Research Article

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Synthesis, Crystal Growth and Characterization of Semi Organic NLO Materials: L-Valine Zinc Chloride as Optic Sensor

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ABSTRACT

A good quality single crystals of L-Valine Zinc Chloride were grown by slow evaporation solution growth technique with different concentrations (0.25, 0.50, 0.75 and 1.0 mole).Single crystal X-ray diffraction technique reveals that the grown single crystals were crystallized in the monoclinic structure.Solid state parameters were calculated for the grown crystals. Kurtz powder technique was used to test the nonlinear optical (NLO) activity of the samples which are semiorganic in nature.The optical properties of the crystals were investigated by UV-Vis. absorption spectroscopy. The results revealed that, the wider bandgap and large transparency in the visible region along with higher polarizability of the grown crystals are highly useful in optoelectronic sensors.

Keywords: Crystal growth, X-ray diffraction, Optical material, Nonlinear optics, Optoelectronic sensors.

1. INTRODUCTION

New nonlinear optical (NLO) frequency conversion materials can have a significant impact on laser technology y (Karas, 2005), optical communication (Anis *et al.* 2014), and optical data storage technology (Feringa *et al.* 1993). Recent efforts at producing new frequency conversion materials have focused primarily on increasing the magnitude of the NLO tensor (d_{ijk}) coefficients to produce structures that can frequency double low peak power sources, such as diode lasers (Karas, 2005). Amino acids are interesting organic materials for NLO applications as they contain zwitterions, which create hydrogen bonds. Amino acids have two or more types of coordination atoms and can act as various bridging ligands (Yukawa *et al.* 1983; Karas, 2005). L-valine is one such amino acid, efforts have been made on the growth of amino acid mixed organic–inorganic complex crystals, in order to improve the chemical stability, laser damage threshold, and linear and non-linear optical properties. A series of studies on semi organic amino acid compounds such as L-arginine phosphate (Haja Hameed *et al.* 1999), L-histidinium bromide (Rajendran *et al.* 2003), L-cystine hydrochloride (Steinrauf *et al.* 1958) as potential NLO crystals have been reported.

In the present work, an attempt has been made to admix L-valine with Zinc chloride in different mole ratios and to study the effect of $ZnCl_2$ on the properties of L-Valine zinc chloride (LVZC) single crystals.

2. EXPERIMENTAL

2.1. Synthesis and Growth of LVZC Single Crystals

LVZC was synthesis from L-valine and zinc chloride hexahydrate were taken in the different molar ratio through 1:0.25, 1:0.5, 1:0.75 and 1:1 and dissolved in double distilled water. The solution was agitated with a magnetic stirring for 2 h continuously. The obtained salt was filtered and dried at room temperature. The required amount of starting materials for the synthesis of LVZC crystal was calculated according to the following reaction:

$$C_5H_{11}NO_2 + ZnCl_2.6H_2O \longrightarrow Zn[C_5H_{11}NO_2]Cl_2$$

The solubility of various concentration of $ZnCl_2$ in $LVZC_x$ (x = 0.25, 0.50, 0.75 and 1.0) salts in double distilled water was determined for six different temperatures(25, 30, 35, 40, 45 and 50 °C). The temperature dependent solubility of various concentrations of $ZnCl_2$ in LVZC crystals is shown in Fig 1. It is observed that the solubility of $ZnCl_2$ mixed LVZC crystals increases with the increase of temperature from 25 °C to 50 °C whereas decreases the increasing concentration of $ZnCl_2$ from 0.25 mole to 1 mole. Solubility is slightly increased for $ZnCl_2$ mixed LVZC samples in comparison to the LVCC samples.

