International Journal of Scientific Research in Physics and Applied Sciences
Vol.11, Issue.4, pp.33-37, August 2023
E-ISSN: 2348-3423
Available online at: www.isroset.org

Research Paper

Growth and Elemental, FTIR Spectroscopic and Thermal Analysis of Pure and Isoleucine Doped Lithium Dihydrogen Phosphate Crystals

H.K. Ladani[1*], V. J. Pandya[2], Radhika Rathod[3], H.O. Jethva[4]

[1,2,3,4]Dept. of Physics, Saurashtra University, Rajkot – 360005, Gujarat India

**Corresponding Author: happyladani18@gmail.com*

Received: 15/Jun/2023; **Accepted**: 17/Jul/2023; **Published**: 31/Aug/2023

Abstract— Pure as well as isoleucine doped lithium dihydrogen phosphate (LDP) crystals are grown at room temperature using the solution growth method. The elemental analysis shows the presence of the atoms of dopant molecule isoleucine and its weight % increases with increase in weight % of the isoleucine, which confirms the successful doping of the isoleucine in the crystal lattice of pure LDP crystal. The FTIR spectra shows the presence of all constitute functional groups of LDP in pure as well as in isoleucine doped LDP crystals. No significant effect of isoleucine doping on the crystal structure of pure LDP is observed except the presence of N – H bending and C – H bending vibrations in the case of 0.6wt% and 0.9wt% isoleucine doped LDP crystals. The thermal analysis of pure and different wt% isoleucine doped LDP crystals indicates that the presence of isoleucine prevents the thermal decomposition of pure LDP at lower temperature and shifts towards higher temperature and reduces the weight loss of pure LDP. The results are discussed and analyzed in detail.

Keywords— Lithium dihydrogen phosphate, isoleucine, Raman spectroscopy, EDAX, FTIR, TGA

1. Introduction

The pure and doped crystals of various phosphate compounds are investigated by the researchers due to their several physical and chemical properties interesting for basic research and practical applications. Among various phosphate compounds, the most widely studied phosphate compounds are the dihydrogen phosphate of ammonium and potassium due to their non-linear optical behavior, while less investigation is reported on the pure and doped dihydrogen phosphate of lithium. The structure of lithium dihydrogen phosphate, commonly known as LDP, consists of tetrahedral groups of PO_4, i.e. phosphate ion and LiO_4, which are bonded together by oxygen ions [1]. Raman spectroscopic data of LDP have been reported by Lee et al [2] between 70 to 300 K and not observed any change in spectra at low temperature, while at high temperature, within range of temperature 170 to 220 ^oC, the Raman spectroscopic data have been reported by R. Dekhili et al [1] and observed intensity breakdown in the monotonous behavior with temperature and two anomalies around 176 ^oC and 210 ^oC temperature for all main Raman lines. These results were found consist with the electrical data reported by Lee et al [3] and confirmed their interpretation. Such type of studies is reported for pure LDP but no reports have been found in the literature for the pure and amino acid doped LDP crystals.

Further, limited data on the decomposition process of LDP crystal is reported, while the decomposition of pure and doped dihydrogen phosphate crystals of ammonium and potassium has been investigated [4,5], with the discussion of the effect of the dopant. The dehydration reaction and the formation of dehydration intermediates of dihydrogen phosphates of several alkali metals have been reported in the literature [6,7], but almost no reports are available in the literature regarding the dehydration and decomposition process of amino acid doped LDP crystals and the effect of dopant in various concentration on the dehydration and decomposition process of LDP crystals.

The present investigation deals with the growth of pure and isoleucine doped LDP crystals and discusses the effect of isoleucine doping in various concentrations on the characteristic vibrations of phosphate by FTIR analysis and on the dehydration and decomposition properties of LDP.

