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Optical, dielectric studies on SR method grown L-Valinium picrate NLO single crystal

R. Uthrakumar[1], G. Ramesh[2], M. Jose[3], S. Jerome Das[4] and C. Inmozhi[1,*]

[1]Department of Physics, T.A.G. Govt. Arts College Tindivanam, Tamilnadu 604 001, India.

[2]Department of Physics (P.Ex.), Periyar University, Salem, Tamilnadu 636 011, India.

[3]Department of Physics, Sacred Heart College, Tirupattur, Tamilnadu 635 601, India.

[4]Department of Physics, Loyola College, Chennai 600 034, Tamilnadu, India.

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ABSTRACT

Bulk single crystal of L-Valinium picrate (LVP) was successfully grown from aqueous solution by Sankaranarayanan -Ramasamy (SR) unidirectional growth method with dimensions of 12 mm diameter and 75 mm length. Single crystal X-ray diffraction studies and powder XRD analysis have been carried out to confirm the structure and perfection of the crystal. The optical absorption window and the cutoff wavelength of the LVP have been identified by UV–Vis–NIR studies. Photoluminescence studies indicate that the grown crystal has a green fluorescence emission. The mechanical asset of the grown crystal has been studied using Vicker's microhardness tester. Dielectric studies have been carried out for the grown crystal and the results were discussed in detail.

Introduction

Non linear optical (NLO) materials are expected to play a key role in the technology of photonics including optical information processing and frequency conversion [1-3]. Inorganic NLO materials have admirable mechanical and thermal properties but possess moderately optical nonlinearity because of the lack of extended π-electron delocalization[4] but organic NLO crystals which have potential applications in signal transmission, data storage, inflorescence, remote sensing, high resolution spectroscopy and optical communication [5]. In the recent years, researchers have shown much interest in the amino acid family of picrate crystals due to their high laser damage threshold, wide transparency windows and high NLO coefficiency [6-10]. Amino acid crystals are potential NLO materials as they have donor carboxyl group and acceptor amino group, which form an extensive hydrogen bond networks within the crystal [11]. L-Valinium picrate is an organic NLO material under amino acid category. The unidirectional Sankaranarayanan-Ramasamy [12,13] solution growth method attracted the researchers due to the growth of defect-free transparent bulk single crystals along a particular axis. Simple experimental techniques, maximum solute-solid conversion and prevention of the microbial growth are the interesting features of this technique. In the present work, we report for bulk single crystal of the title material grown from the unidirectional method. The grown crystals were subjected to single crystal and powder X-ray diffraction (XRD) analysis, UV–Vis–NIR spectral analysis, Photoluminescence studies, Vickers hardness test and dielectric studies.

Experimental

Material synthesis and growth assembly

Single crystals of L-Valinium picrate were grown from aqueous solution by slow evaporation technique. The solution was prepared by dissolving equimolar ratio of picric acid and L-Valine in deionized water and stirred well. The prepared solution was maintained at 37°C in constant temprature bath. Good quality seed crystals with perfect external morphology were obtained within a period of 5 days. Optically good quality seed crystal was chosen for the unidirectional growth [14]. Carefully cut and polished portion of LVP crystal was fixed in the base of the growth ampoule along the growth assembly. The growth ampoule with a seed fitted at the bottom is filled with the saturated solution of LVP. The ampoule is rested in S-R growth setup. The temperature gradient creates a concentration gradient along the ampoule, with a maximum supersaturation at the bottom of the ampoule and a minimum at the top of the ampoule. Due to the rapid evaporation at the top of the ampoule, the over all concentration increased at the bottom and promoted the crystal growth along the ampoule by the specified axis. The growth rate of the crystal was found to be around 3 mm per day. The crystal of 75mm length has been grown successfully within a period of 25 days. The grown crystal shows a cylindrical morphology and the photograph of the grown crystal is showen in Figure 1.

