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ATOMIC SCATTERING FACTOR ESTIMATION OF PURE AND INORGANIC DOPED L-ASPARAGINIUM CHLORIDE MONOHYDRATE CRYSTALS

C. Prasanna Devi[1]*, P. Sumithraj Premkumar[2], V. Sivashankar[3] and G.V. Anuradha[4]*

[1]Department of Physics, CSI Jayaraj Annapackiam College, Nallur, Tenkasi – 627853

[2]Research Department of Physics, St. John's College, Palayamkottai, Tirunelveli-627002, Tamilandu.

[3]Ressearch Department of Physics, St. Xavier's College (Autonomous), (Affiliated to Manonmaniam Sundaranar University, Tirunelveli - 627012), Palayamkottai-627002

[4]Department of Physics, Sriparasakthi College for Women (Autonomous), Courtallam-627802

ABSTRACT

pure, cadmium chloride and zinc chloride doped L- Asparaginium chloride monohydrate crystals grew by slow evaporation method using de-ionized water as solvent. The concentration of Cadmium chloride and Zinc Chloride in the present study is 0.01M. Powder X-ray diffraction data were composed and used for the valuation of lattice parameter and atomic scattering factors. The Debye-Waller factor, Debye temperature, mean-square amplitude of vibration and Debye frequency were also measured. The inorganic doped L-Asparaginium chloride monohydrate crystal's X-ray diffraction pattern were changed little compared to pure L-Asparaginium chloride monohydrate single crystals. The entry of inorganic dopants into the pure L-Asparaginium chloride monohydrate crystal was confirmed by the difference of lattice volume of the grown crystals. The calculated thermal parameter value suggested that the grown crystals are having the active phonon modes with stiffer crystal.

Keywords: inorganic doped crystal, PXRD, lattice volume, Debye-Waller factor, Debye temperature.

INTRODUCTION

Organic materials have piqued interest due to the nonlinear optical effects in materials, providing a chance to design and build novel materials using theoretical modelling and synthetic flexibility.

Crystals from the amino acid family have been studied extensively in recent decades for their nonlinear optical characteristics because of the wide applications in the science and engineering field such as optical networking, digitalization through computation, harmonic generation, optical transmission and frequency modulation [1]. The high nonlinear optical properties of the materials have efficient features of opto-electronic switching for the optical information process the telecommunication field. Therefore, the developments of photonics and opto-electronics fields are needed the developments of advanced molecular and crystal modelling methods for uniting the materials [2].

L-asparagine Monohydrate [$NH_2CO(CH_2)CH(NH_3)CO\text{-}2H_2O$] is an amino acid crystals and it is interesting to analyse such a good efficient material since it crystallizes in a structure containing a complicated hydrogen bond network between asparagine and water molecules. Based on this, some L-Asparagine with L-tartaric acid, picrate, Mn^{2+} doped and cadmium chloride doped materials were synthesized and these materials have evidenced to be potential materials for NLO application [3-7].

The non-destructive technique, X-ray diffraction is a prevailing method to characterize the crystalline materials. The crystalline information such as phases, orientations, structure, crystalline nature, strain, and defects are identified from the XRD data. Experimentally, X-ray diffraction peaks are formed by the constructive interference of an X-rays' monochromatic beam which was scattered at exact angles from each set of lattice planes in a material. Lattice in an atom have fixed the peak intensities of X-ray pattern. Therefore, the X-ray diffraction pattern is the impression of periodic arrangements of atom in a prepared sample. Hence the X-ray diffraction studies of the material is essential in the field of medicines, scientific, physical applications, microelectronics industry, glass engineering, and corrosion investigation [8]. In the present study, the pure and doped L-Asparaginium chloride monohydrate crystals were grown and their thermal parameters were analysed by involving powder X-ray diffraction studies.

MATERIALS AND METHODS

Analytical reagent grade of L- Asparagine monohydrate, $CdCl_2$, zinc chloride and hydrochloric acid were used in the present work for the growth of crystals. Deionized water was used as the solvent.

L Asparagine monohydrate and hydrochloric acid were engaged as 1:1 ratio and crystallized as L-Asparaginium chloride monohydrate through slow evaporation method using deionized water as medium. After it was crystallized, the concentrated L-Asparaginium chloride monohydrate with saturation was prepared as a growth solution at ambient temperature. Then, the required amount of dopant (Cadmium chloride and Zinc Chloride) was mixed separately to the pure solution and stirred for 1 hour to get the homogeneous mixture. The dopant concentrations of Cadmium chloride and Zinc Chloride was 0.01M. The prepared mixture solution was placed in a constant temperature bath at a temperature slightly higher than the ambient. Tiny crystals were seen at the bottom of the beaker after three days and it was allowed to grew larger size at considerable finite time. Good crystals with good morphology were selected and used for the characterization.