2. Experimental Technique

Pure crystals of LDP and different weight%, i.e., 0.3wt%, 0.6wt% and 0.9wt% isoleucine doped LDP crystals are grown using solution growth technique at room temperature by preparing the 100 ml saturated solution of pure LDP in distilled water in four different beakers. One beaker is

selected for the growth of pure LDP crystals and in residual beakers 0.3gm, 0.6gm and 0.9gm isoleucine is added for the growth of 0.3wt%, 0.6wt% and 0.9wt% isoleucine doped LDP crystals. The solutions are stirred well for at least 2 hours for getting the homogeneous solution. Then all the solutions are filtered by using good quality filter papers and put in clean and disturbance free atmosphere. All the beakers are covered by plastic paper having some numbers of pin halls in it for the process of controlled evaporation, which is necessary for the growth of crystals. After about 30 days, good quality, transparent and colorless crystals are observed in each beaker. They are harvested very carefully, washed with distilled water and after drying, photographs are taken by placing the crystals on the graph paper, which are shown in the figure 1.

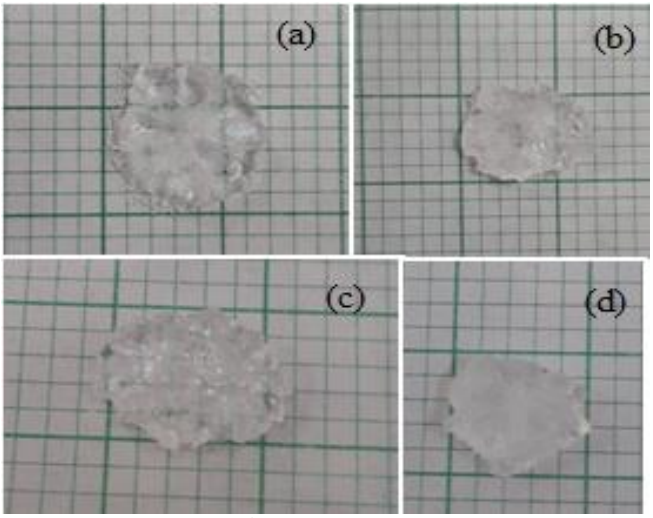

Figure 1: Grown crystals of (a) pure LDP (b) 0.3wt% (c) 0.6wt% and (d) 0.9wt% isoleucine doped LDP

It can be observed from the figure 1, that the grown crystals possess the flower shaped morphology.

All the crystals are analyzed by various analyses. Elemental analysis is carried out in order to find the presence of the atoms of the dopant molecule, in the present case, it is isoleucine. Elemental analysis is carried out by using the Philips XL-30 instrument set up. In order to identify the presence of characteristic vibrations of phosphate and the effect the dopant molecule on the characteristic vibrations of phosphate, Fourier Transform Infra-Red (FTIR) analysis is carried out on Thermo Nicolet Avtar 370 set up within the frequency range 4000cm^{-1} to 400cm^{-1} in KBr medium. In order to find out the presence of various decomposition stages of pure LDP and the effect of doping of isoleucine in different weight% on various decomposition stages of LDP, thermal analysis is carried out on Perkin Elmer STA-8000 set up from room temperature to 700^{o}C at heating rate 15^{o}C/min in the air atmosphere.

3. Result and Discussion

EDAX Analysis

In order to find out the elemental composition of the grown crystals, the EDAX study was carried out. Table 1 shows the wt% of different elements from EDAX, which are present in the grown crystals of pure and different weight% isoleucine doped LDP. The chemical formula of lithium dihydrogen phosphate (LDP) is LiH_2PO_4. The formula suggests that LDP contains both oxygen (O) and phosphorous (P). The chemical formula of dopant isoleucine is $C_6H_{13}NO_2$. Therefore, when isoleucine in different wt% is doped into pure LDP, the presence of carbon (C) and nitrogen (N), along with oxygen (O) and phosphorous (P) of pure LDP confirms the presence of dopant atoms in the LDP crystal. It is worth to mention that the addition of isoleucine in very small quantity, i.e., 0.3gm, 0.6gm and 0.9gm in 100 ml of saturated solution of LDP, the difference in solubility as well as crystal growth rate of LDP and isoleucine may result into the limited amount of dopant that enters into lattice sites of LDP. From the table 1, it is observed that wt% of carbon (C) and nitrogen (N) increase as the weight% of isoleucine increases in LDP, which confirms the successful doping of isoleucine in the crystal lattice of pure LDP.

