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Growth And Studies of Strontium Nitrate Added L-Alanine Crystals

KEYWORDS: Amino acid; Crystal growth; NLO; SHG; microhardness; transmittance; stiffness constant; yield strength

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ABSTRACT *L-alanine crystals added with strontium nitrate (LASN) were grown by solution method with slow evaporation technique. Solubility was determined at different temperatures. The lattice parameters of the grown crystals were determined by X-ray diffraction (XRD) technique. UV-visible transmittance spectrum was recorded to study the optical transparency and band gap of the grown crystal. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique. The microhardness, yield strength and stiffness constant of LASN crystal were determined to understand the mechanical strength.*

Introduction

The search of efficient nonlinear optical (NLO) crystals and the development of NLO materials are extremely important for frequency conversion, optical communication, image processing, optical computing and data storage devices. Amino acid family-type crystals have over the years been subjected to extensive investigation by the researchers for their nonlinear optical properties [1,2]. Alanine is a conditionally essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system [3]. L-alanine is an alpha-amino acid with the chemical formula CH_3CHNH_2COOH with the molecular weight of 89.09 and it is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP [4,5]. In this work, L-alanine is added with strontium nitrate (LASN) to alter its physical and chemical properties. Single crystals of LASN were grown by slow evaporation method at room temperature and they are subjected to different characterization studies and the obtained results are discussed.

Growth and solubility

Strontium nitrate added L-alanine crystals (LASN) were grown from aqueous solutions by taking high purity L-alanine and strontium nitrate in the ratio 1:1. The reactants were dissolved in de-ionized water and stirred well at 45 °C for three hours and the saturated solution at room temperature was allowed to evaporate to get the required seed crystals of LASN. To get the big-sized crystals, seed immersion technique was adopted. The saturated solution was prepared again and stirred well using a hot plate magnetic stirrer and then it was filtered. The filtered solution was taken in a container and it was allowed to evaporate to convert it into the supersaturated solution after 3 days of time. Tiny seed crystals were placed at the bottom of the container containing the supersaturated solution. After a growth period of 25 days, big-sized crystals of LASN were harvested. Solubility study was carried out by gravimetrical method. The measured values of solubility for the sample LASN are 18.45 g/100 ml, 19.88 g/100 ml and 22.10 g/100 ml at 30 °C, 40 °C and 50 °C respectively. From the values, it is noticed that the solubility of sample in water increases with temperature and it has a positive temperature coefficient of solubility. The solubility values are useful in preparing the saturated and supersaturated solutions at a particular temperature and to determine the metastable zone width of LASN sample.

Results and Discussion

Transparency and optical band gap

Optical window width and optical band gap are the important optical constants of NLO crystals. To find these constants, the study of the transmission of electromagnetic waves of the UV–visible–NIR range through the NLO materials is necessary. The optical transmission spectrum of LASN crystal was recorded on a Perkin-Elmer-Lambda 950 UV-vis spectrophotometer in the range 190 nm-1100 nm and it is shown in the figure 1. The spectrum shows that LASN crystal is optically transparent in the UV–vis–NIR region and the low absorption in the entire visible and near infrared region with the low cut-off wavelength at 255 nm suggests that the material is quite suitable for SHG generation and other related optoelectronic applications. Optical band gap of the sample is found to be 4.863 eV. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices.

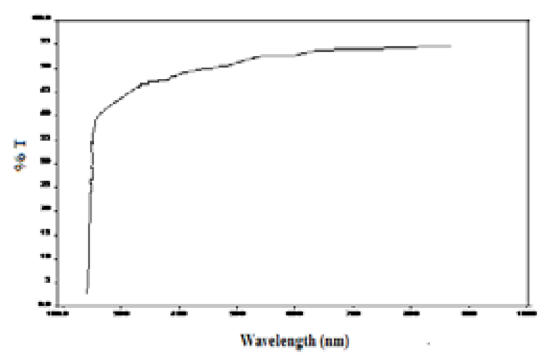

Figure 1: Transmittance spectrum for the grown LASN crystal

SHG efficiency

The second harmonic generation (SHG) efficiency was determined by the powder technique developed by Kurtz and Perry [6], using a Nd:YAG, 10 ns laser with a pulse repetition rate of 10 Hz working at 1064 nm. The sample was ground into fine powder and it was mounted in the path of the laser beam of 9.6 mJ pulse energy obtained by splitting the original laser beam. The output light was passed through a monochromator transmitting only the second harmonic (green) light at 532 nm. Potassium dihydrogen orthophosphate (KDP) ground into sample of identical size was used as reference material in the SHG measurement. SHG conversion efficiency was computed by the ratio of signal amplitude of the LASN sample to that of the KDP signal amplitude recorded for the same input power. The SHG efficiency of the grown LASN crystal was found to be 0.93 times that of KDP.

X-ray diffraction studies

The structure of the grown crystals was identified by using a single-crystal X-ray diffractometer (Model: ENRAF NONIUS CAD-4, MoK_α(α = 0.71069Å) and the lattice parameters were obtained. The obtained values of lattice parameters are a = 5.776 (5) Å, b = 6.027(6) Å, c=12.342(8) Å, α = α = α = 90° and V =429.65(3) Å^3. From the results it is concluded that the grown LASN crystal belongs to the orthorhombic system and the obtained data are found to be in good agreement with the reported data [7].