Using copper k-alpha radiation and scintillation counter, X- ray diffraction data were collected for powder samples at a temperature around 25 °C of pure and inorganic doped L-Asparaginium chloride monohydrate crystals. Powder x [9] software was adopted to index the PXRD patterns. By considering high reflections, the lattice parameters such as volume and constant were calculated from the indexed data of grown crystals.

The Wilson plot method was used to measure the mean Debye-Waller factors (B_{obs}). The structure factors of the grown crystals were determined from the atomic scattering factors which is available in the literature [10-11]. For pure of L Asparaginium chloride monohydrate crystal, the structure factor is:

$$F= 4f_C +11f_H + 2f_N + 4f_O + f_{Cl} \quad \text{……..(1)}$$

Generally, reported that the doping atoms in the doped crystals are positioned in the host lattice or dispersed at random positions particularly on the surface of the grown crystals [12]. The structure factors of cadmium chloride and zinc chloride doped L-Asparaginium chloride monohydrate crystals are:

$$F=4f_C+11f_H+2f_N+4f_O + f_{Cl}+ p\ (f_{Cd} + 2f_{Cl}) \quad \text{……...(2)}$$

$$F=4f_C+11f_H+2f_N+4f_O + f_{Cl}+ p\ (f_{Cd} + 2f_{Cl}) \quad \text{……....(3)}$$

Here 'p' is the dopant concentration. The mean Debye-Waller factor of pure, cadmium chloride and zinc chloride doped L-Asparaginium chloride monohydrate crystals was found by Wilson plot method [13].Then, mean square amplitudes of vibration and mean Debye temperatures were determined using the following relations [14]

$$B=8\pi^2 \langle u^2 \rangle \quad \text{……... (4)}$$

Here $\langle u^2 \rangle$ is the mean square amplitude of vibration.

From the Debye-Waller theory,

$$B = 6h^2W(x)\ (mkT) \quad \text{…..…..(5)}$$

h - Planck's constant, m - mean atomic mass of the crystal, k - Boltzmann's constant and T - absolute temperature.

$$\text{Also, } W(x) = (\phi(x)/x^2) + (x/4) \quad \text{……..(6)}$$

Here $x = \theta_D/T$ (θ_D is the Debye temperature) and

$$\Phi(x) = \int_0^x \left\{\frac{e^y}{1-e^y}\right\} dy \quad \text{……..(7)}$$

The values of W(x) for a range of x was determined and listed by Benson and Gill [15]. Also the x can be determined from the given table. Then, the Debye temperature (θ_D) for the grown crystals were measured from the

value of x. Using the following relation and knowing the Debye temperature, the Debye frequency was determined [16].

$\theta_D = f_D(h/k)$ ……..(8)

where h is Planck's constant and k is Boltzmann's constant.

RESULT AND DISCUSSION

Transparent and extreme size of the grown crystals was collected from the growth vessel. The photograph of the grown pure, cadmium chloride and zinc chloride doped of L- Asparaginium chloride monohydrate crystal are shown in Fig 1, Fig 2 and Fig 3 respectively. It is noted that all the grown crystals such as L- Asparaginium chloride monohydrate crystal, CdCl2 and ZnCl2 doped L-Asparaginium chloride monohydrate crystals are having similar morphology.