Table 1. EDAX Result

Sample Name	Carbon(C) Wt%	Nitrogen(N) Wt%	Oxygen(O) Wt%	Phosphorous (P) Wt%
Pure LDP	-----	-----	64.00	35.00
0.3Wt% Isoleucine doped LDP	9.08	1.11	57.25	30.44
0.6Wt% Isoleucine doped LDP	11.20	2.66	57.94	29.73
0.9Wt% Isoleucine doped LDP	23.95	3.25	48.98	24.40

FTIR spectroscopy analysis

Figure 2 shows the FTIR spectra of pure and different wt% isoleucine doped LDP crystals, while observed absorption frequencies and their assignments in relation to their characteristic vibrational modes are listed in table 2. The crystal of LDP possesses internal as well as external modes of vibrations, elaborately speaking, internal vibrations arise from PO_4 and LiO_4 motion, while the external vibrations (known as lattice vibrations) result from the relative motion between the groups [2]. Dihydrogen phosphate group of crystals possess hydrogen bond network. Hydrogen bond network O – H …… O in solids can be classified as strong, intermediate or weak [8]. The OH stretching frequency depends on the distance between O ….. O and can be classified as 700-2700 cm^{-1} for strong, 2800-3100 cm^{-1} for the intermediate and more than 3200 cm^{-1} for the weak hydrogen bonding. In the present case, the band located at 3080 cm^{-1} and at 2655, 2322, 2114 and 1626 cm^{-1} in the pure LDP crystal can be designated as OH vibration belonging to an intermediate and strong hydrogen bond, respectively [2]. As isoleucine is doped; the band observed at 3080 cm^{-1} is observed to shift slightly towards higher wavenumber and appears at 3084 cm^{-1}. The shifting of this band towards higher wavenumber indicates the reduced strength of the hydrogen bonding due to the presence of isoleucine. This may be the effect of the presence of hydroxy group of isoleucine, exist between neighboring

molecules. The band observed at 1279 cm^{-1} in pure LDP can be attributed to the in-plane deformation vibration of OH [2]. In the isoleucine doped LDP, this vibration is observed at the same wavenumber.

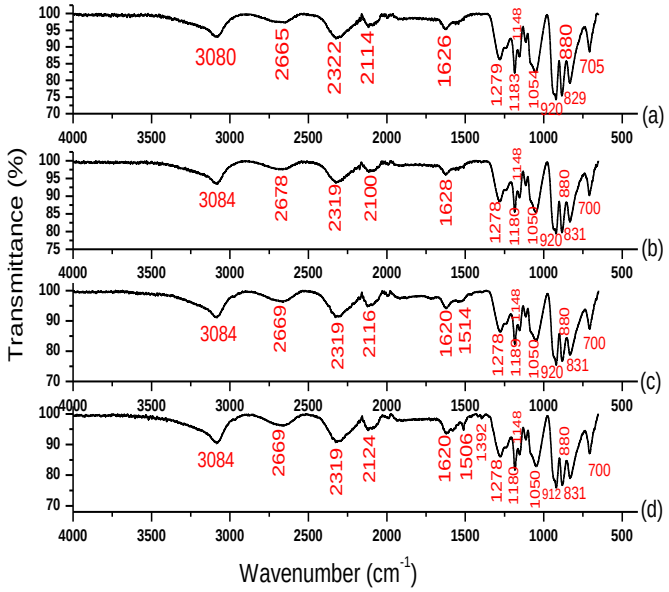

Figure 2. FTIR spectra of (a) Pure LDP (b to d) 0.3wt%, 0.6wt% and 0.9wt% isoleucine doped LDP

