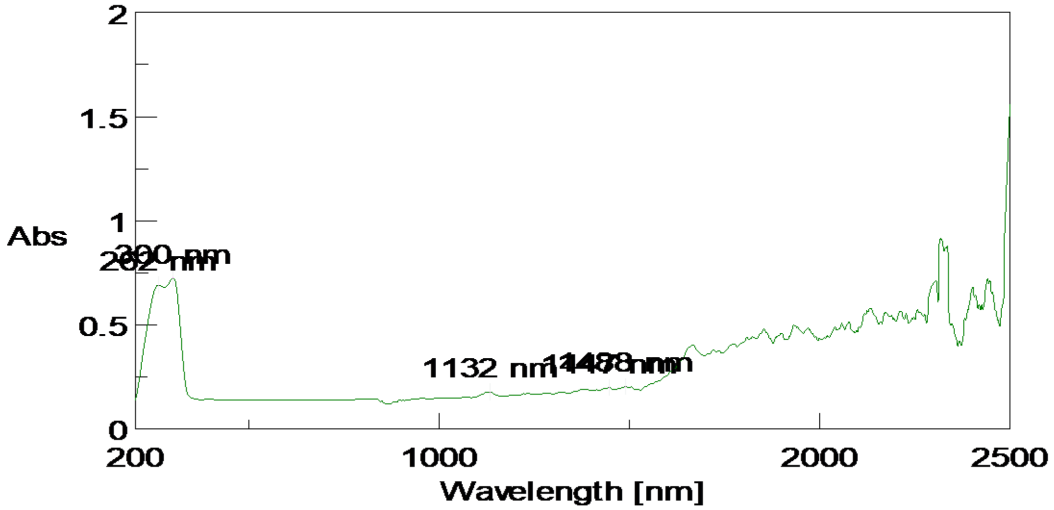

Figure.3 UV-Visible Absorbance spectra of (a) ADP doped Potassium thiocyanate

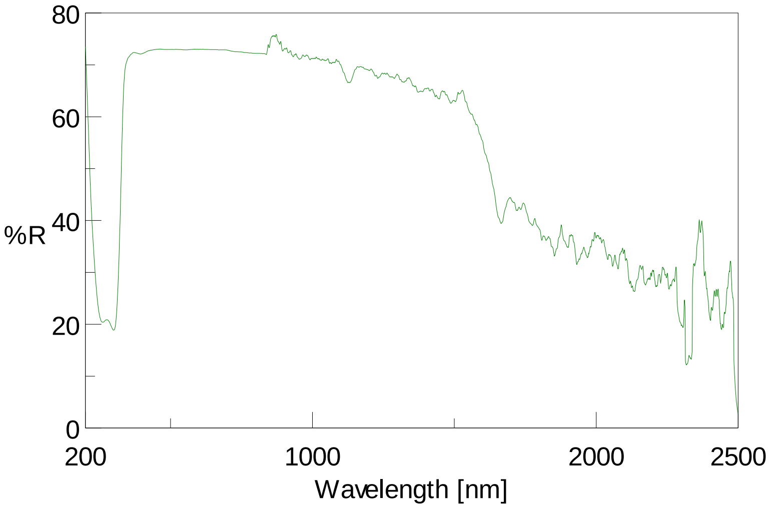

Figure.3 UV-Visible Reflectance spectra of (b) ADP doped Potassium thiocyanate

Table.1 Band gap energy

System	Band gap energy (Eg) eV
Pure ADP	4.01
ADP/POTASSIUM THIOCYANATE	6.15

Thermo gravimetric analysis (TGDTA)

The information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system is studied in TGDTA. The thermal analyses of ADP doped KSCN crystal is shown in Figure.4. In TGA curve there is no weight loss at ~185°C indicating no inclusion of water in the crystal lattice, which is used as a solvent for crystallization. Major weight loss starts at ~ 220°C, indicating the decomposition point of the material. However, above this temperature, no weight loss has been observed. In DTA curve the strong and sharp endothermic peaks located around 200°C and a short one at 290°C shows the good crystallinity of the ADP doped KSCN crystal.

