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Growth and Characterization of Zinc Acetate Doped L-Alanine Single Crystals

***A.SATHYA[1], P.YASOTHA[2], P.SAGUNTHALA[3]**

Department of Physics, Sri Vasavi College, Erode, Tamil Nadu India.
*Corresponding e-mail: sathya91@gmail.com

Abstract

Single crystals of Zinc Acetate doped L-alanine were grown by slow evaporation technique. The size of the grown crystal was upto 5x9x2 mm^3. The powder X-ray diffraction pattern of the grown crystal has been indexed. FT-IR spectral analysis was carried out to identify the various functional groups present in the crystal. The optical transmission study reveals the transparency of the grown crystal in the entire visible region and cutoff wavelength has been found to be 226 nm. In order to determine mechanical strength of crystal Vicker's microhardness measurement was carried out. Dielectric constant and dielectric loss for various frequencies were carried out to the as grown crystal.

Keywords: X-ray diffraction, Single crystals, FT-IR, Dielectric constant.

Introduction

Nonlinear optical materials find a variety of applications to perform functions like frequency conversion, light modulation, optical memory storage, second harmonic generation, and optical switching. In recent years, there has been extensive investigation in the growth of non- linear optical (NLO) materials because of their wide applications in optoelectronics and photonic applications [1, 2]. In the recent years, efforts have been made on the organic material mixed with inorganic crystals, in order to improve their properties.

Amino acids are interesting materials for NLO applications as they contain donor carboxyl acid (COOH) group and the proton acceptor amino (NH_2) group in them (i.e.) known as zwitterions, which create hydrogen bonds, in the form of $N–H^+–O–C$, which are very strong bonds. Hydrogen bonds have also been used in the possible generation of non-centro symmetric structures, which is a prerequisite for an effective second harmonic generation (SHG) crystal [3-5]. Complexes of amino acids with inorganic salts are promising materials for (SHG) as they tend to combine the advantages of organic amino acid and inorganic salt [6].Growing single crystals with required properties is the backbone for development of modern technological device. Hence great attention has been given to grow and characterize pure and doped bulk single crystals to modify their properties for various device applications. Therefore, researchers worldwide have always been in the search of new materials and their single crystal growth. From the stand-point of the search for newer NLO materials, amino acids offer a rich choice [7-9].In the present work, we report the growth of Zinc Acetate doped L-alanine single crystals by slow evaporation technique. The grown crystals were characterized by powder XRD, FT-IR, UV-Visible spectroscopy, Microhardness and Dielectric Studies.

Experimental Procedure

Preparation of solution

The commercially available L-alanine and Zinc Acetate dihydrate (99% purity) salts were used to prepare the crystals. The solutions were prepared using deionized water as the solvent. 100 ml of saturated solutions of L-alanine and Zinc Acetate ($2H_2O$) were prepared separately at room temperature. Then the saturated solutions were filtered twice using a Whatman filter paper and taken in the ratio 1:3. The prepared solution was stirred continuously using magnetic stirrer for 3 hours.

Crystal growth

The growth of Zinc Acetate doped L-alanine single crystal was carried out by slow evaporation method. The prepared solution in the beaker was closed with porously sealed cover and kept in a dust free environment. Then the solution was allowed to evaporate. After 81 days the crystal has been grown. The size of the grown crystals was upto 5mm x 9mm x 2mm and it is shown in Fig 1.

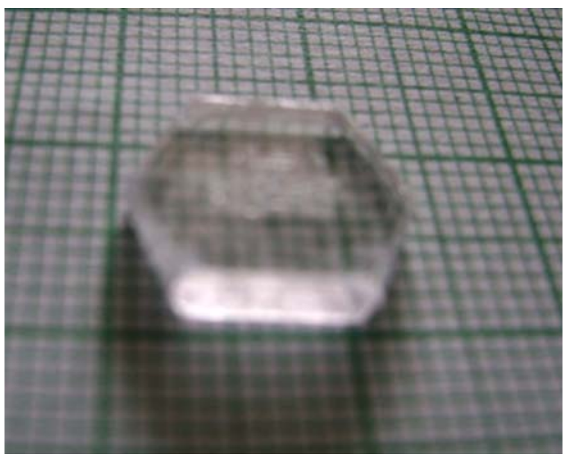

Fig.1. Photograph of L-alanine doped Zinc Acetate crystal

Results and Discussion

Powder X-ray diffraction analysis

X-ray diffraction technique is a powerful tool to analyse the crystalline nature of the materials. If the material to be investigated is crystalline, well defined peaks will be observed. The grown crystals were finely powdered and have been subjected to X-ray diffractometer employing CuKα (1.54058Å) with a scan speed of 1°/min. The indexed powder X-ray diffraction (PXRD) pattern of pure Zinc Acetate and Zinc Acetate doped L-alanine is shown in Fig.2. The well defined, sharp peaks in the (PXRD) patterns signify the good crystalline nature of the compound. But intensities of the peaks are found to be varied (Fig. 2a and 2b).

