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EFFECT OF ACIDS ON GROWTH AND CHARACTERIZATION OF L- VALINE

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Abstract: L-Valine is an aliphatic branched chain essential amino acid which crystallizes in monoclinic system. It has vital role in human metabolism like storage of glycogen in muscles and stimulation of insulin production. The NLO efficiency of L-Valine has already been reported as 0.82 times that of KDP. In order to investigate the role of acids on the morphology, linear and non-linear optical properties of L- Valine, it is crystallized in the presence of acetic acid, citric acid and ortho phosphoric acid. The SHG efficiency of these materials are measured and found to be enhanced.

***Keywords*:** NLO materials; solution growth; SHG efficiency

Introduction : Organic materials are endowed over inorganic materials due to their advanced competence in molecular nonlinearity, inherent flexibility and its easy fabrication towards nonlinear optical (NLO) applications. In an array of organic compounds, amino acids have peculiar characteristics such as molecular chirality, zwitterionic nature and crystallize in non-centrosymmetric space group which are crucial features for second harmonic generation. Also the dipole nature of amino acids boosts the NLO efficiency and are used in optoelectronics, telecommunication, optical logic, optical data storage etc [1-3]. Numerous complexes of amino acids have been crystallized and reported [4-7]. Habit modifications in crystals have strange application in chemical, medical and biological industries. Habit modification is achieved by the addition of additives which usually adsorb or bind on the crystal faces and influence the size and morphology of the crystal [8]. L-Valine is a nonpolar branched-chain essential amino acid, with molecular formula $C_5H_{11}NO_2$ and is present in the human dietary sources such as meat, dairy products and soya beans. Acetic acid is classified as weak organic acid which is used in industry as chemical reagent, industrial chemical and descaling agent in household purpose. Ortho phosphoric acid is an inorganic acid mainly used in fertilizers and soap. Citric acid is a weak organic acid which acts as natural preservative and acidifier in foodstuff. In the present work, we have chosen to crystallize the amino acid, L-Valine in the pure form and in presence of acids such as ortho phosphoric acid, citric acid and acetic acid to study their effect on L-Valine crystals.

1. Experimental procedure

2.1. Crystal growth : The starting material L-Valine was procured from Sigma Aldrich (AR) and all acids were from Merck (AR). The experiments were done using double distilled water as solvent. A saturated solution of L-Valine was prepared at 40°C and the crystals were grown by slow evaporation at room temperature. To grow the L-valine crystals in the presence of additives, the L-Valine and the acid solutions were mixed in 2:1 molar ratio and the crystals grown were named as O-LV, C-LV and A-LV [figure 1].

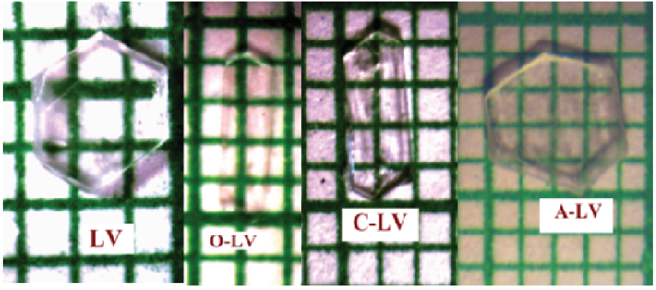

Fig.1 Optical images of the grown crystals

2.2. Characterization techniques : Single crystal X-Ray diffraction studies for the grown crystals were obtained from Enraf (Bruker) Nonius CAD4 single crystal X-ray diffractometer. Powder XRD patterns of the grown crystals were recorded using Rigaku Mini Flex 2 desktop X-ray diffractometer with CuKα radiation of wavelength 1.5418 Å. FT-IR of solid phase samples were studied in Perkin-Elmer RX1 FTIR Spectrometer in the range of 400-3500 cm^{-1} using KBr pellet technique. UV spectrum was recorded using Lambda 35 UV-Vis-NIR spectrometer in the wavelength range190-1100nm at room temperature. Kurtz SHG test was performed to find the NLO property using Q-Switched Nd:YAG laser (1064nm, Quanta ray series with input energy : 2.4 mJ/pulse).

