

Research Article

Optical, Thermal, and Mechanical Properties of L-Serine Phosphate, a Semiorganic Enhanced NLO Single Crystal

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Single crystals of L-serine phosphate (LSP) were grown by slow evaporation technique. The optical studies reveal the transparency of the crystal in the entire visible region. Grown crystal was subjected to single crystal XRD diffraction technique. Thermal studies of LSP confirm the thermal stability of the crystal and it is stable up to 210°C. The functional groups and optical behaviour of the crystal were identified from FT-IR and UV-Vis analysis. The crystals were also characterized by microhardness and photoconductivity to determine the mechanical strength and the optical conductivity. Laser damage threshold and nonlinear optical activity of the grown crystal were confirmed by Q-switched Nd:YAG laser beam.

1. Introduction

The impact of nonlinear optical crystals in science and technology has been recognized recently for several important applications [1, 2]. This includes sensors, waveguide, transmission, infrared detectors, polarizer, transducers, and image processing; apart from that, the growth of high quality NLO materials for optical switches, optical amplifiers, optical parametric oscillators, and frequency multipliers and mixtures opens a new direction in the field of material science for research. Due to the effectiveness in generating new frequencies from existing laser via harmonic generation, tremendous efforts have been made to identify new materials for such process.

During the past decades, organic and semiorganic materials remain the most widely used crystals for frequency conversion. Organic crystals have a large nonlinear coefficient compared to inorganic crystals. But organic crystals are very sensitive to the presence of intrinsic defects and phonon subsystem [3, 4]. Inorganic crystals have high mechanical and thermal stability than that of organic crystals [5, 6]. Semiorganic crystals are those which combine the positive aspects of organic and inorganic materials resulting in desired nonlinear optical properties [7]. Semiorganic crystals have shown potential applications in the field of nonlinear optics.

The importance of nonlinear optics in optical switching, optical memory storage devices, and telecommunication paved the path to identify a suitable and better NLO crystal [8].

Complexes of amino acids with organic and inorganic salts have been identified as promising materials for producing second harmonic generation (SHG) because of their bonding properties with the ions of organic and inorganic salts. Amino acids are playing vital role in the field of nonlinear optics [9]. L-Serine is one of the amino acid family crystals which are easily available in nature [10, 11]. The molecules of L-serine can combine with anionic, cationic, and overall neutral constituents. The study on growth of L-serine crystals from aqueous solution with hydrochloric acid [12], sodium fluoride [13], formic acid [14], sodium nitrate [15], and acetic acid [16] is reported in recent years.

Orthophosphoric acid is highly polar in nature. It is easily miscible with water. Crystal structure of L-serine phosphate ($C_3O_3NH_7 \cdot H_3PO_4$) was reported early [17]. In the present investigation, good optical quality L-serine phosphate (LSP) single crystal has been grown from aqueous solution by slow solvent evaporation method. Single crystal X-ray diffraction study has been carried out to confirm the crystalline nature of the grown crystal. FT-IR, UV-Vis-NIR, microhardness, thermal, and photoconductivity studies were carried out for the grown crystal. Second harmonic generation (SHG) and

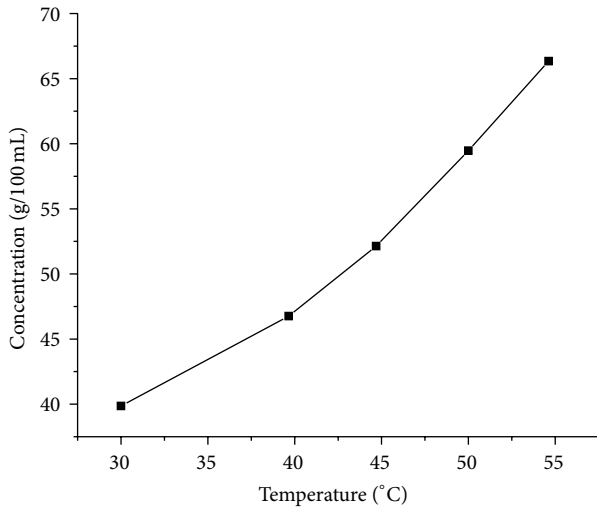


FIGURE 1: Solubility curve of LSP.

