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in recognition of the publication in the edited book entitled

"ADVANCES IN SCIENCE, TECHNOLOGY AND INNOVATIONS"

edited by Dr. M. Anusuya, Dr R Rekha & Dr V Mohan

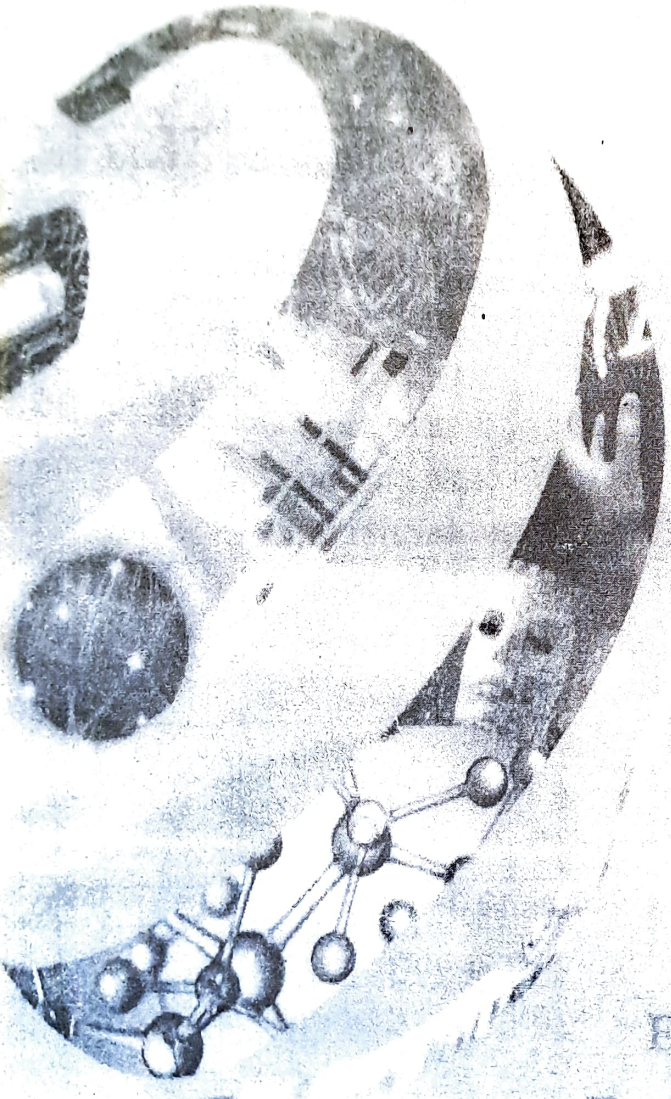
His/Her Chapter Title

"Growth and Characterization of Pure and 2-Picolinic Acid Doped L-Lysine Monohydrochloride Single Crystals"

Published in Category of Book Chapter, February 2022

ISBN: 978-93-93737-59-5

Dr. M. Anusuya
Editor in Chief- Advances in Science, Technology and Innovations
Registrar
Indra Ganesan Group of Institutions



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ADVANCES IN SCIENCE, TECHNOLOGY AND INNOVATIONS
ISBN 978-93-93737-59-5
First Edition 2022
Chapter-15 Pages 212-228

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GROWTH AND CHARACTERIZATION OF PURE AND 2-PICOLINIC ACID DOPED L-LYSINE MONOHYDROCHLORIDESINGLE CRYSTALS

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Abstract

Optically transparent single crystals of 2-picolinic acid doped with L-lysine monohydrochloride (LLM) were grown by slow evaporation solution technique at room temperature using deionized water as solvent. To confirm the presence of dopant various characterizations were studied. The unit cell parameters and the crystallinity nature of the grown crystal were

determined by Single Crystal and Powder X-ray diffraction studies. The presence of functional groups in the crystallized material have confirmed using the FT-IR vibrational spectrum. TGA/DTA and UV-Vis transmission studies are performed to know the thermal properties and optical behaviors of the grown crystal. The mechanical properties of the grown crystals were carried out by Vicker's microhardness measurements. The nonlinear optical property of the crystal have been evaluated using Nd: YAG laser as a source.