3. Results and discussion

3.1 Single crystal X-Ray diffraction : Unit cell parameters of the grown crystals obtained from single crystal X-ray diffraction are tabulated in Table 1.

Table.1. Unit cell parameters of the grown crystals

S.No	Sample	a (Å)	b (Å)	c (Å)	α	β	γ	V (Å^3)
1.	LV	9.72	5.29	12.12	90°	90.8°	90°	623
2.	O- LV	9.67	5.27	12.04	90°	90.78°	90°	614
3.	C-LV	9.68	5.28	12.20	90°	90.81°	90°	614
4.	A-LV	10.08	5.47	12.40	90°	90.70°	90°	684

It was found that all the grown crystals crystallize in monoclinic system with space group $P2_1$.The crystal grown in presence of acetic acid showed increase in values of lattice parameters.

3.2. Powder XRD

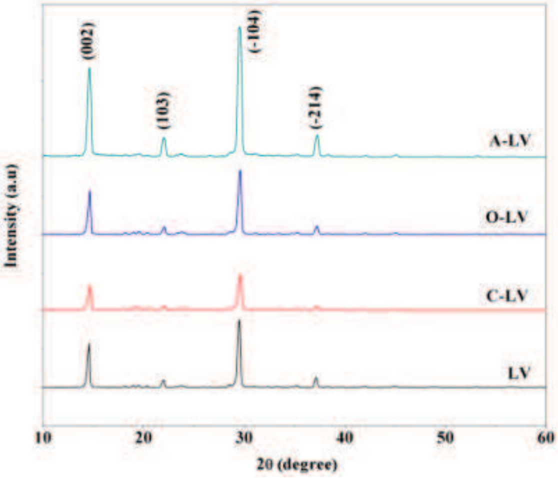

Fig.2. XRD pattern of pure and acid added L-Valine single crystals

All the observed reflections were indexed by comparing the data with K.Torii,Y.Iitaka etal for LV. Powder XRD pattern of pure LV matched well with that of the crystals grown in the presence of acids. No new reflections were observed, but the intensity of the peaks obtained for A-LV increased significantly.

3.3. FT-IR spectral analysis

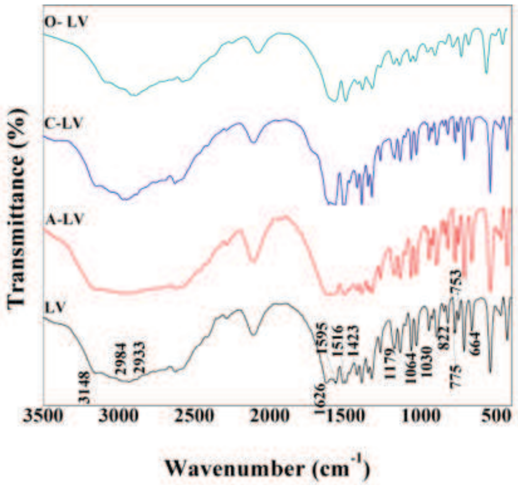

Fig.3. FT-IR spectra of pure and acids added L-Valine

FT-IR spectra of L-Valine and acids added L-Valine samples were recorded at room temperature and shown in figure 3. Protonated NH_3^+ group produces characteristic peaks at 3148 cm^{-1}(asymmetric stretching), 1626 cm^{-1} and 1516 cm^{-1} (deformation bands), NH_3^+ stretching and C-H overlaps to form broadband between 3100 - 2600 cm^{-1}. Zwitterionic nature is confirmed from deprotonated COO^- peak at 1595 cm^{-1}(asymmetric stretching) and 1423 cm^{-1}(symmetric stretching). Peak at 2984 cm^{-1}(asymmetric stretching) is due to methyl group and at 2933 cm^{-1} (symmetric stretching) is due to methylene group. Peaks at 1179 cm^{-1} and 1030 cm^{-1} are due to C-C stretching. Skeletal vibration stretching is observed at 775 cm^{-1}, C-H out-of plane bending at 822 cm^{-1}, 753 $cm^{-1}$and 664 $cm^{-1}$and C-N stretching at 1064 cm^{-1}. No peaks corresponding to the acids are observed which indicaties that the acids did not enter into the crystals of LV.