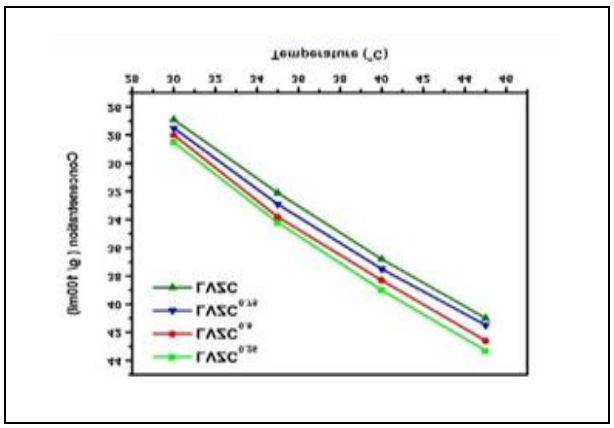

Fig. 1: Solubility curve for LVZC.

The supersaturated solution of different concentration of $ZnCl_2$ admixed L-valine (LVZC) was prepared as per solubility data. Thus prepared solution was allowed to evaporate at room temperature and crystals of good optical qualities have been harvested from the solution between 24 - 27 days.A recrystallization process was carried out in order to eliminate impurities in the LVZC crystals. The obtained LVZC single crystals with different concentration of $ZnCl_2$ (0.25, 0.50, 0.75 and 1.0) are shown in Fig 2.

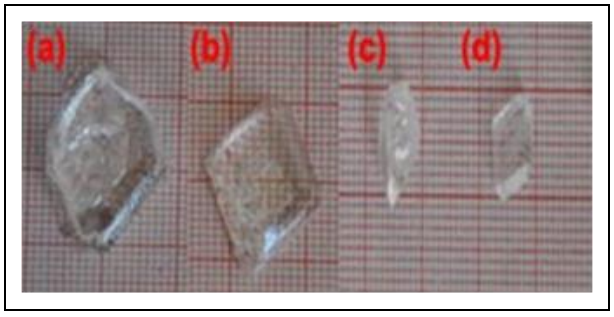

Fig. 2: Photograph of recorded in the range of 190–1100 nm (a) $LVZC_{0.25}$ (b) $LVZC_{0.50}$ (c) $LVZC_{0.75}$ (d) LVZC single crystals.

2.2 Characterization

The single crystal XRD data were collected using an automated 4-circle diffractometer (EnrafNonius CAD4). SEM and EDX analyses were carried out to study the morphology and elemental compositions. The UV-Vis-NIR spectra were using a Shimadzu UV-2400 PC spectrometer. NLO efficiency of the grown crystals were tested by the Kurtz powder method. Solid state parameters of the grown crystals were calculated.

3. RSULTS & DISCUSSION

3.1. Single Crystal XRD

The single crystal XRD data of the LVZC crystals with different concentration of $ZnCl_2$ are presented in Table 1. It is observed that the different concentration of $ZnCl_2$ admixed LVZC crystals has a monoclinic structure with a space group of $P2_1$. The increasing concentration of $ZnCl_2$ in L-valine matrices reduces the overall unit cell volume of LVZC crystals. Significant change in the unit cell parameters and decrease in unit cell volume confirms the formation of admixed crystals of LVZC and the variation of concentration of $ZnCl_2$ modify the lattice parameters.

Table 1: Single crystal XRD data of LVZC crystals with different concentration of $ZnCl_2$ in L-Valine.

DATA	L-valine (Moitra *et al.* 2010)	LV (ZC) $_{0.25}$	LV (ZC) $_{0.50}$	LV (ZC) $_{0.75}$	LVZC
a (Å)	9.701	9.621	9.545	9.487	9.511
b (Å)	5.261	5.274	5.253	5.124	5.104
c (Å)	11.953	11.821	11.683	11.531	11.439
V(Å^3)	610.004	599.734	585.573	560.233	554.643
α (º)	90	90	90	90	90
β (º)	90.66	90.92	91.54	91.89	92.78
γ (º)	90	90	90	90	90
Crystal System	Monoclinic				
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$

