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Growth and characterization of nonlinear optical L – Bis valine selenate single crystals

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ABSTRACT

Single crystals of L-Bis Valine selenate (L-BVS) were grown by slow evaporation method. The grown crystals are characterized by single X – ray diffraction analysis. The vibrational frequencies of various functional groups of the crystal are analyzed from FTIR spectrum. The optical transmission of the material is ascertained by recording UV – VIS – NIR spectrum. Micro hardness and dielectric studies were also carried out on the grown crystals. Thermal behavior of the crystals has been investigated by DTA and TGA analysis. The NLO property of the grown crystals has been confirmed by Kurtz-powder SHG test.

Keywords: NLO, amino acid, valine selenate, micro hardness.

INTRODUCTION

The development of highly efficient non-linear optical (NLO) crystals for visible and ultraviolet (UV) region is extremely important for both laser spectroscopy and laser processing. In view of this, it is desired to find new NLO materials, which have a shorter cutoff wavelength. High quality NLO organic crystals must possess high second-order optical non linearity, lower laser damage threshold power, transparency in UV region and easy growth with larger dimension. However, most organic NLO crystals have usually poor mechanical and thermal properties and are susceptible to damage during processing. It is also difficult to grow large optical quality crystals of these materials for device application [1-3].

Recently, complexes of amino acids have been explored. Amino acids are interesting materials for NLO applications. Complexes of amino acids with inorganic acids and salts are promising material for optical second harmonic generation (SHG), as they tend to combine the advantage of the organic amino acid with that of the inorganic acid [4]. The importance of amino acids in NLO applications is due to the fact that all the amino acid has chiral symmetry and crystallizes in noncentro-symmetric space groups [5].

In the present investigation, high quality bulk single inorganic crystals of L-BVS have been grown from aqueous solution by slow evaporation method. Grown good quality L-BVS crystals were subjected to characterization studies such as single XRD, FT-IR, micro hardness, dielectric and UV-VIS-NIR. Thermal stability of the grown crystal was found out by TGA and DTA analysis. The SHG efficiency of the L-BVS crystals were also studied using Nd: YAG Q-switched laser.

MATERIALS AND METHODS

2.1 EXPERIMENTAL PROCEDURE

L-Valine and selenic acid were taken in 2:1 ratio and mixed in doubled distilled ionized water to obtain clear solution. The super saturated solution was prepared by stirring for 5 hours. The saturated solution was filtered and allowed to evaporate at room temperature under optimized conditions. Seed crystals were obtained in a period of one month. Good quality crystals of L-BVS were obtained by successive recrystallization. The grown crystals were further characterized by various characterization techniques. The photograph of the as grown L-BVS crystals is shown in Fig.i.