The phosphate group shows various modes of vibrations such as a symmetric stretching mode (ν_1), an anti-symmetric stretching mode (ν_3), a symmetric bending mode (ν_2) and (ν_4) [9] and they are observed modified slightly due to the surrounding crystalline field. The bands observed around 1180 and 1050 cm^{-1} in pure and isoleucine doped LDP can be assigned to anti-symmetric stretching mode (ν_3) of PO_4 or out-of-plane bending vibrations of OH group [2]. A symmetric stretching mode (ν_1) of PO_4 is observed around 920 and 880 cm^{-1} in pure and isoleucine doped LDP crystals. The vibrations observed around 830 and 705 cm^{-1} can be ascribed to the overtone of PO_4 or LiO_4 [2]. The assignment of LiO_4 is based on the fact that the crystal structure of LDP is composed of LiO_4 and $H_2PO_4^{-1}$, which share oxygen atoms. The effect of isoleucine doping is clearly observed in the case of 0.6wt% and 0.9wt% isoleucine doped LDP. In the case of 0.6wt% isoleucine doped LDP crystal, one additional absorption band at wave number 1514 cm^{-1} is observed, which can be assigned to the bending vibration of N – H bond, while in the case of 0.9wt% isoleucine doped LDP, crystal, two additional absorption bands at wave number 1506 and 1392 cm^{-1} are observed, which can be assigned to the bending vibration of N – H bond and symmetrical bending vibration of methyl C – H bond, respectively [10,11]. The FTIR analysis shows that there is no significant effect of doping of isoleucine on the crystal structure of pure LDP, except reducing the strength of hydrogen bonding and the presence of N – H bending and C – H bending vibrations in the case of 0.6wt% and 0.9wt% isoleucine doped LDP crystals.

Table 2. Assignments of functional groups with frequency

Assignments	Wave numbers (cm^{-1})			
	Pure LDP	0.3wt% isoleucine doped LDP	0.6wt% isoleucine doped LDP	0.9wt% isoleucine doped LDP
O – H stretching vibrations of intermediate H bond	3080	3084	3084	3084
O – H stretching vibrations of strong H bond	2665, 2322, 2114, 1626	2678, 2319, 2100, 1628	2669, 2319, 2116, 1620	2669, 2319, 2124, 1620
Bending vibration of N – H bond	-------	-------	1514	1506
Bending vibration of methyl C – H bond	-------	-------	-------	1392
O – H in-plane deformation vibration	1279	1278	1278	1278
Anti-symmetric stretching mode (ν_3) of PO_4 and/or out-of-plane bending vibrations of OH	1183, 1054	1180, 1050	1189, 1050	1180, 1050
symmetric stretching mode (ν_1) of PO_4	920, 880	920, 880	920, 880	912, 880
overtone of PO_4 or LiO_4	829, 705	831, 700	831, 700	831, 700

Thermal analysis

The curves of Thermogravimetry of pure and different wt% isoleucine doped LDP crystals are shown in the figure 3, while the remaining weight loss% are given in the table 3.

The curve of thermogravimetry of pure LDP crystal shows the thermal stability up to 200 ^oC, which indicates good stability compared to the reported in the literature [12] with good agreement with the result reported in the literature [13]. Then within range of temperature 200 to 345 ^oC, pure LDP crystal looses 18% weight. The thermal analysis shows that this weight loss is the result of the conversion of LDP into $LiPO_3$. Then, up to the higher temperature limit, which is 600 ^oC in this investigation, the product remains as it is. This also shows good agreement with the literature [13]. The thermal decomposition of acid phosphates of alkali metals, having general formula MH_2PO_4, generally includes more than one step [13]. In the present analysis, one step process is observed for the conversion of LDP into $LiPO_3$ within mentioned temperature range.