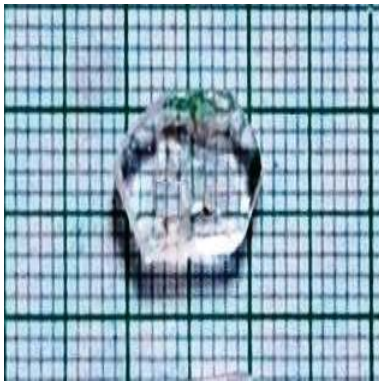


FIGURE 2: Photograph of as-grown LSP crystal.

laser damage threshold (LDT) studies were carried out for the LSP crystal.

2. Experimental

L-serine phosphate single crystal was formed in aqueous solution containing L-serine and phosphoric acid in equimolar ratio 1:1 at room temperature. The solution was stirred 9 hours continuously and filtered. The filtered solution is allowed for complete evaporation. The solubility of LSP in deionized water was assessed as a function of temperature in the range of 25°C–50°C. The solubility was gravimetrically analyzed and was found to increase with increase in temperature which is shown in Figure 1. Seed crystals were obtained in a period of 8 days. The quality of the crystal was improved by successive recrystallization process. Optically good quality single crystal was harvested after 35 days from the day of recrystallization. The grown crystal with dimension $12 \times 8 \times 2 \text{ mm}^3$ is shown in Figure 2.

3. Results and Discussion

3.1. X-Ray Diffraction Study. Single crystal X-ray diffraction studies were carried out using Enraf Nonius CAD-4/MACH

TABLE 1: XRD data of LSP crystal.

Cell parameters	Present work	Reported values
a	9.129 Å	9.134 (5) Å
b	9.407 Å	9.489 (5) Å
c	4.626 Å	4.615 (5) Å
Crystal system	Monoclinic	Monoclinic
$\alpha = \beta$	90°	90°
γ	98.46°	99.54 (5)°
Space group	$P2_1$	$P2_1$

3 diffractometer, with $\text{MoK}\alpha$ radiation to determine the lattice parameters and space group. The crystal belongs to monoclinic crystal system with the space group $P2_1$. Cell parameters and space group of the grown crystal are in good agreement with the reported value [17]. XRD data of the grown crystal with reported values are shown in Table 1.

3.2. FT-IR Study. In order to analyze the presence of functional groups in LSP crystal, Fourier transform infrared (FTIR) spectrum was recorded using the Perkin Elmer Infrared spectrophotometer. The fine powder sample of grown L-serine phosphate crystal was subjected to FT-IR analysis. The characteristic absorption peaks are observed in the range from 400 to 4000 cm^{-1} and are shown in Figure 3.

The strong absorption peak at 3426 cm^{-1} indicates the presence of amine in the grown crystal. NH_2 plane deformation of primary amine is observed at 1561 cm^{-1} and 1622 cm^{-1} . The P–O stretching frequency and deformation of orthophosphoric acid were identified at the peaks 1047 cm^{-1} and 496 cm^{-1} , respectively. This confirms the presence of phosphate ion in the grown crystal lattice [18]. The intense peaks at 2860 and 2950 cm^{-1} are due to C–H stretching [19]. The absorption peak at 1470 cm^{-1} corresponds to CH_3 antisymmetric deformation.

4. Linear and Nonlinear Optical Studies

4.1. UV-Visible Analysis. UV-Vis-NIR studies give important structural information of a given material because absorption of UV and visible light involves promotion of the electrons in π and n orbital from the ground state to higher energy states [20].

The optical absorption spectrum of LSP crystal is shown in Figure 4. The lower cutoff wavelength of the crystal is found as 214 nm. No absorption was found in the visible region of the UV-Vis spectrum. The absence of strong absorption in the entire visible range suggests that the grown LSP crystal is a useful material for the SHG applications [21].

Hence, it is concluded that the grown crystal can be used for optoelectronic applications. The optical absorption coefficient (α) of the crystal was calculated from the UV visible experimental data, using the formula

$$\alpha = \frac{1}{t} \log \frac{1}{T}, \quad (1)$$

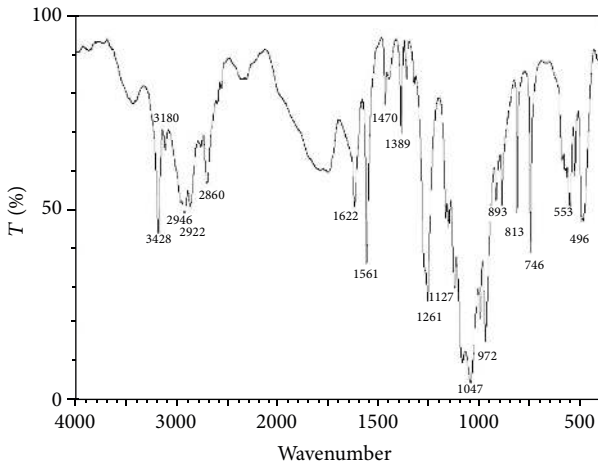


FIGURE 3: FT-IR spectrum of LSP crystal.