3.4. Optical characteristics

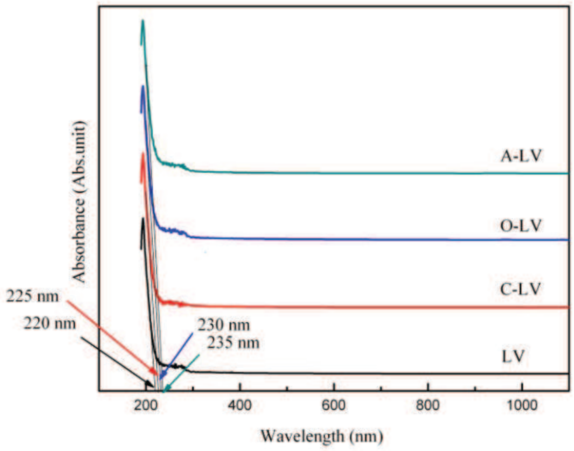

Fig.4. Absorption spectra of pure and acid added L-valine

For optoelectronic applications it is necessary to investigate the optical behavior of the crystals. From the optical parameters like optical band gap (E_g) and absorption co-efficient (α) of the crystals the linear optical characteristics of the material can be inferred [9]. The UV- Vis-NIR absorption spectra of LV, C-LV, O-LV and A-LV are shown in figure 4. All the crystals shows wide transparency range between 300 - 1100nm. An absorption peak was found at 194 nm due to $n\rightarrow\pi^*$ transition of C=O of the carboxyl group. The cut-off wavelength values (λ_{max}) were 220 nm (LV), 225nm (C-LV), 230 nm(O-LV) and 235 nm(A-LV). Significant increase in cut-off wavelength of acid added L-valine crystals were observed and had maximum wavelength for acetic acid added L-valine.

Determination of band gap

Band gap of the crystals were calculated using the relation

$$E_g = \frac{hc}{\lambda_{max}} \qquad (1)$$

where λ_{max} is the cut-off wavelength.

E_g values calculated are 5.65 eV, 5.52 eV, 5.40 eV, and 5.29 eV for LV, C-LV, O-LV and A-LV respectively. The band gap values decreased for acid added L-valine when compared to pure and the minimum value is obtained for acetic acid added L-valine.

The relationship between absorption coefficient (α) and absorbance is given by the equation

$$\alpha = \frac{2.303\times \mathrm{Abs}(\lambda)}{t} \qquad (2)$$

The absorption coefficient at λ =1100 nm was calculated to be 2.118 (LV), 0.184 (C-LV), 2.2565 (O-LV) and 0.6443(A-LV). If the value of the absorption coefficient is large, the energy dissipation in the materials is high which may lead to thermal effect which is undesirable. Least value of α is favorable for SHG efficiency and blue region application. Addition of citric and acetic acid makes the crystal most desirable for SHG conversion.

3.5. Second Harmonic generation efficiency

KDP was used as reference material for SHG measurement and the output signal measured for the crystals are tabulated in Table 2. LV crystals exhibited less SHG efficiency whereas the crystals grown in presence of acids showed SHG efficiency higher than1.5 times that of the reference used. The SHG efficiency mainly depends on intermolecular interaction, crystal packing nature and charge transfer across chromophore of the material. The mechanism behind is being investigated.

Table.2. SHG efficiency of the grown crystals

S.No.	Nonlinear optical crystal	Output signal (mV)	SHG efficiency
1.	KDP	33	1.00 times
2.	LV	27	0.83 times
3.	O-LV	50	1.51 times
4.	A-LV	52	1.58 times
5.	C-LV	53	1.60 times

Conclusions : Single crystals of L-Valine were grown in the absence and presence of acids such as ortho phosphoric acid, citric acid and acetic acid. XRD and FT-IR analyses confirmed that the acids are not incorporated into the lattice of the crystal. The morphology of the crystal was affected by ortho phosphoric acid and citric acid. Enhancement in SHG efficiency was observed for all the three cases. Optical absorption coefficient values also exhibited the same order of enhancement. L-valine crystals grown in presence of acids are found to be better than that grown in the absence.

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