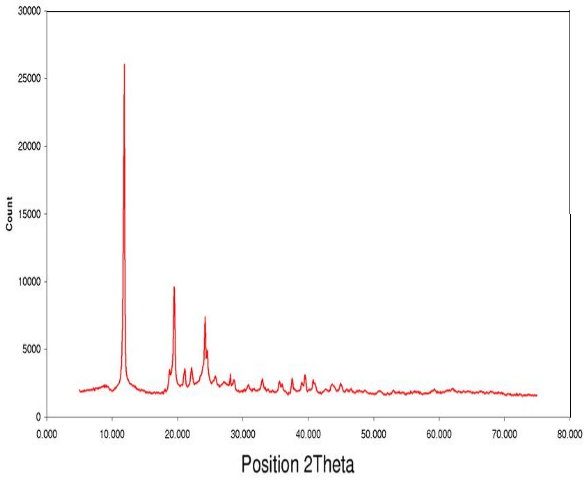

Fig.2 (a).PXRD pattern of Zinc acetate

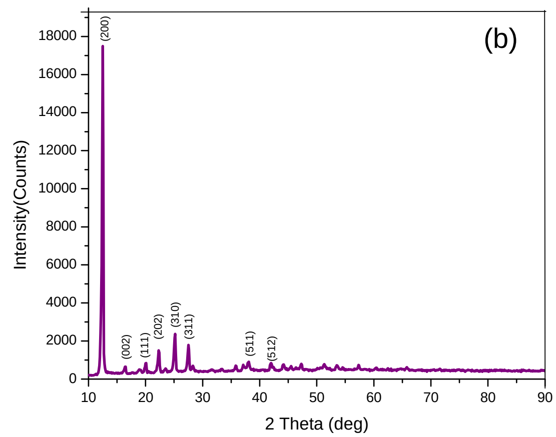

Fig.2 (b) PXRD of Zinc Acetate doped L-alanine crystal.

FT-IR spectral analysis

The infrared Spectroscopy is a technique that provides information about the chemical bonding and to identify the functional groups present in the synthesized samples. FT-IR spectrum of grown crystals was recorded by the KBr pellet technique using a Perkin Elmer FT-IR spectrometer in the range 4000–400cm^{-1}. The recorded FTIR spectrum is shown in the Fig.3. The peak appearing at 1342 cm^{-1} is due to the plane bending of O-H group vibrations. The peak observed at 1026 cm^{-1} is assigned for C-N stretching. The other peaks at 686 cm^{-1} and 948 cm^{-1} are due to the out of plane bending of C-H and O-H group vibrations.

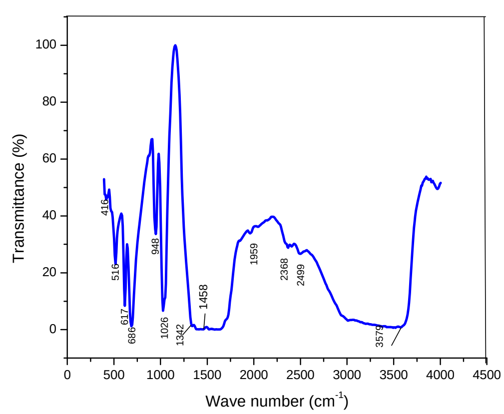

Fig.3.FT-IR spectrum of grown crystal.

The stretching vibrations of the water molecule of Zinc acetate dihydrate are expected in the region 3600-3000 cm^{-1}[10]. Assignments of IR frequencies (cm^{-1}) are given in table 1.

Table.1. Assignment of IR frequencies (cm^{-1}) for Zinc Acetate doped L-alanine crystal.

Band frequencies wave number(cm^{-1})	**Assignment**
686	C-H out of plane bending
948	O-H out of plane bending
1026	C-N stretching
1342	O-H in plane bending

UV-Visible Spectroscopy

The optical behavior of the material basically includes the interaction of light radiation over the range of the electromagnetic spectrum. The ultra violet light absorbed by the sample gives information about the transparency window which is very essential in many optoelectronic applications [11]. The optical transmission and absorption spectrum of the grown crystals were recorded in the wavelength range 200 to 800 nm using a Perkin Elmer lambda 35 UV-Vis spectrometer. The optical transmission and absorption spectrum for Zinc Acetate doped L-alanine is shown in the Fig.4. The lower cut off wave length is around 226 nm. It is observed from the figure 4(a) that the grown crystals show good transparency in the entire visible region.