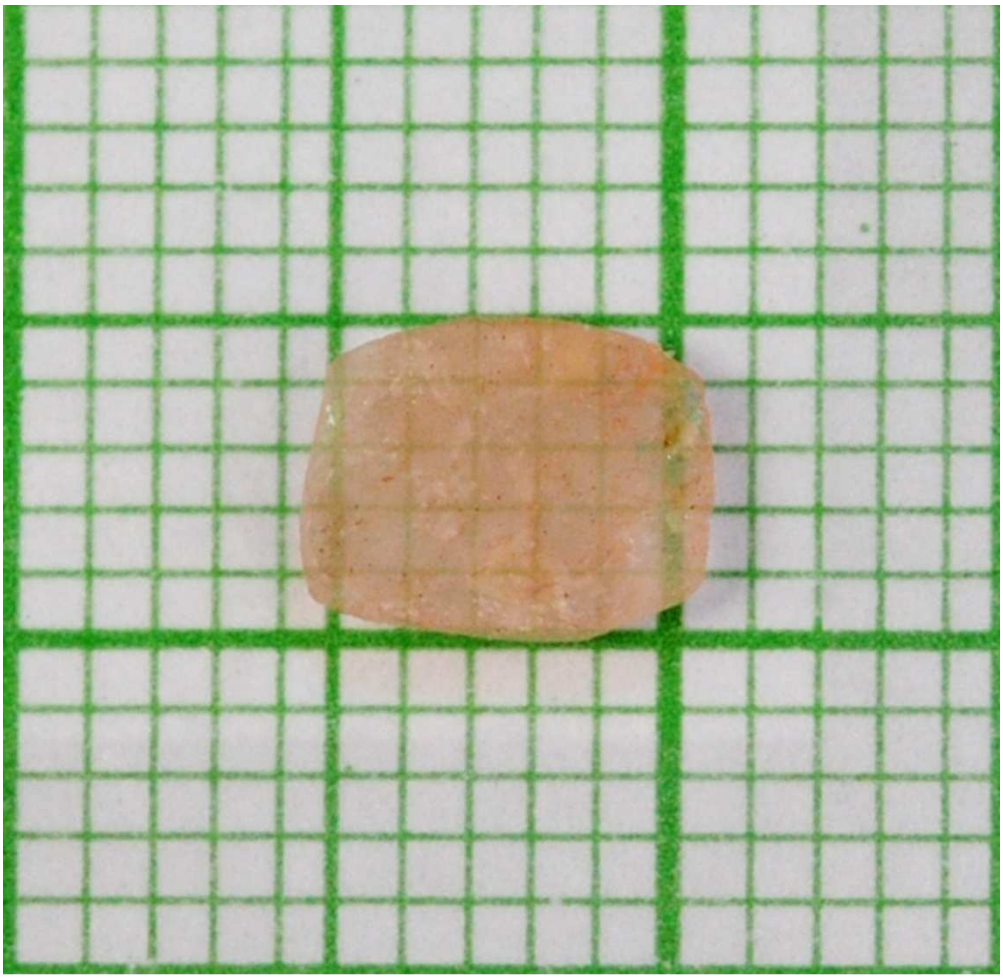

Fig. i. Photograph of the as grown crystal L-BVS

RESULTS AND DISCUSSION

3.1. Single X – ray diffraction studies

Single crystal X-ray diffraction studies of L-BVS crystals were carried out using MESSRS ENRAF NONIUS CAD4-F, single X-ray diffractometer. It is observed from the X-ray diffraction data that the L-BVS sample is monoclinic in structure with space group of $P2_1$. The lattice parameter values are tabulated in table i.

3.2. UV analysis

The optical absorption spectrum of good quality L-BVS crystal was recorded in the wavelength range of 200 nm and 2500 nm using lambda 35 UV spectrophotometer. The absorption spectrum of L-BVS crystal is shown in fig.ii. The UV spectrum shows the presence of a wide transparency window lying between 320 nm and 2250 nm. The lower cut off wavelength of grown crystal is at 320 nm. The analysis of absorption spectrum shows that the grown crystal is transparent in the entire visible region, which is the key requirement for any nonlinear optical crystal having applications in second harmonic generation, parametric oscillation, etc.

Table I: Lattice parameters of L-BVS crystals

Lattice parameter	L- Bis valine selenate
Empirical formula	$2C_5H_{11}NO_{2+}H_2SeO_4$
Crystal system	monoclinic
Space group	$P2_1$
a (Å)	1.11
b (Å)	5.17
c (Å)	13.03
α°	90
β°	111
γ°	90
Volume (Å^3)	696