Keywords: Crystal growth from solution, XRD, Vibrational analysis, Thermal analysis

Introduction

Nonlinear optical (NLO) materials have been attracting a great deal of interests due to their applications such as high speed information processing, optical communications, optoelectronics and optical data storage [1]. In semiorganic materials the organic ligand is ionically bonded with inorganic host, the semi organic crystals provides a high degree of mechanical integrity and increase the properties of crystals. An aminoacid exists as a dipolar ion in which carboxyl group is present as carboxylate ion and amino group is present as ammonium ion. Due to this dipolar nature, they possess good mechanical and physical properties, viz., crystal hardness and high melting point, which make them ideal candidates for NLO applications [2]. L-lysine based compounds contain an optically active carbon atom having basic chain and therefore all of them form accentric crystal. L-lysine-based crystals such as L-lysine monohydrochloride [3-4] can be used as novel elasto-electro optical materials. The crystal structure and characterization studies of L-lysine monohydrochloride dihydrate have been reported [5-12]. Motivated by the earlier reports on doping [13-18]. Picolinic acid (pyridine 2-carboxylic acid), is a widely explored multidentate ligand and is very often used in NLO studies as

it has the ease of protonation in acid solution [19-20]. It is one of the most chelating agents present in the human body and they are involved in several essential biochemical processes [21-22]. It is a pyridine compound, an isomer of nicotinic acid with a carboxyl side chain at the 2nd & 3rd position. Interest in picolinic acid is also focused on the ability of the o-carboxylic acid group to form five member intramolecular O-H...N rings. The authors has reported that doping NLO crystals can alter various physical and chemical properties and find wide applications in optoelectronic devices compared to pure crystals [23-24]. For the first time we report the 3 wt % 2-picolinic acid doped L-lysine monohydrochloride (LLM) single crystals.

Experimental

Synthesis and Crystal Growth

Calculated amount of the reactants containing, Analar reagent (AR) of L-lysine monohydrochloride ($C_6H_{14}N_2O_2$) and 2-picolinic acid ($C_6H_5NO_2$) were purchased from (Loba Chemie) and 3 wt % 2-picolinic acid is taken as a dopant quantity and deionized water was used as solvent. The calculated amount of samples are prepared in water. The mixture was stirred well to avoid co-precipitation of multiple phases which yields the pure and 2-picolinic acid doped LLM. The solution was filtered by using Whatman filter paper and transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation solution growth technique at room temperature especially in undisturbed region. Good quality pure and doped LLM crystals are obtained by repeated recrystallization. Pure and 3 wt % 2-picolinic acid doped LLM crystals were harvested in 28 days and 30 days respectively. The grown crystals are non

hygroscopic and good transparent. The photograph of grown crystals are shown in Fig. 1.

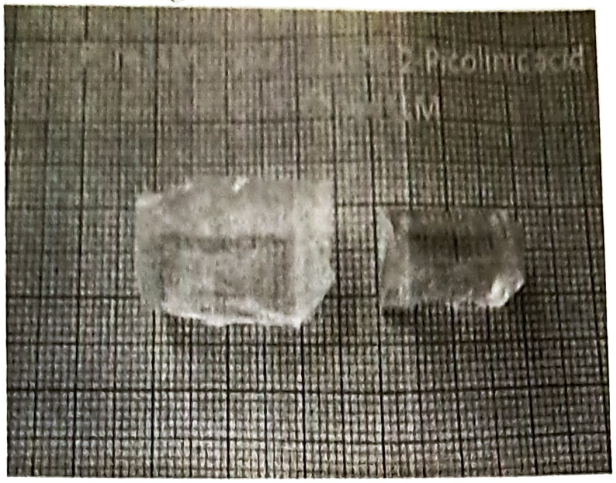

Fig. 1 Photograph of grown pure and 2-picolinic acid doped LLM crystals

Characterization Studies

The grown pure and doped LLM single crystals have been subjected to various characterization studies. The Bruker kappa APEXII single crystal X-ray diffractometer was used to estimate the cell parameters and the powder X-ray diffraction pattern was checked by XPERT-PRO X-ray diffractometer. The FT-IR spectrum is recorded using a 8400S Shimadzu infrared spectrophotometer using KBr pellet technique in the region 4000-400 cm^{-1}. The TGA/DTA studies showed the thermal properties of grown crystal carried using TA instruments, model:Q600 SDT thermal analyzer are carried between the room temperature to 700 °C at a heating rate of 10 °C/min in the nitrogen atmosphere. The transmittance spectrum was studied in the range 200–1200 nm by Perkin Elmer Lambda 35 UV–Vis spectrometer. In order to investigate the mechanical properties, microhardness measurements was carried out using Leitz-Wetzlar Vicker's microhardness tester fitted with a diamond pyramidal indenter attached to an optical microscope in the range 25–100

ğ. Nonlinear optical property of the crystal was confirmed using the Kurtz and Perry powder technique and a study of its SHG efficiency in comparison with KDP.