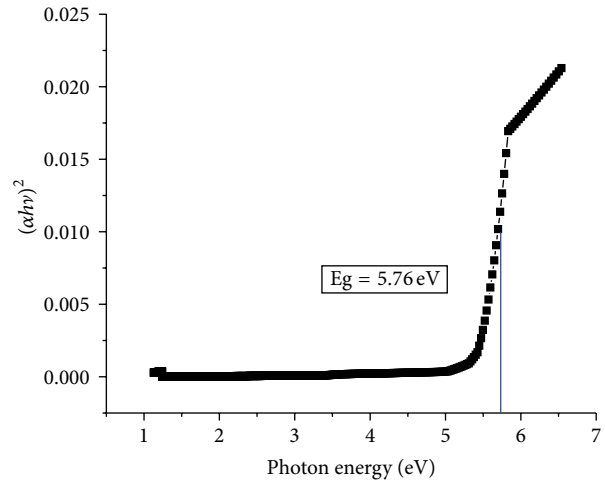


FIGURE 5: Optical band gap energy of LSP.

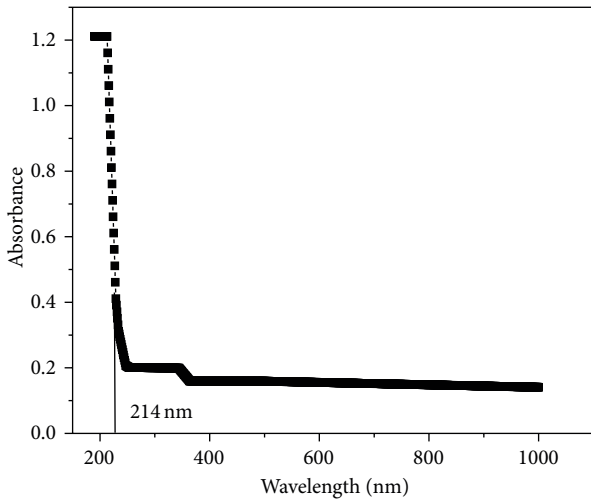


FIGURE 4: UV-Vis spectrum of LSP crystal.

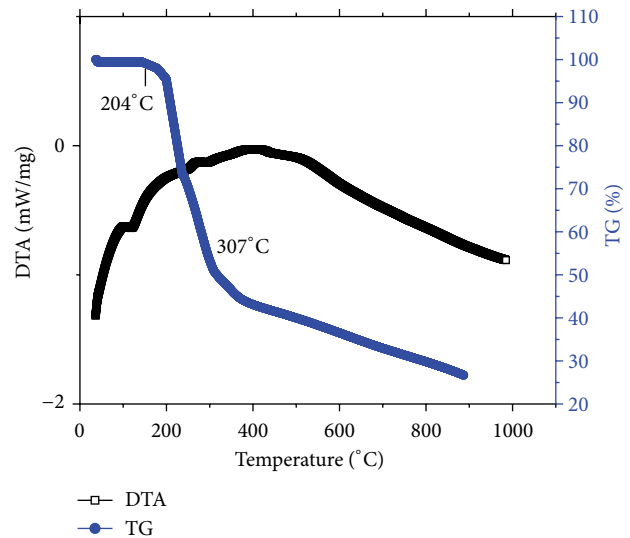


FIGURE 6: TGA and DTA traces of LSP crystal.

where t is the thickness of the crystal and T is the transmittance of the crystal. The optical band gap energy of the crystal can be calculated from Tauc's plot. The optical energy gap (E_g) of the grown LSP crystal was calculated as 5.76 eV from Tauc's plot of $h\nu$ versus $(\alpha h\nu)^2$ which is shown in Figure 5.