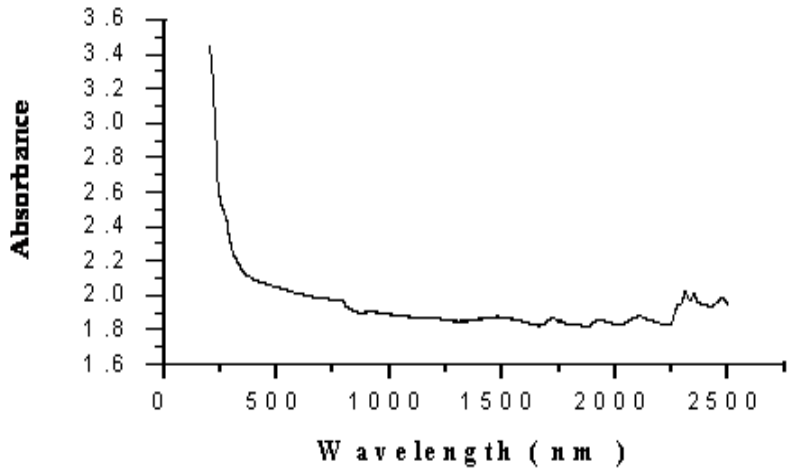

Fig.ii. UV-Vis - NIR spectrum of L-BVS crystal

3.3. Fourier Transform – Infra Red spectroscopy (FT – IR) spectral analysis

The FT-IR spectrum of L-BVS crystal carried out at room temperature in the spectral range of 500 cm^{-1} - 4000 cm^{-1} by employing BRUKKER IFS 66V FT-IR spectrometer, using KBr pellet method is shown in Fig.iii. The broad peak at 3018 cm^{-1} is due to N-H primary amines. The peak at 1991 cm^{-1} corresponding to NH_3^+ asymmetric bending. The sharp peak at 1701 cm^{-1} is attributed due to C=O stretching. The peak at 1473 cm^{-1} represents the C-H stretching vibration. The wave number 1155 cm^{-1} indicates the presence of secondary alcohols (C-O).

Table Ii: Vibrational assignment of L-BVS crystals

WAVE NUMBER (cm^{-1})	ASSIGNMENT
3018	N-H primary amines
1991	NH_3^+ asymmetric bending
1701	C=O stretching
1473	C-H stretching vibration.
1155	C-O stretching vibration.

3.4. Micro hardness measurements

Hardness is an important solid state property and plays a vital role in device fabrication. In order to evaluate the vicker's hardness number, as grown crystals of L-BVS were subjected to the static indentation test at room temperature using a HMV SHIMADZU micro hardness tester fitted with a vicker's diamond pyramidal indentor. Several indentation were made on the [1 0 0] face of L-BVS crystal. The vicker's hardness number was calculated using the expression,

$$H_V=1.8544(P/d^2)\ kg/mm^2$$

Where H_V is the vicker's hardness number in kg/mm^2, P is the applied load and d is the average diagonal length of the indentation. At lower loads there is an increase in the hardness number, which can be attributed to the electrostatic attraction between the zwitterions present in the molecule. This favours all amino acids for their good

mechanical strength [6]. Fig.iv shows the dependence of hardness on load for the L-BVS crystals. At higher loads the hardness shows a sharp decrease, and beyond 40 g significantly cracking occurs, which may be due to the release of internal stress generated locally by indentation. The working hardness coefficient (n) for L-BVS crystal was calculated and it is 1.2. According to onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft material [7]. Hence, it is concluded that the L-BVS crystal belongs to hard material category.