Results and Discussions

Single Crystal X-ray Diffraction

Single crystal X-ray diffraction were carried with MoK_α radiation (λ=0.71073 Å). The single crystal X-ray diffraction study was carried out to confirm the unit cell parameters of pure and doped LLM crystal. The lattice parameters were calculated by least square refined with atleast no of reflections as it is shown in Table 1. The values of pure LLM crystal are in good agreement with the reported values [6].

Table 1: Crystallographic data of pure and doped LLM crystal

Crystallographic data	Pure LLM	2-picolinic acid doped LLM	Already reported pure LLM [6]
Crystal system	Monoclinic	Monoclinic	Monoclinic
Unit cell	a= 5.884 Å	a= 5.953 Å	a= 5.884 Å
dimensions	b = 13.33 Å	b = 13.82 Å	b = 13.33 Å
	c = 7.501 Å	c = 7.599 Å	c = 7.501 Å
	$\alpha=\gamma=90°\neq\beta$	$\alpha=\gamma=90°\neq\beta$	$\alpha=\gamma=90°\neq\beta$
Volume	583 $Å^3$	599 $Å^3$	583 $Å^3$
Crystal size	24 x 14 x 6 mm^3	18 x 10 x 7 mm^3	18 x12 x 3 mm^3

Powder X-ray Diffraction Studies

To confirm the obtained values of unit cell parameters, powder XRD studies were also carried out for the sample. The crystalline nature of the pure and doped crystals was identified by taking the X-ray diffraction pattern of powder samples with CuK_α (λ=1.54060 Å) radiation. The sample was

scanned 2θ in the range of 10° - 70° at the scan rate of 0.04 count per minute. The XRD patterns were indexed with the TWOTHETA software package. The indexed powder XRD pattern is shown in Fig. 2. The appearance of sharp and well-defined Bragg's peaks confirmed the crystalline nature of the grown crystal.

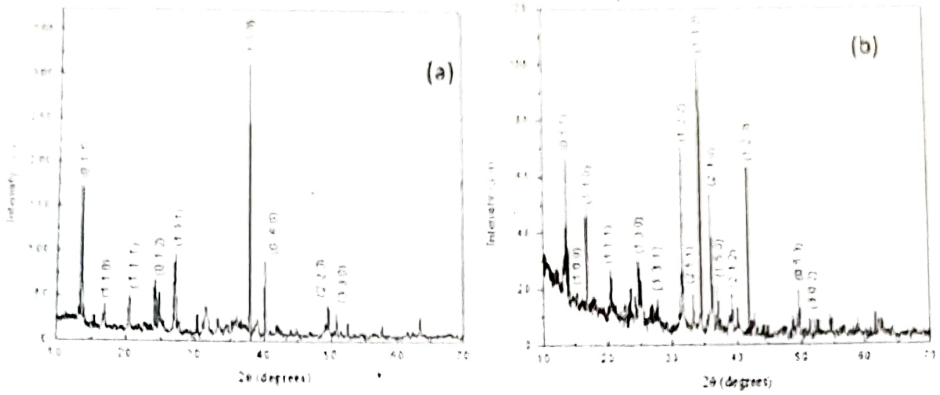

Fig. 2 Powder XRD pattern of (a) pure LLM crystal (b) doped LLM crystal

FT-IR Spectral Analysis

The recorded infrared spectrum of pure and doped LLM is shown in Fig. 3.The characteristic vibrational bands in the spectrum were compared with the corresponding bands of picolinic acid. The stretching frequency around 3425 cm^{-1} clearly indicates O–H stretching of carboxylic acid group and the presence of hydrogen bonding and water molecule in the crystal lattice [25]. The weak band at 3163 cm^{-1} is assigned to the asymmetric vibrations of the NH_3^+ group. The strong but broad peak at 2931 cm^{-1} is due to the presence of C–H asymmetric stretching. The intensity of C–H stretching vibrations at 2623 cm^{-1} may be attributed to electronic effects. The band 2337 cm^{-1} may be assigned to a combination of torsional oscillation of the NH_3^+ group. The carbonyl stretching bands at 1867 cm^{-1} corresponding to picolinium cation presence, confirms the picolinic acid incorporated in