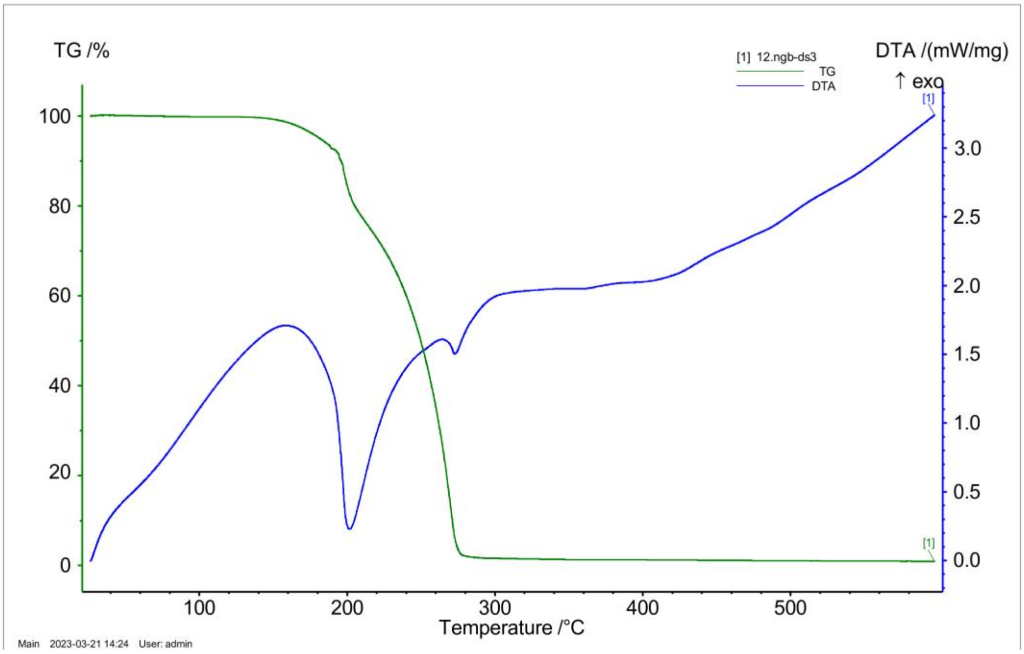

Figure.4 TG-DTA curve of ADP doped KSCN Crystal.

Powder X-Ray Diffraction studies

Powder X - ray diffraction analysis of ADP doped Potassiumthiocyanate crystal was performed with a graphite monochromated Cuk$_\alpha$ radiation and respective XRD patterns are given in the figure.5. The ADP doped Potassiumthiocyanate crystal gives high crystallinity with increase in their relative intensities of the peaks and they are shifted to higher counts due to the higher incorporation of Potassiumthiocyanate to ADP crystalline matrix. The particle size of the crystal is calculated due to doping by using scherrer equation:

$$\mathbf{t = K\lambda/(\beta\cos\theta)}$$

Where: t- Averaged dimension of crystallites,

k - Scherer constant, (it is usually assumed to be1)

λ - Wave length of X- ray,

ϴ - Peak position measured in radian,

β - Integral breadth of reflection (in radian 2ϴ) located at 2ϴ.

The granularity or partical size of ADP doped Potassiumthiocyanate crystal is calculated as 17.36nm. In ADP doped doped Potassiumthiocyanate graph (27.466^0, 31.076 and 38.17^0) the peak intensities of higher order reflections are decreased at (52.734^0, 48.491^0) which implies that there is shift in peak positions and peak broadening in higher order reflections and intensity. The minute changes in the peak intensities, peak shifts in the observed XRD graph could be attributed to the strain developed by the incorporation of the metal Potassium in Potassiumthiocyanate taken as dopant to ADP crystalline matrix.