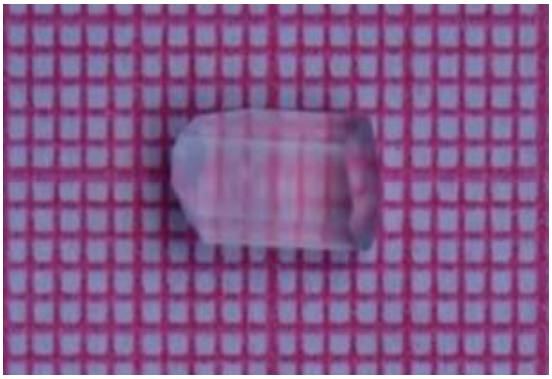

Figure 1: Photograph of pure L Asparaginium chloride monohydrate crystal

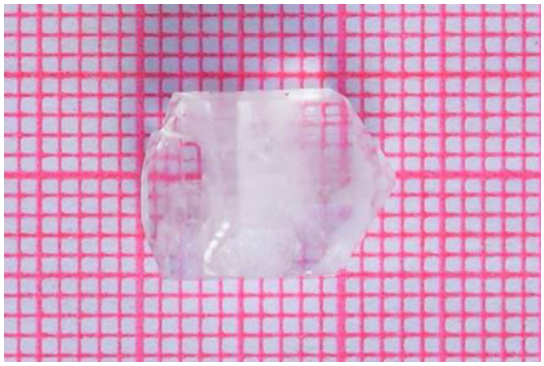

Figure 2: Photograph of the $CdCl_2$ doped L Asparaginium chloride monohydrate crystal

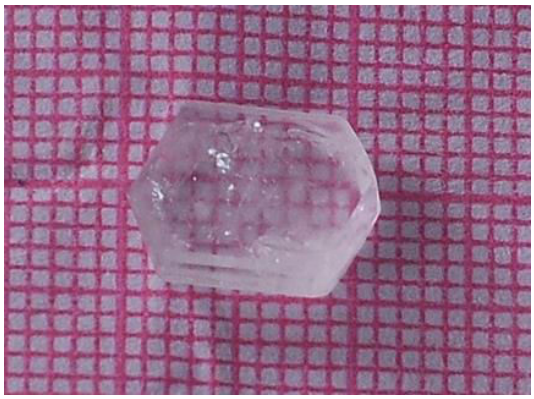

Figure 3: Photograph of the $ZnCl_2$ doped L Asparaginium chloride monohydrate crystal

The obtained power X-ray diffraction pattern were indexed using powder X software. The indexed XRD pattern of pure, cadmium chloride and zinc Chloride doped L- Asparaginium chloride monohydrate crystals are presented in the figures 4-6.

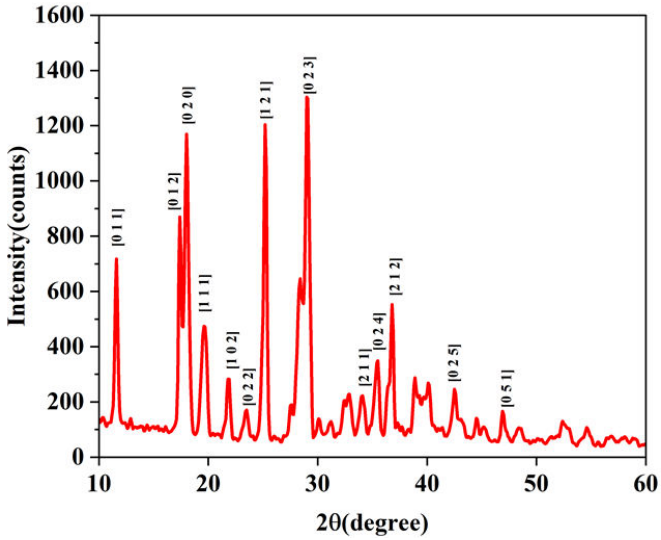

Figure 4: XRD pattern of pure L Asparaginium chloride monohydrate crystal

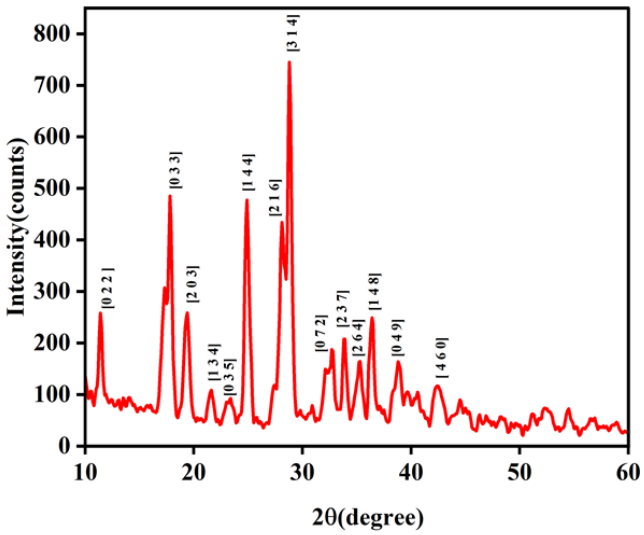

Figure 5: XRD pattern of the $CdCl_2$ doped L Asparaginium chloride monohydrate crystal

The X-ray pattern of $CdCl_2$, $ZnCl_2$ doped L Asparaginium chloride monohydrate crystals are somewhat fluctuated from their relative strengths of pure L Asparaginium chloride monohydrate ingle crystals. Lattice parameters such as lattice constant and lattice volume of the pure, $CdCl_2$, and $ZnCl_2$ doped L-Asparaginium chloride monohydrate single crystals were estimated and are given in table 1.