3.2 PXRD Analysis

The grown crystals of LVZC is powdered well and subjected to powder X- ray diffraction (PXRD) analysis, using an X- ray powder diffractometer. The samples were scanned over the range of 10 - 80° at a rate of one degree/minute. The PXRD pattern of $LVZC_{0.25}$, $LVZC_{0.50}$, $LVZC_{0.75}$ and LVZC could be indexed with DICVOL 04 software (Filinchuk *et al.* 2009) using the first 10 more intense and better resolved reflections (located using the derivative based peak search algorithm provided with FULLPROF 2K (Wu *et al.* 2006). The absolute error on each 2θ line is fixed with 0.02º and the unit cell was inspected using CHECKCELL (Laugier and Bochu, 2002), which indicated as monoclinic structure with space group *P21*. The indexed PXRD patterns of $LVZC_{0.25}$, $LVZC_{0.50}$, $LVZC_{0.75}$ and LVZC are shown in Fig. 3. The lattice parameters are calculated from the indexed pattern by using the software powder X (Dragoe, 2001) and are summarized in Table 2.

Table 2. Lattice parameters of $LVZC_{0.25}$, $LVZC_{0.50}$, $LVZC_{0.75}$ and LVZC single crystals obtained from powder XRD.

Sample name	Calculated lattice parameters				
	a Å	B Å	C Å	B Degree	Volume $Å^3$
$LVZC_{0.25}$	9.6537	5.1838	11.7633	90.54	588.64
$LVZC_{0.50}$	9.4831	5.2247	11.6018	90.91	574.75
$LVZC_{0.75}$	9.3984	5.1728	11.4762	91.28	557.79
LVZC	9.4565	5.0876	11.3974	91.97	548.02

From Fig. 3, it is revealed that the diffraction peak of the planes (2 0 -1) and (2 1 2) gradually shifted to the higher angle side with the increasing concentration of $ZnCl_2$ in the L-valine matrices. Besides, Also, as the increasing concentration of $ZnCl_2$ in L-valine matrices increase the intensity of dominant reflection peaks of the PXRD patterns, which reveals that the crystallinity of the LVZC crystals are improved when the concentration of $ZnCl_2$ increases. The observed prominent peaks confirm the crystalline property of the grown $ZnCl_2$ admixed L-valine crystals (LVZC). The calculated lattice parameter values are well agreed with the data received from the single crystal XRD.

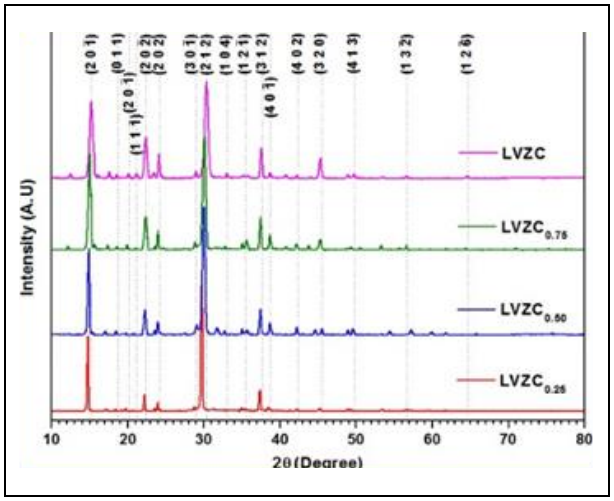

Fig. 3: Indexed powder XRD patterns of LVZC crystals.

3.3. UV–Vis–NIR Spectral Analysis

The optical properties of the crystals were investigated by UV-Vis. absorption spectroscopy. The optical absorption spectrum of LVZC crystals with different concentration of $ZnCl_2$ in the wavelength range from 190 - 1100 nm is shown in Fig. 4-7. No absorption was observed in the visible region of the observed UV–Vis spectra. UV–Vis studies also give important structural information because absorption of UV and visible light involves promotion the electrons in π and n orbital from the ground state to higher energy states (Perkampus *et al.* 2013). From the UV-vis absorbance spectra we have observed that the shape and position of the absorption peaks of LVZC crystals have some significant blue shift as the increasing concentration $ZnCl_2$ in L-valine matrices. Besides, all the grown crystals have low percentage of absorption while making use of these crystals for Laser transmission in the rage 200-800nm. In the case of LVZC crystal, the absorbance is less than 210 nm and the optical absorbance with the lower cut-off wavelength is less than 210 nm which may be attributed to π→π* or n→π* transitions. The absence of strong absorption in the region between 240 nm to 800 nm in UV–Vis. spectrum shows that the grown LVZC with different concentration of $ZnCl_2$ crystals are useful for the SHG application.