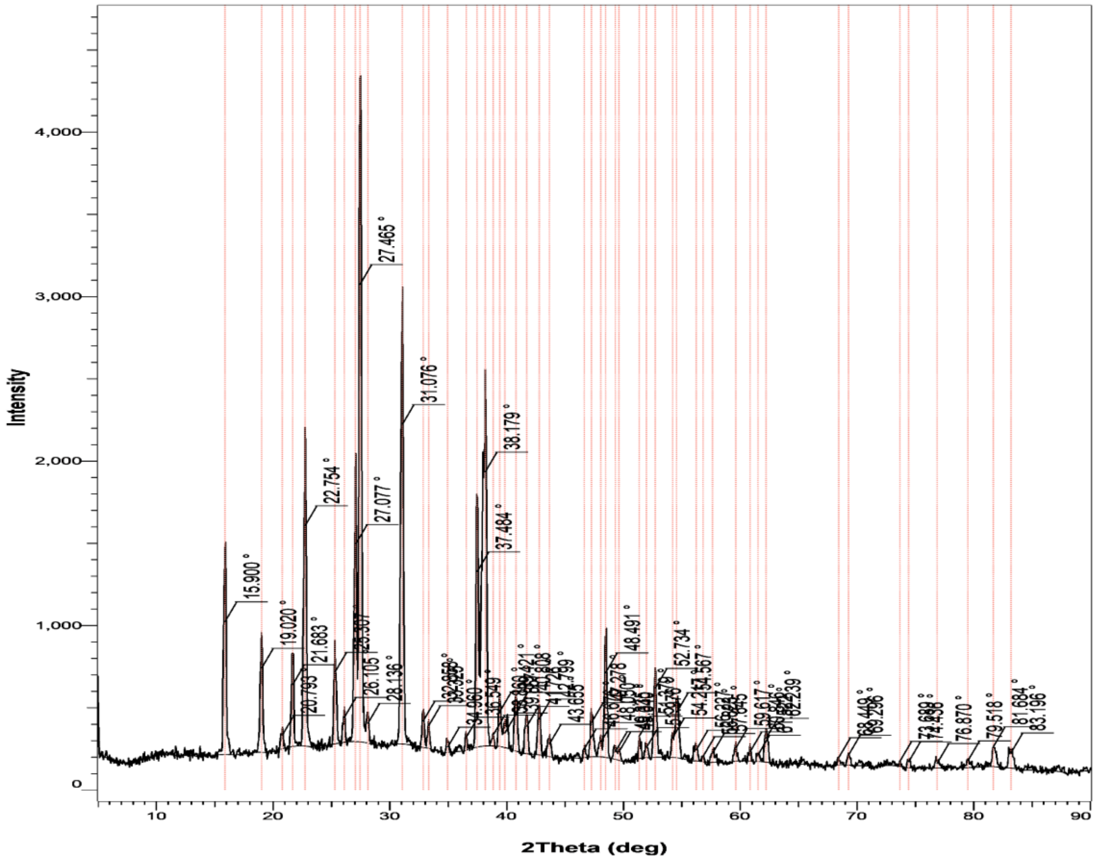

Figure.5 Powder XRD of ADP doped KSCN Crystal.

SINGLE CRYSTAL XRD ANALYSIS

The Single crystal X-ray diffraction analysis is done by Bruker AXS (Kappa Apex II) X-ray diffractometer. Here the unit cell values of Ammonium Dihydrogen Phosphate pure and ADP doped Potassium thiocyanate are determined. The table.2 shows the unit cell values of both Ammonium Dihydrogen Phosphate pure and Potassium thiocyanate crystals.

Table -2- cell parameters values of Ammonium Dihydrogen Phosphate pure and ADP doped Potassium thiocyanate crystals.

Lattice Parameter Values	**$a_A{}^0$**	**$b_A{}^0$**	**$c_A{}^0$**	**$v\ A^{03}$**	**System/space group/Beta angle**
Ammonium Dihydrogen Phosphate	7.502	7.480	7.554	421	Tetragonal/I-42d/ 90degree
ADP doped Potassium thiocyanate	5.07	14.32	9.63	698	Monoclinic/ $P2_1/c$ /93.21degree

In the above table, the cell parameter values is a=7.502A˚, b=7.480A˚,

c=7.554A˚ and v=421A$^{˚3}$ with Tetragonal system and angles α=β=γ=90˚.

for pure Ammonium Dihydrogen Phosphate crystals. The cell parameter values are moderately modified due to the change in occupational sites of the metal Potassium of Potassium thiocyanate in ADP matrix, ADP doped Potassium thiocyanate cell parameter values are a=5.07A˚, b=14.32A˚, c=9.63A˚ and

v=698A$^{3˚}$ with change in system or space group as Monoclinic with angles α=γ=90˚, β=93.21˚ differing forms a new mixed crystal.

CONCLUTION

New mixed crystals of ADP doped Potassium thiocyanate crystals have been synthesized by slow evaporation solution growth process using triply distilled water as solvent. A close observation of FTIR and Powder XRD profiles of ADP doped Potassium thiocyanate crystals reveal some minor structural variations. TG/DTA studies reports the purity of the sample and no decomposition is observed below the melting point. Optical studies reveal that the doped ADP crystals have good transmittance with higher band gap energy than undoped ADP crystals with high optical quality concluded that ADP doped Potassium thiocyanate crystal the optical property is too high making it vital role in Optoelectronic and Photonic industries. In

Single crystal X-ray diffraction of ADP doped Potassium thiocyanate the cell parameter values have change in system or space group as Monoclinic with angles α=γ=90˚, β=93.21˚ forming a new mixed crystal than the values of pure ADP crystal .