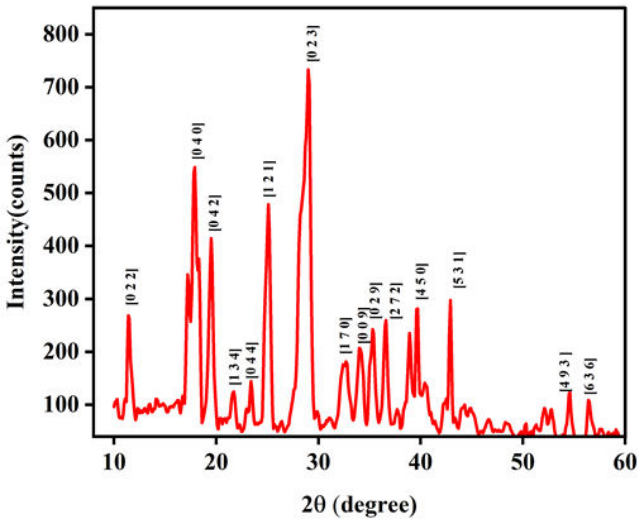

Figure 6: XRD pattern of the $ZnCl_2$ doped L Asparaginium chloride monohydrate crystal

Table 1: Lattice Parameter of Pure And $Cdcl_2$, $Zncl_2$, Doped L Asparaginium Chloride Monohydrate Single Crystals

Crystals	Lattice Constant			Lattice Volume (Å^3)
	a (Å)	b (Å)	c (Å)	
Pure L-Asparaginium chloride monohydrate	11.06	19.63	23.62	5131.70
$CdCl_2$ doped Pure L-Asparaginium chloride monohydrate	12.65	19.17	23.73	5758.98
$ZnCl_2$ doped Pure L-Asparaginium chloride monohydrate	11.19	19.77	23.53	5210.08

x-ray diffraction data of intended and detected intensities for all the reflections of the present work along with the respective $(\text{Sin}\ \theta\ /\lambda)^2$ values were taken to calculate the mean Debye-Waller factors. The observed intensity (A) and the corresponding θ values are measured from x-ray diffraction data and λ =1.5418Å. However it should be determined the calculated intensity values for all the reflections. For this, the atomic scattering factors for all the constituent atoms for various sin θ / λ of the observed reflections were used and relations were found using the formula,

$$\ln(A/I_c)=\ln(k) - 2B(\sin\theta/\lambda)^2 \quad \text{.....(9)}$$

The above equation shows that if $1n(A/I_c)$ is plotted against $(\text{Sin}\ \theta/\lambda)^2$ a straight line should be obtained and it is represented in figure 7-9.

The calculated Debye temperature (θ_D) and Debye frequency (f_D) values of pure and $CdCl_2$, $ZnCl_2$ doped L-Asparaginium chloride monohydrate crystals are listed in Table 2.