Floatation method

Floatation method was used to find the density of crystals. This method is sensitive to point defects and insensitive to dislocations in crystals. Liquids like xylene and bromoform are used for floatation method. After mixing the liquids xylene and bromoform in a suitable proportion in a specific gravity bottle, a small piece of the crystal was immersed in the liquid mixture. When the sample had attained a state of mechanical equilibrium, the density of the crystal was equal to the density of liquid mixture. The density was calculated using the relation (w3 –w1) / (w2 – w1) where w1 is the weight of the empty specific gravity bottle, w2 is the weight of the specific gravity bottle with full of water and w3 is the weight of specific gravity bottle full of the mixture of xylene and bromoform. The density of the grown LASN crystal was found to be 1.38 g/cc.

Mechanical constants

Hardness, yield strength and stiffness constant are some of the mechanical constants and these properties can be determined by carrying out microhardness studies. Microhardness property was measured using a Vickers microhardness tester, fitted with a Vickers diamond pyramidal indenter. The well polished LASN crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied in a fixed interval of time. The indentation time was kept 10 s for all the loads. Vickers microhardness values have been calculated by using the formula $H_v = 1.8544\ P / d^2$ kg/mm^2 where H_v is the Vickers microhardness number, P is the applied load in kg, d is the mean diagonal length of the indentation in mm and 1.8544 is a constant for the geometrical shape of diamond pyramidal indenter [8]. The variation of Vickers hardness number with a load for the grown crystal is shown in the figure 2. The result shows that the hardness increases with increase in the load and this can be explained on the basis of depth of penetration of the indenter. When the load increases, a few surface layers are penetrated initially and then inner surface layers are penetrated by the indenter with increase in the load. The measured hardness is the characteristics of these layers and the increase in the hardness number is due to the overall effect on the surface and inner layers of the sample and it is called as the reverse indentation size effect. Yield strength is the maximum stress that can be developed in a material without causing plastic deformation and it is the stress at which a material exhibits a specified permanent deformation and is a practical approximation of elastic limit. Stiffness is the rigidity of an object and its complementary concept is flexibility. The more flexible an object is, the less stiff it is. Stiffness is a measure of the resistance offered by an elastic body to deformation or pliability. Using the microhardness data, the yield strength and stiffness constant have been determined. Yield strength of the material can be found out using the relation, yield strength (σ_y) = (H_v / 3) and the stiffness constant (C_{11}) for different loads was calculated the formula $C_{11} = H_v^{7/4}$ where H_v is the microhardness of the material. The results show that the values of yield strength and stiffness constant are observed to be increasing with the increase of applied load to the sample. As the values of yield strength are high, the resistance of plastic to bending and tightness of bonding between neighboring atoms will be high. The large values of stiffness constant indicate that the grown LASN crystal has the strong binding forces between the ions in the lattice [9, 10].

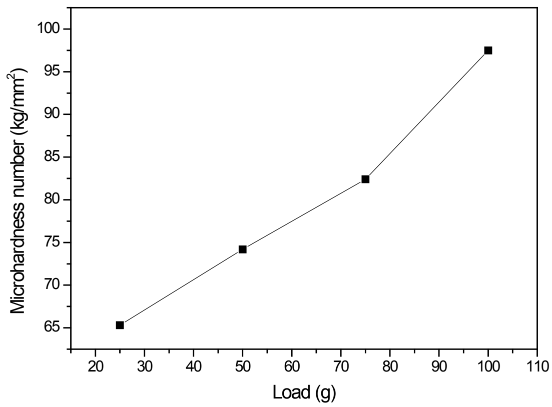

Figure 2: Variation of hardness number with applied load for the grown LASN crystal

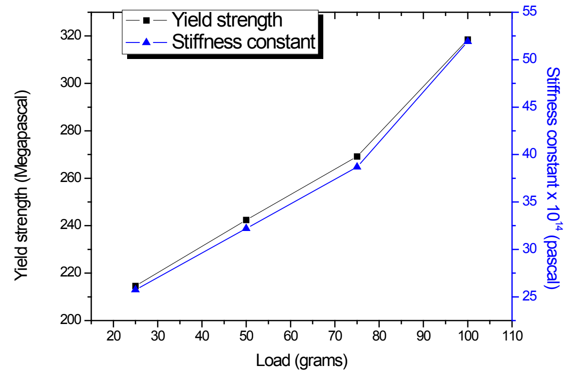

Figure 3: Variation of yield strength and stiffness constant with load for LASN crystal

Conclusion

Growth crystals of L-alanine added with strontium nitrate (LASN) was carried out by solution method with slow evaporation technique. The solubility of LASN crystal is observed to be increasing with increase in temperature. The crystal structure of LASN crystal is found to be orthorhombic and the values of lattice parameters of the grown crystal are well coincided with those of undoped L-alanine crystal. SHG efficiency of LASN sample is found to be 0.93 times that of KDP. Optical transmittance, cut-off wavelength and band gap values were calculated for LASN crystal. Vickers microhardness studies were carried out for the grown LASN crystal to determine values of yield strength and stiffness constant. The density of the grown crystal by floatation method was found to be 1.38 g/cc.

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