4.2. Nonlinear Optical (NLO) Studies. Kurtz powder technique was performed on LSP crystal to confirm the second harmonic generation efficiency [22]. Potassium dihydrogen phosphate (KDP) crystal was used as a reference material for second harmonic generation test. The output SHG signal of 79.7 mV for the LSP crystal was obtained for an input energy of 5 mJ/pulse, whereas the KDP crystal gave an output of 27.6 mV for the same input signal. Thus the SHG efficiency of the LSP crystal is 2.9 times greater than KDP crystal.

4.3. Laser Damage Threshold Test. LDT measurement of the LSP crystal has been carried out using a Q-switched Nd:YAG laser beam of wavelength 1064 nm with the pulse width of 10 ns. The repetition rate of the LDT measurement is 10 Hz.

The laser beam of focal length 1 mm is focused on the sample of 0.7 mm. The LDT value of the grown crystal is found to be 5.27 GW/cm².

Hence, the crystal has a high LDT value; it is observed that L-serine phosphate crystal can be used for high power frequency conversion application [23].

4.4. Thermal Analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of L-serine phosphate single crystal were carried out using a NETZSCH STA 409°C thermal analyzer. The sample was heated in the temperature ranges between 10°C and 1000°C at a heating rate of 10 K/min in nitrogen atmosphere.

The TGA and DTA traces of LSP crystal are shown in Figure 6. From the plot it is found that the first stage of decomposition of the grown crystal starts at 204°C and the crystal starts to decompose further in weight due to the liberation of volatile gases and compounds. It is concluded

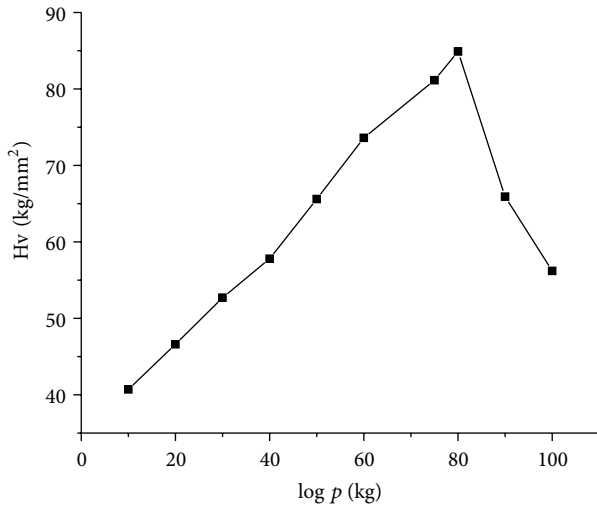
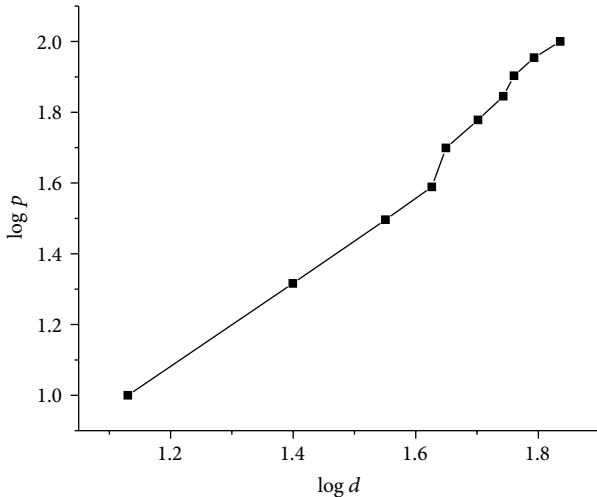


FIGURE 7: Hardness number plot of LSP.

FIGURE 8: Plot of indentation (d) versus load (p).

that the LSP crystal is thermally stable up to 204°C. Almost 50% weight of the starting material is lost around 307°C. Further the crystal is fully decomposed around 900°C.

4.5. Vickers Microhardness Study. Mechanical stability of the crystal was found using Vickers microhardness tester. To get accurate results of hardness of the grown crystal, indentations were made on the LSP crystals with applied load ranging from 10 g to 100 g. The values of Vickers microhardness at different loads were calculated and a graph was drawn between hardness number and the applied load and is shown in Figure 7.

The hardness number was found to increase with the applied load up to 80 g and then decreases gradually due to the microcracks developed in the crystal.