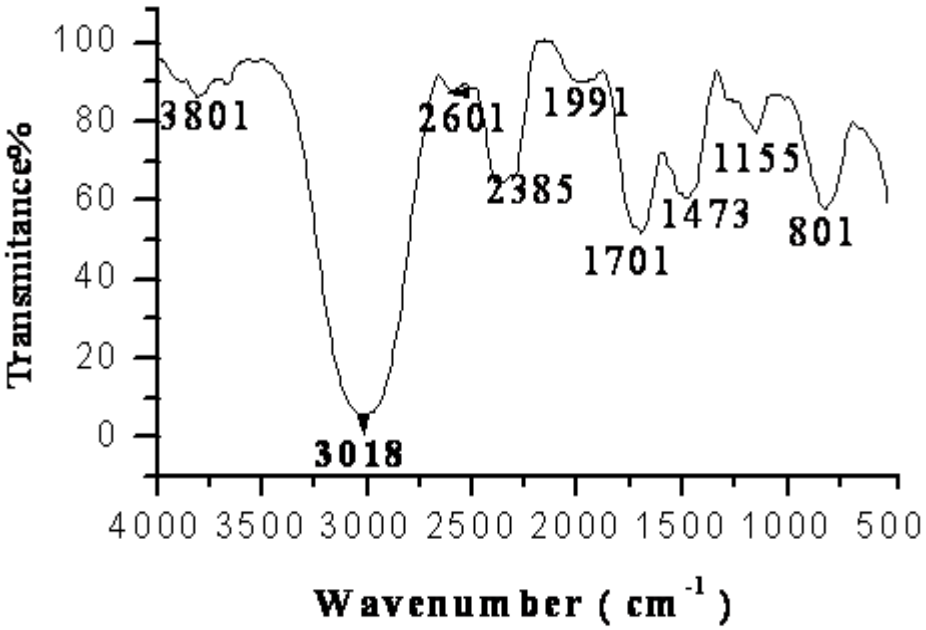

Fig.III. FT-IR spectrum of L-BVS crystal

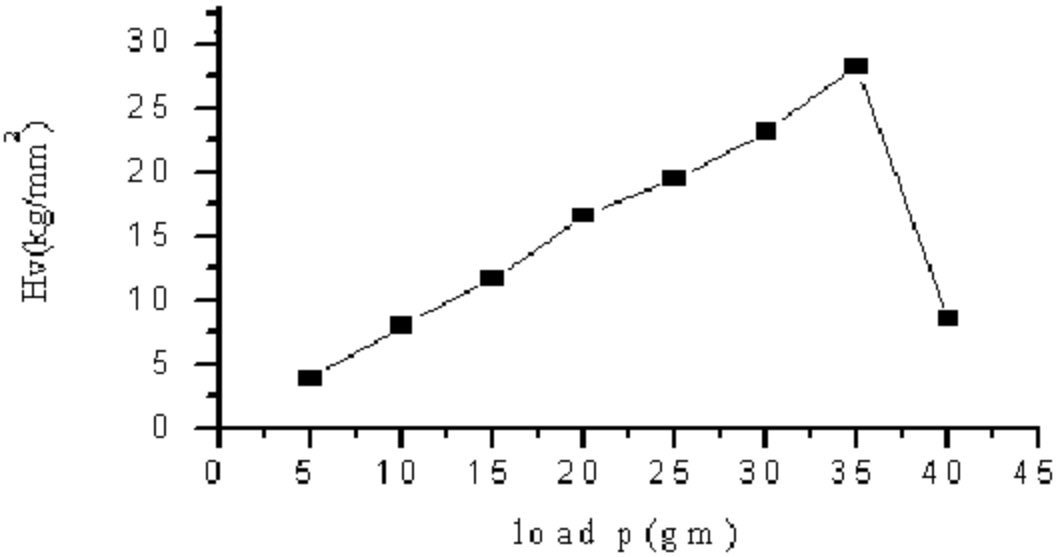

Fig.IV. Load (P) Vs Hardness number (Hv)

3.5. Dielectric studies

The dielectric study of L-BVS single crystals were carried out using the HIOKI 3532- 50 LCR HITESTER instrument. The capacitance of crystals is found for frequency range of 50 Hz to

5 MHz at room temperature. Fig. v & vi. Shows the variation of dielectric constant and dielectric loss with log frequency for L-BVS crystals. It is observed from the plot that the dielectric constant and dielectric loss decreases with increasing log frequency and attained a constant value in the high frequency region. At different temperatures, the dielectric constant and dielectric loss decreases with applied frequency. In L-BVS crystal the low dielectric constant and dielectric loss with high frequency suggests that the crystal possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications [8].