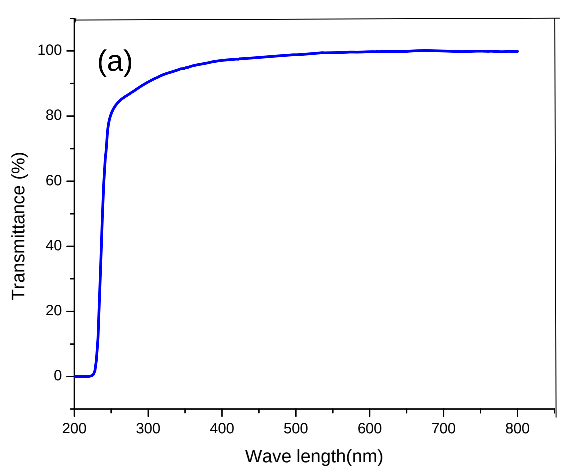

Fig.4 (a). UV- Vis spectrum for transmittance

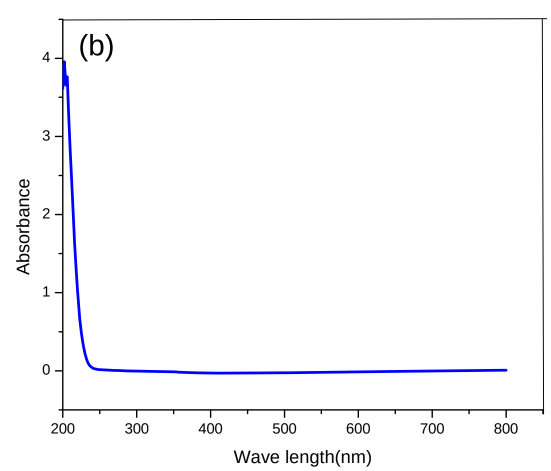

Fig.4 (b). UV-Vis spectrum for absorbance

The suitability of the grown crystals for photonic and optical applications is confirmed by the absence of absorption bands in the visible region. Effect of various additives in Zinc acetate is given in the table 2.

Table.2. Effect of various additives in Zinc acetate.

Dopant	Transparency cut off (nm)	Ref
γ- glycine	212	[12]
L-Threonine	350	[10]
L-Alanine (present work)	226	Present work
Bis-thiourea	260	[13]

3.4 Microhardness Measurements

Micro hardness testing provides useful information concerning the mechanical behavior of solids. The indentation hardness was measured as the ratio of applied load to the surface area of the indentation. Indentations were carried out using indenter for varying loads. Vickers micro-hardness number was determined by using the relation

$$H_v = \frac{1.8544\,P}{d^2}\ \frac{kg}{mm^2}$$

A plot between the hardness number and corresponding loads is shown in Fig. 5(a). The plot of log P against log d is a straight line and it is shown in Fig.5 (b), which is in good agreement with Mayer's law, $P = k_1 d^n$ [14] where k_1 is the material's constant and n the Mayer's index or work hardening coefficient.