The value of working hardness coefficient of the material was calculated from the slope of the plot between $\log p$ and $\log d$ (Figure 8) and it is found to be 1.17. According to

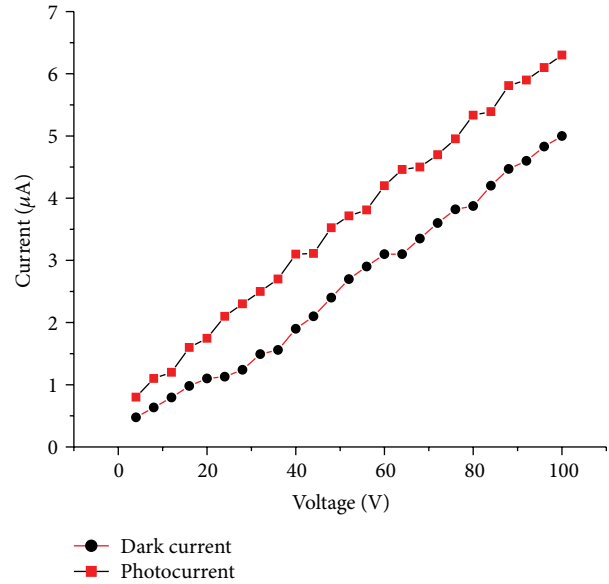


FIGURE 9: Photoconductivity plot of LSP.

Onitsch, n lies between 1 and 1.6 for hard materials, and n is greater than 1.6 for soft materials [24]. Hence, it is concluded that the LSP crystal belongs to hard material category.

4.6. Photoconductivity Study. Photoconductivity studies were carried out for the LSP crystal using Keithley 485 Picoammeter at room temperature. The dark current (I_d) of the sample was measured using DC power supply and picoammeter. The power from the halogen lamp incident on the crystal is 100 W. Photocurrent of the sample was measured using halogen lamp containing iodine vapor. The light from halogen lamp is focused on the material using convex and the photocurrent is measured. DC supply is increased step by step from 10 V to 100 V and the photocurrent (I_p) was measured.

Figure 9 shows the variation of photocurrent and dark current as a function of applied field. It is observed from the plot that the dark current (I_d) and photocurrent (I_p) of the sample increase linearly with the applied field. The photocurrent is always higher than the dark current. This phenomenon is known as positive photoconductivity [25].

5. Conclusion

A potential semiorganic nonlinear optical single crystal of L-serine phosphate was grown by slow evaporation technique. Single crystal X-ray diffraction study confirms that the grown crystal belongs to monoclinic system with space group $P2_1$.

FT-IR studies confirm the various functional groups present in the crystal and they give the evident of anharmonic phonons in the vibrational spectrum of the crystal. These anharmonic phonons are responsible for nonlinearity in noncentrosymmetric crystals. The grown LSP has a wide transparency window in the entire visible region with a lower cutoff wavelength of 214 nm thus confirming the suitability

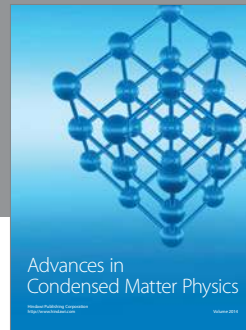
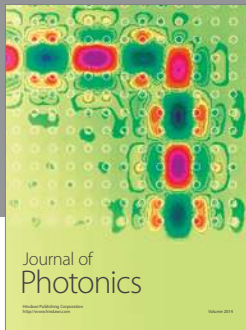
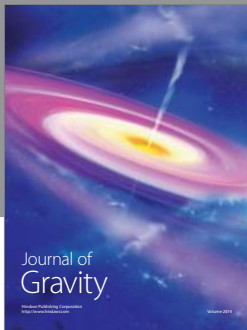
of this material for various optoelectronic and photoelectric applications. The hardness of the material indicates that the material belongs to hard material category, which can be useful for the high frequency conversion devices. Thermal studies revealed that LSP crystal is thermally stable up to 204°C. Photoconductivity studies show that the material exhibits positive photoconductivity. Positive photoconductivity is achieved at anion interstitials. The powder SHG efficiency of LSP crystal is about 3 times that of KDP. It is concluded that LSP crystal is a suitable material for NLO applications with higher efficiency. Laser damage threshold value of the crystal is calculated from the experimental data and it is found to be 5.27 GW/cm². It is concluded that the grown LSP crystal can be used in potential applications in the field of optoelectronic sensors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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