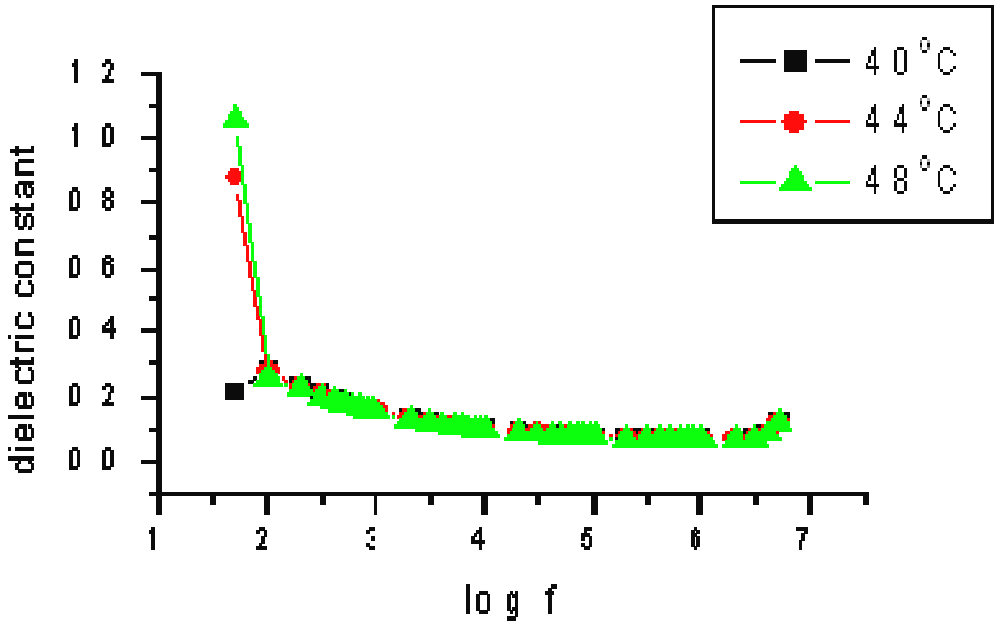

Fig.v. Variation of dielectric constant with log frequency at different temperatures for L-BVS crystals

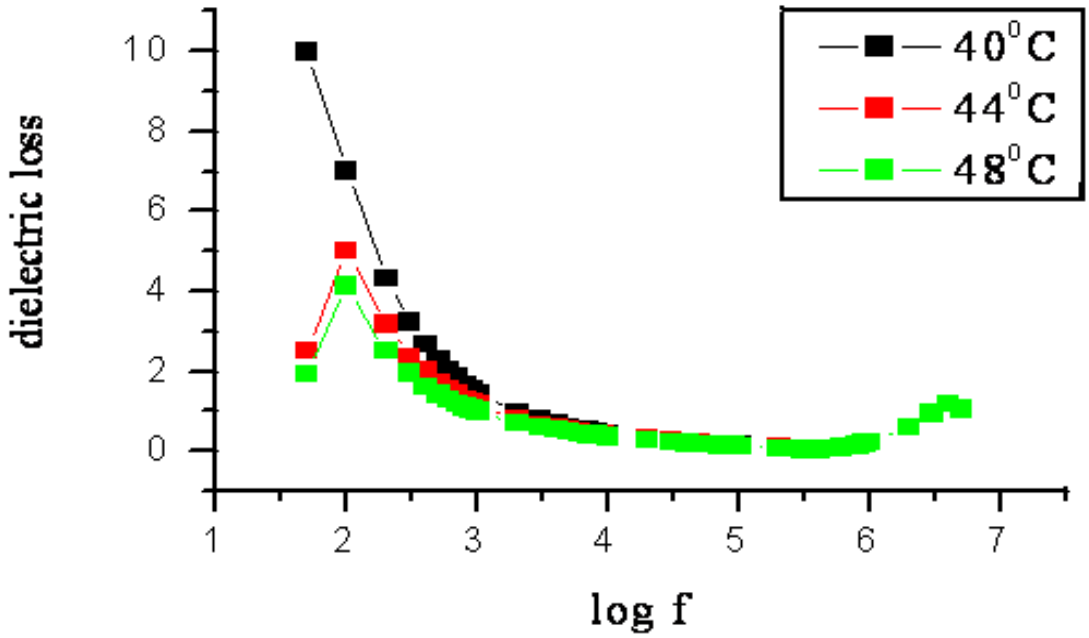

Fig.vi. Variation of dielectric loss with log frequency at different temperature for L-BVS crystals

3.6. Thermal studies

The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of the crystal were taken using the instrument NETSZCH STA 409 ^{o}C, in nitrogen atmosphere. The sample was heated at a rate of 25 ^{o}C/ min. The

TGA and DTA trace of L-BVS crystal is shown in the Fig.vii. There is a sharp weight loss at 259 ^{o}C. Below the onset of decomposition, no weight loss is observed and hence the crystal is completely free from physically observed water or water of crystallization. The thermal studies indicate that L-BVS crystal is thermally more stable up to 259 ^{o}C.