References

1. Jagatheesan,A.; Neelakantaprasad,B.; Murugan,J.; Rajarajan,G. Int. J comp. appl. **2012**, 53, 15-18.

2. Zaitseva,N.; Carman,L. Prog. cryst. growth charact. **2001**, 43, 1-118.

3. Glasser,L. Chem. Rev. **1975**, 75, 21-65.

4. Gunning,M.J.; Raab,R.E.; Kucharczyk,W. J.opt.soc.Am**. 2001**, 18, 1092.

5. Rushton,E. Br. J.Appi.Phys.**1961**,12, 417.

6. Peres,N.; Boukhis,A.; Souhassou,M.; Gavoille,G.; Lecomte,C. Acta Cryst**. 1999**, 55, 1038.

7. Ledzion,R.; Bondarczuk,K.; Kucharezyk,W. Cryt. Res. Technol. **2004**, 39,161.

8. Galass,A.M.; Lines,M.E. Principles and Applications of Ferroelectric and Related Materials; oxford university press; oxford**, 1977**; pp.293.

9. Courtens,E. Helv.Phys.Acta. **1983**, 56, 705.

10. Ermerl,D. Ferroelectrics. Ferroelectrics. **1987**, 72, 95.

11. Zajtseva, N.P.; Bogatyreva, S.V. J. Crystal growth. **1995**, 148, 276.

12. Dmitriev,V.G.; Gurzadyan,G.G.; Nikogosyan,D.N.In Hand book of nonlinear optical crystal; Berlin; Heidelberg, **1991**, pp.14-35.

13. Jayarama,A.; Dharmaprakash,S.M. Applied Surface Science. **2006**, 253, 944-949. 14. Wankhede,P.M.; Gundale,S.A.; Rode,M.N.; Muley,G.G. Int. J. Basic and App. Res. **2012**, special issue, 290-292.

15. Bhagavannarayana,G.; Kushwaha,S.K.; Parthiban,S.; Subbiah Meenakshisundaram. J. Crystal growth. **2009**, 311, 960-965.

16. Meenakshisundaram,S.P.; Parthiban,S.; Madhurambal,G.; Dhanasekaran,R.; Mojumdar,S.C. J.Therm.Anal.Calorim. **2008**, 94, 15-20.

17. Bhagavannarayana,G.; Parthiban,S.; Subbiah Meenakshisundaram. Cryst.Growth Des. **2008**, 8, 446-451.

18. Peng,W.Q.; Qu,S.C.; CongG.W. J.crystal growth. **2005**, 279, 454.

19. Venkataramanan,V.; Dhanaraj,G.; Wadhawan,V.K.; Sherwood,J.N.; Bhat,H.L. J.crystal growth. **1995**, 154, 92.

20. Jouini,A.; Yoshikawa,A.; Fukuda,T.; Boulon,G. J. crystal growth. **2006**, 293, 517. 21. Davey,R.J.; Mullin,J.W. J. crystal growth. 1974, 26, 45.

22. Yumashe,K.V.; Appl. Opt. **1999**, 38, 6343.

23. Natasha, A. N.; Sopyan, I.; Mel, M.; Ramesh, S. Med. J Malaysia. **2008**, 63, 85- 86.

24. Cheng, J. J.; Wu, J. M. Mater. chem. phys. **1999,** 48, 129.

25. Xiandong Wang.; Zhenquan Liu.; Andra Ambrosini.; Antoine Maignan.; Charlotte L. Stern.; Kenneth R. Poeppelmeier.; Vinayak P. Dravid. Solid State Sciences. **2000**, 2, 99-107.

26. Santos,D.A.A.; Rocha,A.D.P.; Duque,J.G.S.; Macedo,M.A. J. Physics. **2010**, Conference series 200 IOP Publishing Ltd.

27. Bhagavannarayana,G.; Kushwaha,S.K.; Parthiban,S.; Subbaih Meenakshisundaram. J. crystal growth, **2009**, 311, 960- 965.

28. Nishitha Prabhu., et. al, Journal of Optics, **2025**, 964

29. Srinivasan Karuppanan., Materials Chemistry and Physics, **2014**, 144, 293-300.

30. Jyotsna Pandey, Deep Sagar, IJARESM, **2023**, 11, 218-223.

31. Girija.P., Materials Today Proceedings, **2022**, 49, 2569-2573.

32. Girija.P., GJSR, **2024**, 1, 1-9.