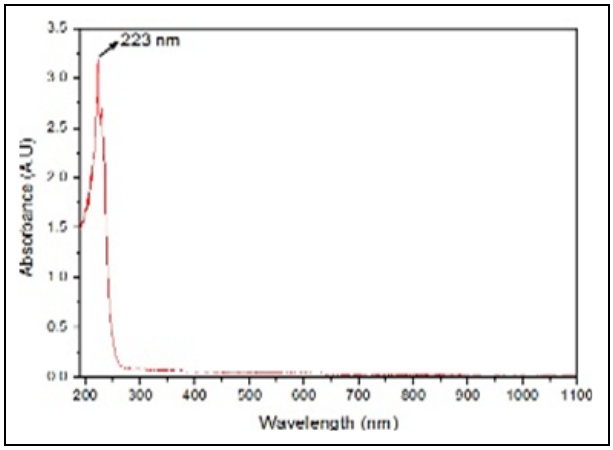

Fig. 4: Optical absorbance spectrum of $LVZC_{0.25}$ crystal.

The optical band gap (E_g) has been evaluated from the absorbance spectra and the optical absorption coefficient (α) near the absorption edge is also calculated.Plot of optical bandgap determination from UV-Vis.-NIR absorption data of $LVZC_{0.25}$, $LVZC_{0.5}$, $LVZC_{0.75}$ and LVZC single crystals were shown in Fig. 8. The bandgap energy of crystals $LVZC_{0.25}$, $LVZC_{0.5}$, $LVZC_{0.75}$ and LVZC are found to be 5.016, 5.145, 5.465 and 5.500 eV respectively.

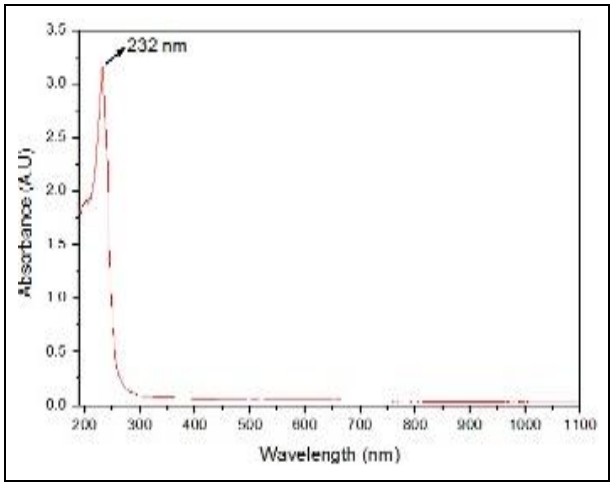

Fig. 5: Optical absorbance spectrum of $LVZC_{0.50}$ crystal.

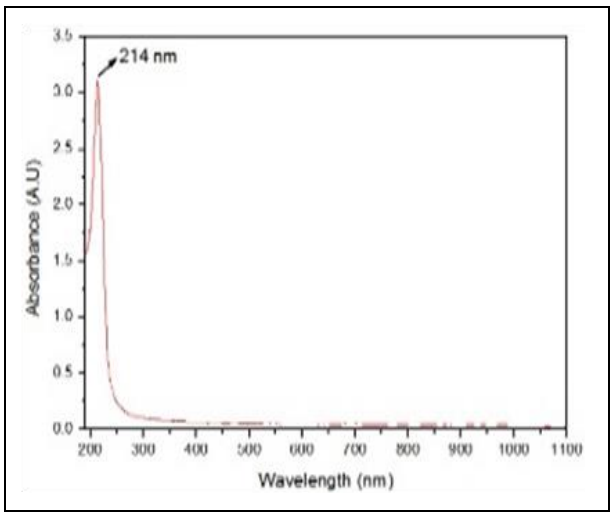

Fig. 6: Optical absorbance spectrum of $LVZC_{0.75}$ crystal.