the doped sample. The wavenumbers corresponding to bending vibrations fall in the range 1500-450 cm^{-1}. In this region, skeletal vibrations of amino acids are all coupled together. The CO_2^- symmetric stretching was observed with wavenumber of 1404 cm^{-1}. The C–H bending band was found in LLM with wavenumber 1319 cm^{-1}. The C–H in-plane bending vibrational mode is observed at 1219 cm^{-1}. The peak with wavenumber at 1180 cm^{-1} was observed for the rocking of NH_3 structure [6]. The band observed with wavenumber of 1095 cm^{-1} is due to C–C–N asymmetric stretching vibration. The C–C stretching vibrations of the compound is identified at bands with wavenumber of 910 cm^{-1}. The intense band at 864 cm^{-1} is observed in the IR spectrum which relates to a stretching of C–C–N structure. Also the band with wavenumber 709 cm^{-1} is due to wagging vibration of CO_2^- structure. The NH_3^+ torsion is observed at 555 cm^{-1} and another associated with C–C–N deformation structure is also observed with a wavenumber of 424 cm^{-1}.

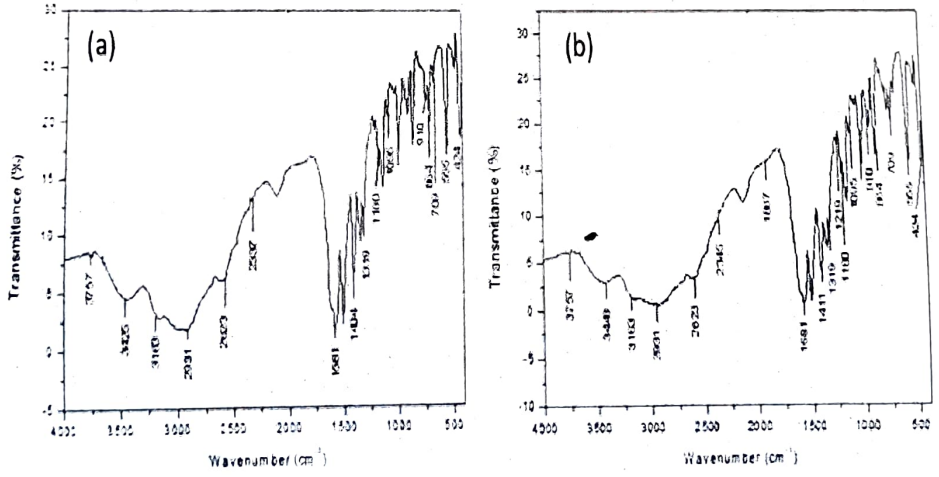

Fig. 3 Recorded FTIR spectrum of pure and doped LLM

Thermal Analysis

The results of TGA/DTA of pure and doped LLM crystals are illustrated in Fig. 4. An Al_2O_3 (alumina) crucible was used and it served as a reference for the sample. The weight loss of about 14.7 % at 78 °C is assigned due to loss of water of crystallization. It is observed that there is major weight loss

starts at 263 °C due to decomposition of the sample which is left over after the major weight loss. The weight loss of 79.9 % of tightly bonded organic molecules occurred and the exothermic peak at 666 °C may be due to heat evolution after decomposition of all substances. The endotherm with maximum at 263 °C corresponds to degradation of 2-picolinic acid doped LLM, since there is no endotherm corresponding to melting point in the DTA trace [6]. Based on the results of TGA/DTA, it is found that the pure and doped crystals can be exploited for NLO applications below 78 °C.