Isoleucine doped LDP shows noticeable change in the thermogravimetry, particularly in the case of 0.9wt% isoleucine doped LDP. The 0.3wt% and 0.6wt% isoleucine doped LDP crystals show almost same thermal stability as that of pure LDP, while 0.9wt% isoleucine doped LDP crystals show initial weight loss of 1% within room temperature to 180 ^oC, which can be ascribed to the probability of insertion of some molecules of water, used for the process of crystallization. Then after, all the three isoleucine doped LDP show the decomposition process completed within single step followed by stability region. Discussing for the particular isoleucine doped LDP, 0.3wt% and 0.6wt% isoleucine doped LDP shows 18% weight loss

within temperature range 200 to 417 ^{o}C and then remains stable up to 600 ^{o}C temperature. While, 0.9wt% isoleucine doped LDP shows only 4% weight loss within temperature range 180 ^{o}C to 405 ^{o}C and then remains stable up to 600 ^{o}C temperature. It can be concluded from the above discussion that the presence of isoleucine in the amount of 0.3wt% and 0.6wt% increases the temperature of conversion of LDP into $LiPO_3$ from 200 to 345 ^{o}C to 200 to 417 ^{o}C. After that the weight of the residual product increases from 18% (in the case of pure LDP and 0.3wt% and 0.6wt% isoleucine doped LDP) to 95% in the case of 0.9wt% isoleucine doped LDP. It shows that the presence of isoleucine impedes the thermal decomposition of pure LDP at lower temperature (345 ^{o}C) and shifts towards higher temperature (417 ^{o}C) and reduces the weight loss of pure LDP from 18% (in the case of pure LDP and 0.3wt% and 0.6wt% isoleucine doped LDP) to only 4% in the case of 0.9wt% isoleucine doped LDP. The increased temperature region of conversion of LDP into $LiPO_3$ can be allocated to the increase in bond energy due to the presence of dopant isoleucine.

The thermal analysis of pure and isoleucine doped LDP shows the conversion of LDP into $LiPO_3$. According to literature, $LiPO_3$ can be synthesized directly from reacting metaphosphoric acid with LiOH in solution [14] or from the solid state reaction of different phosphates of ammonium with lithium sources [15]. But these methods have the disadvantages of producing west water in the former and ammonia gas in the latter, which may create environmental and safety problems [13].

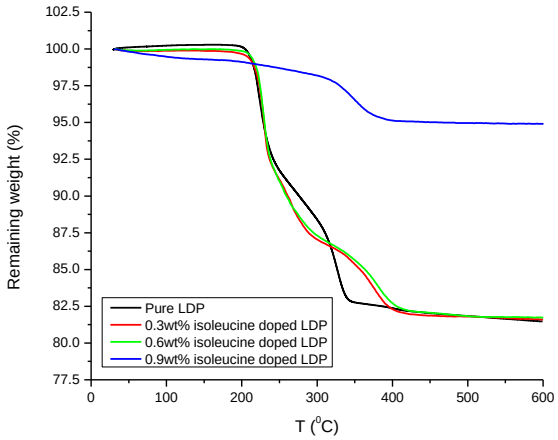

Figure 3. TG curves of pure and isoleucine doped LDP crystals

. **Table 3.** Thermogram result

Sample	Temperature range (^{o}C)	Remaining weight (%)
Pure LDP	From RT to 200	100
	From 200 to 345	82
	From 345 to 600	82
0.3wt% isoleucine doped LDP	From RT to 200	100
	From 200 to 417	82
	From 417 to 600	82
0.6wt% isoleucine doped LDP	From RT to 200	100
	From 200 to 417	82
	From 417 to 600	82
0.9wt% isoleucine doped LDP	From RT to 180	99
	From 180 to 405	95
	From 405 to 600	95