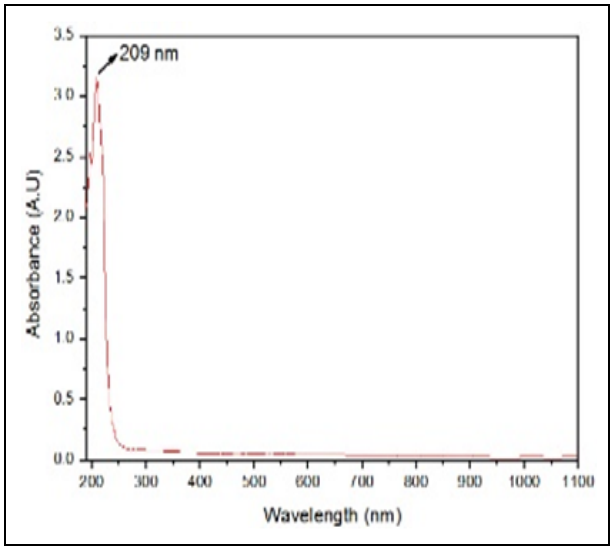

Fig. 7: Optical absorbance spectrum of LVZC crystal.

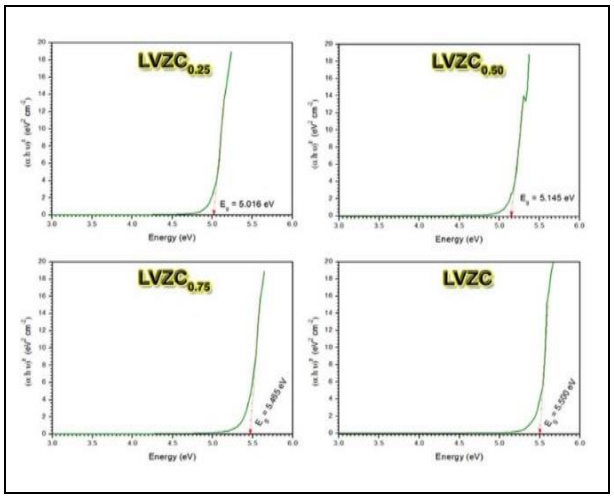

Fig. 8: Plot of optical bandgap determination from UV-Vis absorption data of different concentration of $ZnCl_2$ admixed LVZC single crystals.

Fig. 9 shows the plot of extinction coefficient (K) against wavelength. It could be noticed that K decreases abruptly as the wavelength increases from 200 nm to 280 nm and saturates beyond the wavelength of 300 nm.

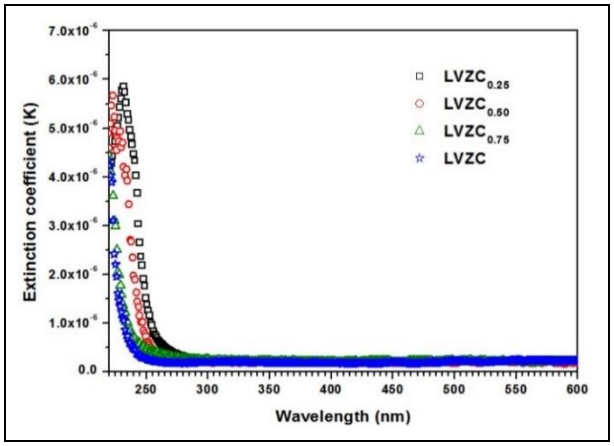

Fig. 9: Variation of Extinction coefficient with wavelength for different concentration of $ZnCl_2$ admixed LVZC single crystals.