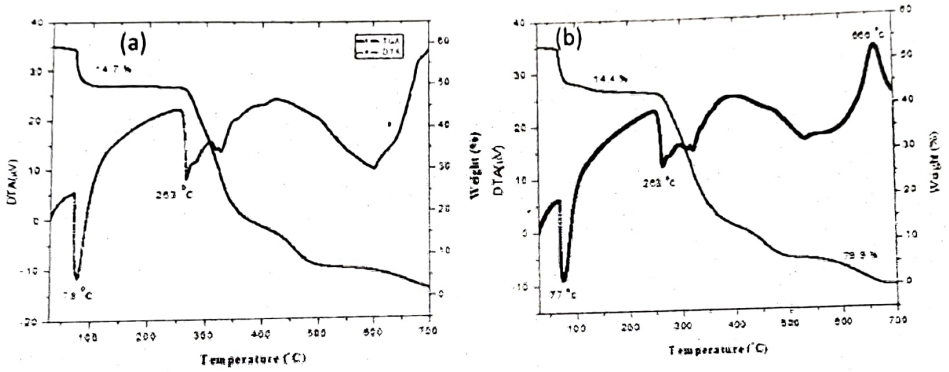

Fig 4: TGA/DTA spectra of (a) pure and (b) doped LLM crystals

UV-Vis Spectral Analysis

The optical transmission range, transparency cut-off and absorbance band are the most optical parameters for laser frequency conversion applications. A crystal of thickness 2 mm was used for UV–Vis spectrum is shown in Fig. 5. The pure crystal has good transparency of about 50 % and the lower cut-off wavelength was found to be 330 nm and the doped crystal has good transparency of about 38 %. While adding 2-picolinic acid as dopant, the transmission wavenumber is reduced to 310 nm. From this measurement, it is noted that there is no significant absorption in the entire

visible region, which enables it to be a potential candidate for optoelectronic applications [17, 26].

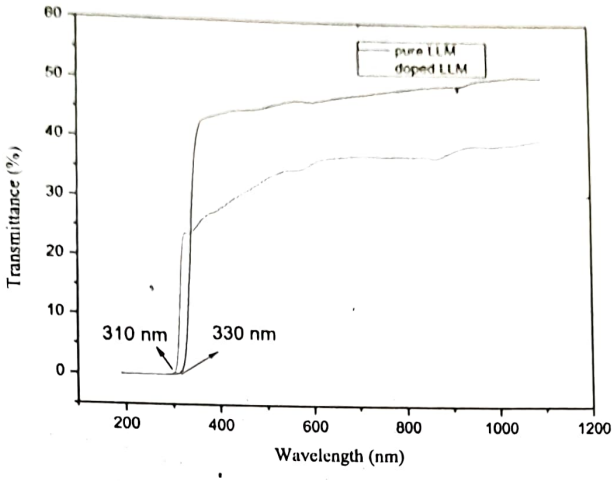

Fig. 5 UV-Vis transmittance spectrum of pure and doped LLM crystal

The measured transmission (T) was used to calculate the absorption coefficient (α) based on the following relation,

$$\alpha = \frac{2.3026}{t}\log(1/T) \quad \ldots\ldots\ldots (1)$$

Where, t is the thickness of the crystal.

In the high photon energy region, the energy dependence of absorption coefficient suggests the occurrence of direct band gap of the crystal obeying the following equation for high photon energies (hv) [27],

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad \ldots\ldots\ldots (2)$$

Where, E_g is the optical band gap of the crystal and A is a constant. The band gap of the crystal was evaluated by plotting $(\alpha h\nu)^2$ versus hv [28] as shown in Fig. 6 and it was found to be for pure 3.69 eV and doped 3.92 eV.

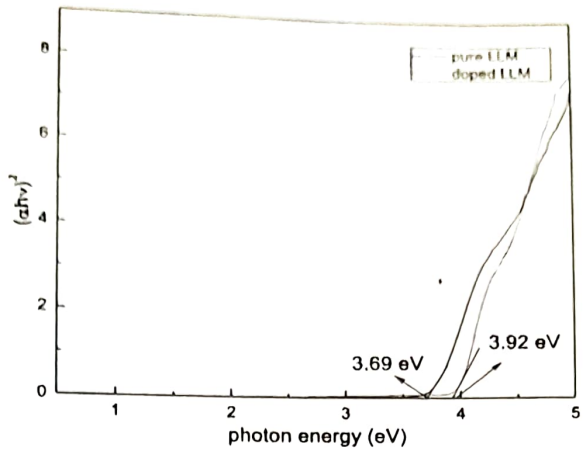

Fig. 6 Plot of (αhv)² vs. photon energy for pure and doped LLM crystal

Extinction coefficient is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. In electromagnetic terms, the extinction coefficient can be explained as the decay or damping of the amplitude of the incident electric and magnetic fields. The extinction coefficient (K) obtained from the following equation,