6. Conclusion and Future Scope

Pure and isoleucine doped LDP crystals are grown at room temperature by the solution growth method. The elemental analysis confirms the presence of dopant isoleucine atoms with increase in weight% of atoms with increase in the weight% of isoleucine. This confirms the successful doping of isoleucine in the crystal lattice of pure LDP. FTIR spectroscopic analysis shows the presence of characteristic vibrations of phosphate group in pure and isoleucine doped LDP crystals. The effect of doping and increase in its weight% is clearly observed in terms of the presence of N – H bending and C – H bending vibrations in the case of 0.6wt% and 0.9wt% isoleucine doped LDP crystals. The thermogravimetry of pure and different wt% isoleucine doped LDP crystals clearly indicates the effect of doping of isoleucine in terms of the elimination of the conversion LDP at lower temperature, shifts towards higher temperature with observed reduction of the weight loss of pure LDP from 18% (in the case of pure LDP and 0.3wt% and 0.6wt% isoleucine doped LDP) to only 4% in the case of 0.9wt% isoleucine doped LDP.

Data Availability
The raw data required to ongoing study; hence it cannot be shared.

Conflict of Interest
The authors declare that there are no competing interests.

Funding Source
The author(s) received no financial support for the research, authorship, and/or publication of this article.

Authors' Contributions
Authors are required to include a statement of responsibility in the manuscript that specifies the contribution of every author. The level of detail varies; some disciplines produce manuscripts that comprise discrete efforts readily articulated in detail, whereas other fields operate as group efforts at all stages.

For Example- Author-1 researched literature and conceived the study. Author-2 involved in protocol development, gaining ethical approval, patient recruitment, and data analysis. Author-3 wrote the first draft of the manuscript. All authors reviewed and edited the manuscript and approved the final version of the manuscript.

Acknowledgements
Experimental, conceptual study and data collection: Hepi Ladani, V. J. Pandya and Radhika Rathod; Analysis and Interpretation of Results: Hepi Ladani and Prof. H. O. Jethva;

Draft manuscript design: Hepi Ladani; Supervising and editing manuscript: Prof. H. O. Jethva.

References

[1]. R. Dekhili, T. H. Kuffmann, H. Aroui, M. D. Fontana, "Phase transformations in LiH_2PO_4 (LDP) revealed by Raman spectroscopy", *Solid State Commun.,* Vol. **279, pp. 22-26, 2018**

[2]. Kwang-Sei Lee, Jae-Hyeon Ko, Joonhee Moon et al., "Raman spectroscopic study of LiH_2PO_4", *Solid State Commun.,* Vol. **145, pp. 487-492, 2008**

[3]. Kwang-Sei Lee, Joonhee Moon, Jisu Lee et al, "High-temperature phase transformations in LiH_2PO_4 and possible solid-state polymerization", *Solid State Commun.,* Vol. **147, pp.74-77, 2008**

[4]. K. V. Vadhel, V. J. Pandya, M. J. Joshi, H. O. Jethva, "Growth and characterization of pure and l-ornithine monohydrochloride doped ADP crystals", Int. J. Sci. Res. in Physics and Applied Sciences, Vol. **10(3), pp.19-25, 2022**

[5]. H. Bhuva, H. O. Jethva, "EDAX, Thermal, UV-Vis and SHG studies of pure and creatinine doped KDP crystals", *Journal of Physics and Chemistry of Materials,* Vol. **10(1), pp.01-06, 2023**

[6]. P. K. Gallagher, "A study of the thermal decomposition of some alkali metal dihydrogen phosphates and arsenates", *Thermochimica Acta,* Vol. **14(1-2), pp.131-139, 1976**

[7]. Jong-Ho Park, Kwang-Sei Lee, Byung-Chun Choi, "High temperature transformation in KH_2PO_4 and RbH_2PO_4 crystals", *J. Phys.: Condens. Matter,* Vol. **13(42), pp.9411, 2001**