3.4. NLO Studies

The grown crystals were subjected to SHG studies by Kurtz and Perry powder technique. Using Nd:YAG Q-switched laser source, the crystal was illuminated by laser beam with a wavelength of 1064 nm. A SHG signal of 15.22, 19.09, 19.18, and 22.08 mJ was obtained for $LVZC_{0.25}$, $LVZC_{0.5}$, $LVZC_{0.75}$ and LVZC crystals respectively, when compared to 8.8 mJ of that of standard KDP crystal for the same input energy of 6.5 mJ/pulse. The SHG efficiency of the grown crystals was compared to that of KDP crystal and the results are tabulated in Table 3.

Table 3: SHG efficiency values of different concentration of ZnCl2 admixed LVZC single crystals.

Sample name	Input power mJ	Output power mJ	SHG efficiency (compared with KDP)
$LVZC_{0.25}$	6.5	15.82	1.79
$LVZC_{0.50}$	6.5	18.09	2.06
$LVZC_{0.75}$	6.5	20.78	2.36
LVZC	6.5	24.08	3.08

From the table it's revealed that the SHG efficiency of the grown LVZC crystals increases with the increasing concentration of $ZnCl_2$ in the L-valine matrices. The SHG efficiency of the LVZC crystal is found to be higher than that of $LVZC_{0.25}$ crystal by the order of ~ 2.

3.5. Solid State Parameters

Solid state parameters such as valence electron plasma energy, Fermi energy, Pen gap energy and electronic polarizability is calculated using the relations [17]. The calculated theoretical values of SHG efficiency is well matched with the experimental results.

Table 4. Calculated solid state parameters for LVZC single crystals with different concentrations of $ZnCl_2$

Solid state parameter		LV (ZC) 0.25	LV (ZC) 0.50	LV (ZC) 0.75	LVZC	KDP (Vas udevan et al. 2013)
Plasma energy (eV)		26.228	23.471	21.279	20.522	17.33
Penn gap (eV)		2.949	2.655	2.455	2.231	2.39
Fermi energy (eV)		22.724	19.604	17.207	16.397	12.02
Polarizability ($x10^{-23}$)		3.7222	4.646	5.649	6.072	2.14
Polarizability from Clausius-Mosotti ($x10^{-23}$)		3.593	4.484	5.448	5.882	2.18
SHG	Theoretical	1.73	2.17	2.64	2.84	1
	Experimental	1.79	2.06	2.36	3.08	1

It was observed that the addition $ZnCl_2$ increases the polarizability whereas it decreases the Penn gap energy and Fermi energy considerably when compared with the standard KDP NLO material. Thus, the effect of $ZnCl_2$ favours the NLO property of L-valaine crystals. Besides, the polarizability value determined using Penn gap agreed very well with the polarizability value obtained using Clausius- Mossotti relation.

4. CONCLUSION

Single crystals of $ZnCl_2$ admixed LVZC, were successfully grown from amino acid family by slow evaporation technique at room temperature. All the grown crystals were confirmed by X-ray diffraction analysis and it is found that the crystal belongs to the monoclinic system with space group $P2_1$. Lattice parameters obtained from the powder X-Ray diffraction analysis well matched with the single crystal studies. The overall unit cell volume of LVZC crystals decreases with increasing concentration of $ZnCl_2$ in LV matrices. The optical absorption spectral studies confirm that all the LVZC crystals have very good transmission in entire visible region, with lower UV cut-off around 240 nm. The transparency nature of the grown crystals in the Visible and Infrared regions confirms the NLO property of the crystals. The SHG test confirms the second harmonic conversion efficiency of all the grown crystals. The 1 mole $ZnCl_2$ admixed L-Valine (LVZC) crystal it is found to be better than that of KDP crystals by the order of 3. All these studies indicate that the $ZnCl_2$ admixed LVZC crystals can be considered as a potential candidate for the NLO applications and fabrication of optoelectronic devices.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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