$$K = \frac{\alpha\lambda}{4\pi} \quad \ldots\ldots\ldots (3)$$

The transmittance (T) is given by the following relation [29],

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

The reflectance (R) in terms of the absorption coefficient (α) can be derived from the relations [30],

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad \ldots\ldots\ldots (5)$$

The refractive index (n) can be determined from reflectance data using the following relation [31],

$$n = \frac{-(R+1) \pm 2\sqrt{R}}{(R-1)} \quad \ldots\ldots\ldots (6)$$

Fig. 7a and 7b represent the variation of refractive index and extinction coefficient with respect to photon energy respectively. From the graph, it is cleared that the extinction coefficient depends on the photon energy. Since the internal energy of the device also depends on the photon energy, by tailoring the photon energy one can achieve the desired material to fabricate the optoelectronic devices. The estimated refractive index (n) of crystals from the graph for pure LLM is 1.639 and doped LLM is 1.759 at 632 nm.

From the optical constants, the electric susceptibility (χ_c) can be calculated according to the relation [30],

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_c = n^2\text{-}k^2 \quad \ldots\ldots\ldots (7)$$

$$\chi_c = \frac{n^2-k^2-\varepsilon_0}{4\pi} \quad \ldots\ldots\ldots (8)$$

Where, ε_0 is the dielectric constant in the absence of any contribution from free carriers. The estimated electric susceptibility (χ_c) is found to be for pure 0.200 and doped 0.236 at 1100 nm.

The real and imaginary dielectric constants, ε_r and ε_i can be calculated from the following relations [32],

$$\varepsilon_r = n^2\text{-}k^2 \text{ and } \varepsilon_i = 2nk \quad \ldots\ldots\ldots (9)$$

The value of real ε_r and imaginary ε_i dielectric constants at λ=1100 nm were found to be for pure 2.518 and 0.93×10^{-3} and doped 2.968 and 1.379×10^{-3} respectively.

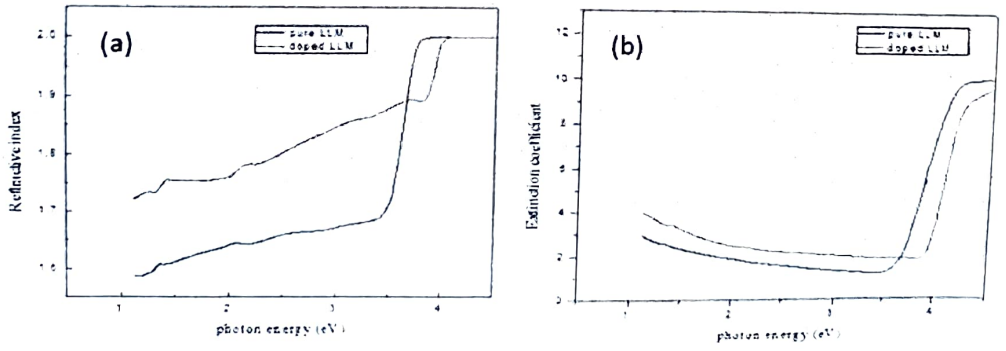

Fig 7a Refractive index and
7b Extinction coefficient of pure and doped LLM crystal

Vicker's Microhardness Measurements

The mechanical properties of crystalline materials are closely related with their other physical properties, and determine the performance of devices prepared from that material.