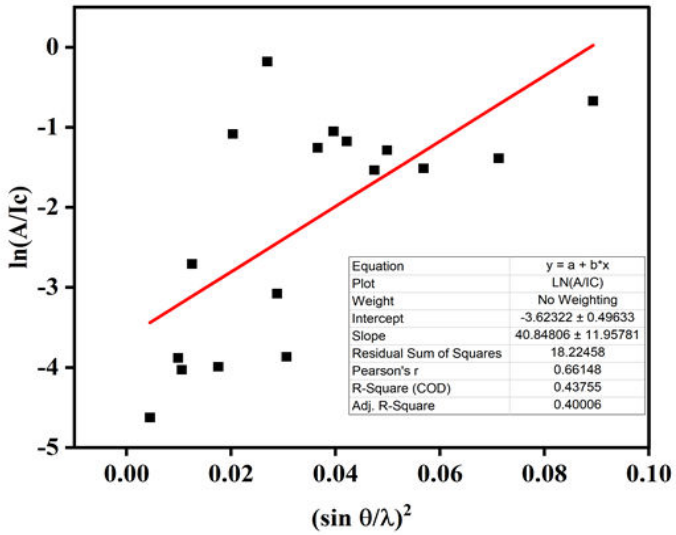

Figure 7: Wilson plot of L Asparaginium chloride monohydrate Crystal

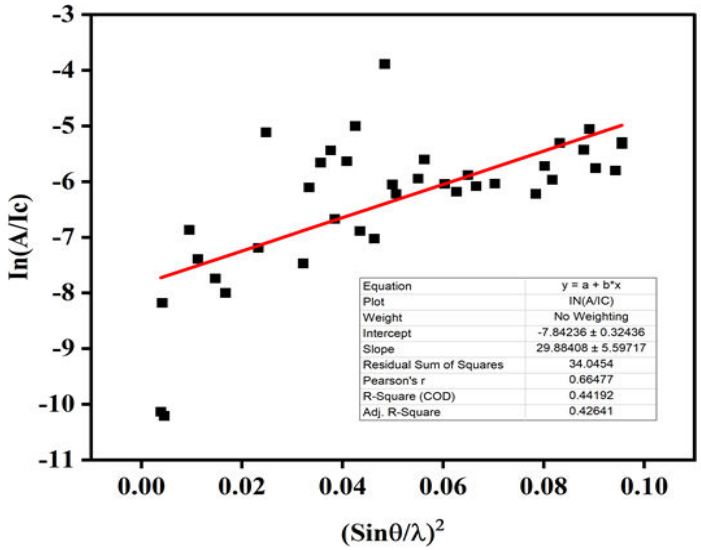

Figure 8: Wilson plot of $CdCl_2$ doped L Asparaginium chloride monohydrate Crystal

From the table 2, it is understood that there is no significance difference between the thermal parameter's values of pure and doped L-Asparaginium chloride monohydrate crystals. However, these obtained values suggested that all the grown crystals are having the active phonons. The observed Debye frequencies of pure and inorganic doped L-Asparaginium chloride monohydrate crystals present in the infrared range. Comparable results have been observed for the other crystals systems such as impurity added potassium dihydrogen orthophosphate, triglycine formate and triglycine oxalate crystals [17-18].

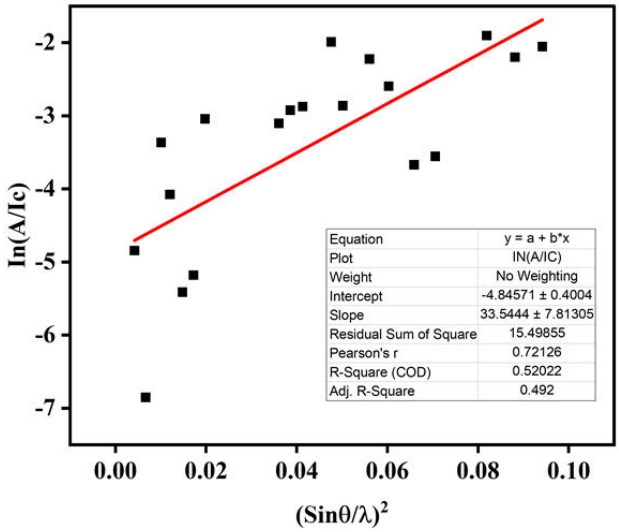

Figure 9: Wilson plot of $ZnCl_2$ doped L Asparaginium chloride monohydrate Crystal

Table 2: Thermal Parameters for Pure and Doped L-Asparaginium Chloride Monohydrate Crystals

Crystals	B ($Å^2$)	$<u^2>$ ($Å^2$)	θ_D(K)	$f_D(10^{12}Hz)$
Pure L-Asparaginium chloride monohydrate	20.42	0.2588	1770	36.8811
$CdCl_2$ doped Pure L-Asparaginium chloride monohydrate	14.94	0.1894	1180	24.5874
$ZnCl_2$ doped Pure L-Asparaginium chloride monohydrate	16.77	0.2126	1475	30.7342

CONCLUSIONS

Pure, $CdCl_2$ and $ZnCl_2$ doped L-Asparaginium chloride monohydrate crystals were grown from aqueous solution. The concentration of both dopants in the present study is 0.01M. X ray diffraction studies of all the grown crystals reveals the existence of tetragonal structure. The change in lattice volume of inorganic doped L-Asparaginium chloride monohydrate crystals were confirmed the entry of dopant into the pure L-Asparaginium chloride monohydrate crystal lattice. The thermal parameters of pure, $CdCl_2$ and $ZnCl_2$ doped L- Asparaginium chloride monohydrate crystals were calculated and no particular order was not followed by the calculated thermal parameters in the present study. However, it showed the active phonons presents in the crystal lattice

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