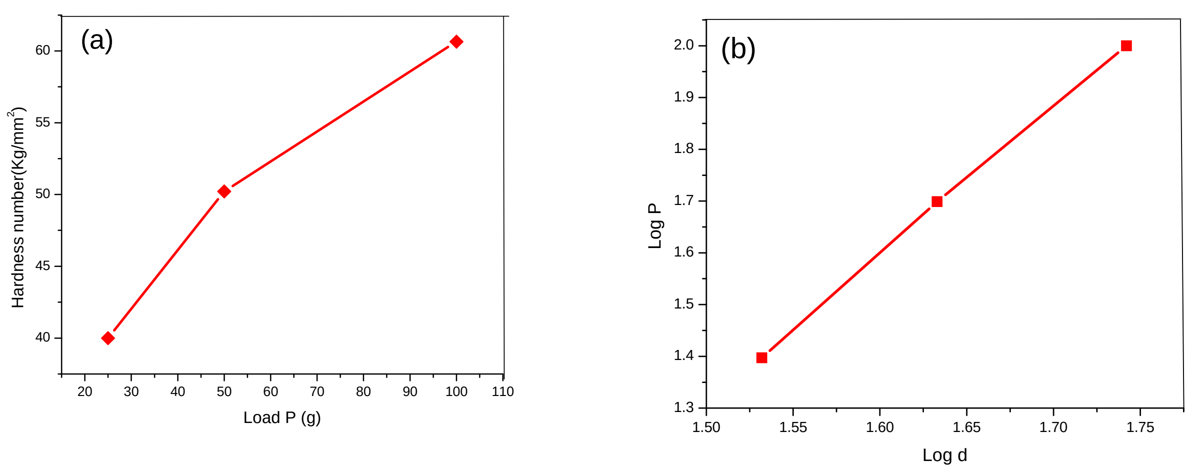

Fig.5. (a) Variation of microhardness number with load. (b) Plot of log P Vs log d.

The slope of the graph gives n and it is determined to be 3.00. According to Onitsch and Hanneman, n should be between 1 and 1.6 for hard materials and above 1.6 for softer ones. Hence the grown crystal belongs to softer material category.

Dielectric Measurements

The dielectric constant is one of the basic electrical properties of solids [15]. The dielectric properties of the grown crystals were studied at room temperature using an LCR meter in the frequency region 50Hz – 5 KHz. The opposite parallel faces of the crystals were coated with high-grade silver paste placed between two copper electrodes and thus a parallel plate capacitor was formed. The values (Cp) and loss were obtained from the dielectric measurement. The dielectric constant of the crystal was calculated using the relation

$$\varepsilon_r = \frac{C_{crys}}{C_{air}}$$

Where, C_{crys} is the capacitance of the crystal and C_{air} is the capacitance of the same dimension of air. Fig 6 (a) shows the variation of dielectric constant with frequency. From the frequency response of the dielectric constant, it was found that the dielectric constant increases initially at low frequencies and finally it becomes almost constant at higher frequencies. The relatively high dielectric constant of the material at room temperature is a good indication for NLO effects.

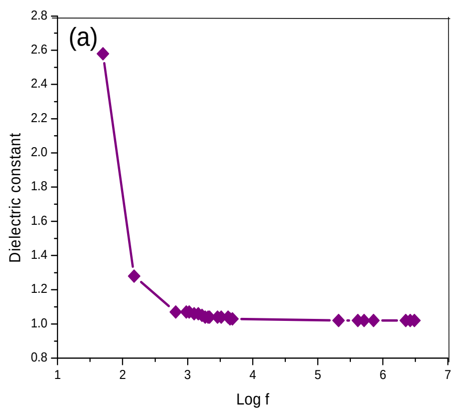

Fig.6.(a). Variation of dielectric constant with frequency

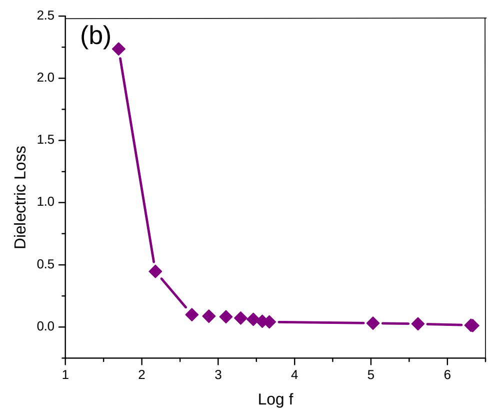

Fig.6. (b) Variation of dielectric loss with frequency

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Fig.6 (b) shows the variation of dielectric loss of the grown crystals with frequency. It is observed from the studies that the dielectric loss decreases with increasing the frequency. The behavior of low dielectric loss with high frequency for the sample suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of NLO devices [16].

Conclusion

Zinc Acetate doped L-alanine single crystals have been successfully grown by slow evaporation technique. PXRD analysis confirms the crystalline nature of the grown crystal. From the FTIR spectroscopy analysis, the various functional groups present in the grown crystals were identified. From the UV-visible spectroscopy analysis, the grown crystals are transparent in the visible region and the cut-off wavelength is 226nm. The crystal possesses moderate mechanical stability which is confirmed by the Vickers microhardness analysis. By Meyer's law, the value of Meyer's index n estimated which indicates that the crystal belongs to soft material category of the grown crystals. The dielectric property studied at room temperature indicates that the dielectric constant and dielectric loss decreases with the increase in frequency which is the normal behavior of nonlinear optical materials. The characteristics of low dielectric loss with high frequency for a given sample suggest that the sample possesses enhanced optical quality with lesser defects and this parameter is vital for various NLO materials and their applications.

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