The load is applied for 25 gm, 50 gm and 100 gm and their corresponding Vicker's hardness number is calculated. The graph is plotted between Vicker's hardness (H_v) number and load as shown in Fig. 8a . Vicker's hardness (H_v) number increases initially with load upto 100 g and cracks were observed beyond 100 g. This type of load variation of hardness is termed as reverse indentation size effect [33]. The hardness value of 2-picolinic acid doped LLM single crystal is increased as compared to pure crystal for all applied loads. At low loads, the indenter penetrates only the top surface layers generating dislocations, which results in the increase of hardness in this region. The load independence of hardness at higher loads can be attributed to the mutual interaction or rearrangement of dislocations. The reason for this type of behaviour is the elastic nature of the crystal lattices. The relation between load and the size of indentation can be correlated using Meyer's law, $P = k_1 d^n$, where k_1 is a constant and 'n' is the Meyer's index. The slope of log P versus log d gives the work hardening coefficient (n) and it was calculated and represented in Fig.8b. This value found is to be 1.9, which indicates that crystal belongs to soft material category. n value lies between 1.0 and 1.6 for moderately hard materials and it is more than 1.6 for soft materials [34-36]. From these observations, it can be concluded that the doped crystal has better mechanical stability when compared to pure LLM single crystal.

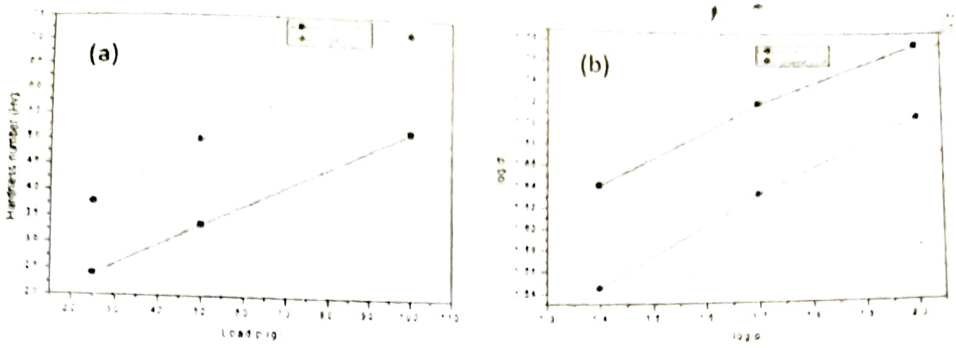

Fig 8a. Plot of Vicker's hardness (H_v) vs load (P) 8b. log P vs. log d of pure and doped LLM crystal

SHG Studies

In this experiment Q-switched Nd:YAG laser (1064 nm, Quanta ray series, USA) emitting a fundamental wavelength of 1064 nm was used [37]. The grown single crystal is powdered with a uniform particle size of 125–150 μm, and then packed in a microcapillary of uniform bore and exposed to the laser radiation. The SHG was confirmed by the emission of green radiation (532 nm). The input laser energy incident on the sample was 0.68 J, an energy level optimized to cause any chemical decomposition of the sample. Various physical properties of LLM single crystal were reported earlier and the powder SHG efficiency is 0.39 times that of urea [15]. The KDP is used as a reference material for the present measurement. The SHG efficiency of pure and doped LLM is shown below in Table 2 with reference to the KDP 8.8 mJ. The efficient SHG demands specific molecular alignment of the crystal and this is to be achieved facilitating nonlinearity in the presence of dopant.

Table 2: Values of relative SHG efficiency of pure and doped LLM crystal

Sample	Relative SHG efficiency	Reference
Pure LLM	4.4 mJ (0.39 times that of KDP)	[6]
3 wt % 2-picolinic acid doped LLM	5.4 mJ (0.48 times that of KDP)	Present work

Conclusions

The single crystals of pure and doped LLM crystals are grown by slow evaporation solution growth technique at room temperature. The single crystal X-ray diffraction study estimated cell parameters suggested that the pure and doped LLM crystals belongs to monoclinic system. Powder XRD studies will give ideas of diffraction planes of the crystals and it is indexed. In the FT-IR spectra, the stretching frequency around 3425 cm^{-1} clearly indicates O-H stretching of carboxylic acid group and the presence of hydrogen bonding and water molecule in the crystal lattice. The weight loss of about 14.7 % at 78 °C is assigned due to loss of water of crystallization. The lower cut-off wavelength was found to be for pure 330 nm and doped 310 nm and the band gap of the crystal was found to be for pure 3.69 eV and doped 3.92 eV. The work hardening coefficient (n) value is found to be 1.9, it can be concluded that the doped crystal have better mechanical stability than pure. The 2-picolinic acid doped sample act as active SHG efficiency and it is compared with the KDP.

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