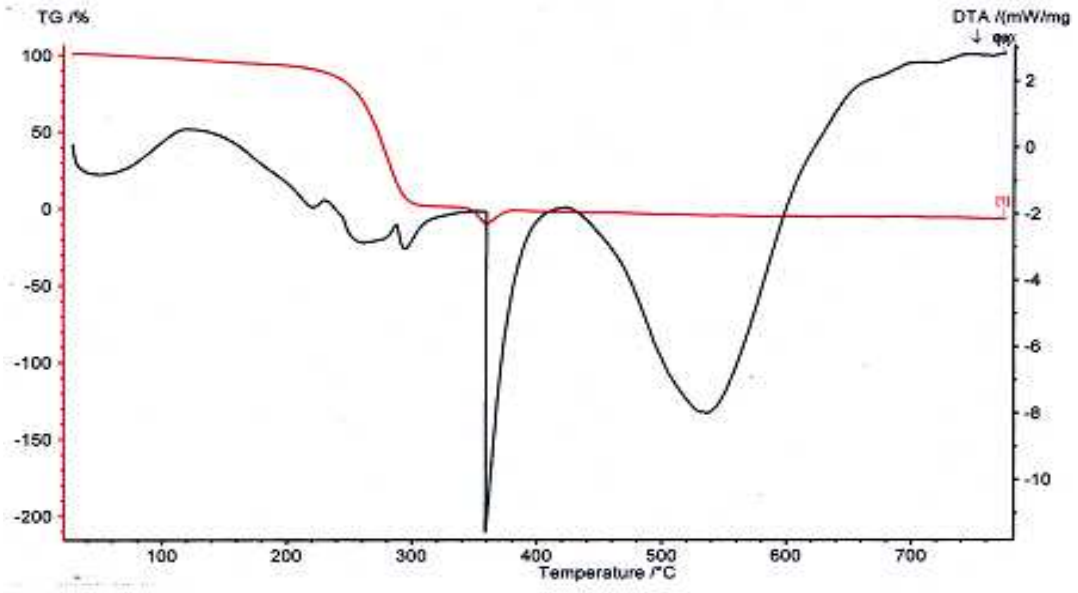

Fig.vii. TG – DTA curves of L-BVS crystal

3.7. NLO property studies

The SHG efficiency of L-BVS has been found by Kurtz powder technique. The fine powdered sample of the grown crystal was taken for NLO test. The sample is subjected to Nd: YAG laser beam (1064 nm, quanta ray) with a input pulse of 0.68 J. The frequency conversion is confirmed by the emission of green light from the powder sample [9]. The output pulse obtained from the experiment for KDP and L-BVS are respectively 8.8 mJ and 5.01 mJ. The efficiency of L-BVS is 0.56 times as that of KDP. The result confirmed the L-BVS crystal is a suitable material for optical conversion applications.

CONCLUSION

A crystal L-BVS has been synthesized by slow evaporation technique. Single crystal XRD analysis shows that grown material is crystallized in monoclinic crystal system with a space group $P2_1$. The presence of functional groups has been confirmed by FTIR analysis. Hardness value of the crystal has been measured on the prominent plane. Hardness test revealed that the grown crystal L-BVS is belonging to hard crystal category. The dielectric studies reveal that the dielectric constant decreases with log frequency, owing to its total transparency in the visible region. The TGA and DTA studies reveal that the material is thermally stable up to 259 ^{o}C. The NLO efficiency of L-BVS crystal found to be 0.56 times that of KDP crystal. Thus, it is concluded that L-BVS is a promising material for NLO applications.

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