[8]. A. Novak, "Structure and Bonding", Springer, Vol. **18, pp.177, 1974**

[9]. Ray L. Frost, Andres Lopez, Yunfei Xi, Ricardo Scholz, "Vibrational spectroscopic characterization of the phosphate mineral althausite Mg2(PO4)(OH,F,O)-Implications for the molecular structure", *Spectrochim. Acta A: Mol. Biomol. Spectrosc.,* Vol. **120, pp.252-256, 2014**

[10]. A. Stanila, A. Marcu, D. Rusu, M. Rusu, L. David, "Spectroscopic studies of some copper(II) complexes with amino acids", *J. Mol. Struct*., Vol. **834-836, pp.364-368, 2007**

[11]. John Coats; Interpretation of Infrared Spectra, A Practical Approach, R. A. Meyers (Ed), John Wiley & Sons Ltd., Chichester, **pp.10815-10837, 2000**

[12]. R. Benkhoucha, B. Wunderlich, "Crystallization during polymerization of of lithium dihydrogen phosphate. I. Nucleation of the macromolecular crystal from the oligomer melt", *Z. Anorg. Allg. Chem.,* Vol. **444, pp.256-266, 1978**

[13]. Bahman Yari, Pierre Sauriol, Jamal Chaouki, "Kinetics of the dehydration of lithium dihydrogen phosphate", *Can. J. Chem. Eng*., Vol. **97(8), pp.2273-2286, 2019**

[14]. S. Prakash, G. D. Tuli, S. K. Basu, R. D. Madan, "Advanced Inorganic Chemistry", 17th Ed., S. Chand & Co. Ltd., New Delhi, Vol. **1, 2000**

[15]. S. Angaiah, V. Thiagarajan, G. Ramaiyer, R. Meenakshisundaram, Council of Scientific & Industrial Research, invs.:US. 6656441B2, **2003**

AUTHORS PROFILE

Ms. Hepi Ladani pursued Bachelor of Science in Physics from the Saurashtra University, Rajkot, Gujarat and Master of Science in Physics from the same university in the year 2015 and 2017, respectively. She is currently pursuing Ph.D. and currently working as an Assistant Professor in Physics at the Atmiya University, Rajkot, Gujarat. She holds 5 years of experience of teaching physics to undergraduate students and 3 years of research experience

Dr. H. O. Jethva is a post graduate from the Saurashtra University, Rajkot, Gujarat and Doctorate from the same university. He has published forty research papers in International Journals of repute and five books for the undergraduate students of the same university. He holds an experience of teaching Physics to undergraduate and postgraduate students of twenty-seven years. He is currently working as a Professor in the Department of Physics at the same university.

Ms. V. J. Pandya has gained Bachelor of Science in Physics and Master of Science in Physics from the Saurashtra University, Rajkot, Gujarat in the year 2016 and 2018, respectively. She has also pursued Master of Philosophy in Physics from the same University in the year 2020. She is currently pursuing Ph.D with main research work focus on Crystallography and Condensed Matter Physics. She has 2 years of teaching experience and 3 years of research experience.

Ms. Radhika Rathod is a post graduate in Education from the Saurashtra University, Rajkot, Gujarat in the year 2020 and post graduate in Physics from the RK University, Rajkot, Gujarat in the year 2022. She is currently pursuing Ph.D. with main research work focused on growth and characterization of pure and doped metal sulphate crystals.

Call for Papers:
Authors are cordially invited to submit their original research papers, based on theoretical or experimental works for publication in the journal.

Make a Submission

All submissions:
- must be **original**
- must be **previously unpublished research results**
- must be **experimental or theoretical**
- must be in **the journal's prescribed Word template**
- and will be **peer-reviewed**
- may not be **considered for publication elsewhere at any time during the review period**