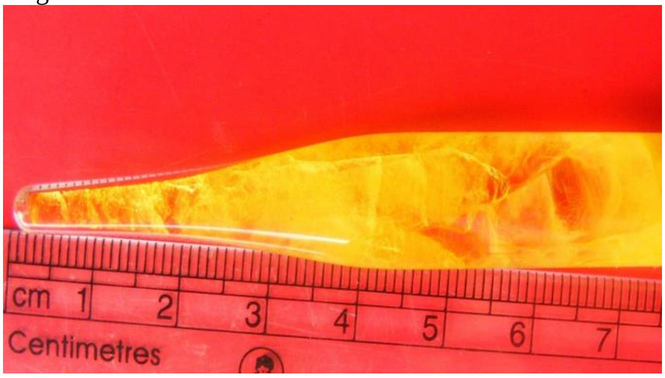

Figure 1. Photograph of the LVP uniaxial single crystal

Results and discussion

Single crystal X-ray analysis

Single crystal X-raydiffraction analysis for the grown L-valinium picrate (LVP) crystal has been carried out to confirm the crystallinity and also to identify the unit cell parameters

Tele:
E-mail addresses: cvesta19@yahoo.com

using Bruker Kappa APEX-2 diffractometer with MoKα (λ=71073Å) radiation. The title crystal belongs to monoclinic crystal system with space group $P2_1$, the lattice parameters are a = 9.967Å; b = 6.235Å; c =12.641Å, β =110. 50° and is well matched with the reported literature [15].

Powder X-ray diffraction studies

The unidirectional grown single crystal of LVP has been subjected to powder X-ray diffraction analysis. Powder form of the above mentioned crystal was taken for the studies using a REICH SEIFERT powder X-ray diffractometer with a scan speed of 1°/ min. The indexed powder X-ray diffraction pattern of the grown crystal is given in Figure 2. The sharp and well defined Bragg's peaks at specific 2y angles testimonies the good crystalline nature of the grown crystal.

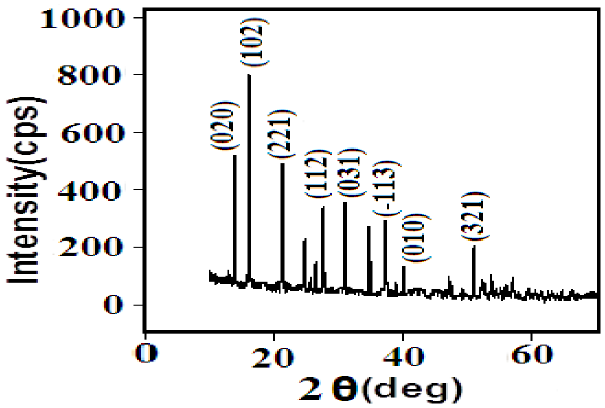

Figure 2. Powder XRD pattern of grown crystal

Optical absorption studies

Optical absorption studies for the unidirectional grown LVP single crystal was recorded in the range 200-1200 nm using VARIAN CARY 5E spectrophotometer and the resultant spectrum is shown in Figure 3. The resultant spectrum illustrates that the very low absorption in the entire visible and NIR region. The UV cut-off wavelength for unidirectional grown LVP crystal was found to be at 430 nm. The low absorption throughout the entire visible region is one of the desired properties for the fabrication of optoelectronic devices [16]. Hence LVP crystal can be used for optical applications.

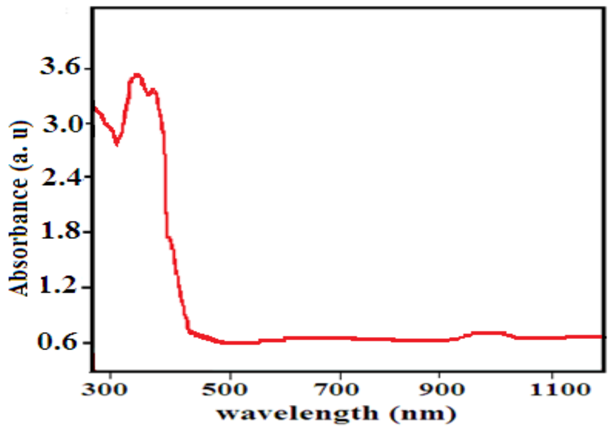

Figure 3. Optical absorption spectrum of LVP single crystal

Photoluminescence (PL) spectroscopy

The PL emission spectrum provides information concerning the point defect nature of the crystal. Observation of near-band-edge emission provides approximate determination of the bandgap energy (Eg) and thus the composition. The photoluminescence spectrum was recorded using JOBIN YVON FLUROLOG-3-11 Spectroflurometer at room temperature. Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light Photons produced as a result of the various recombinations of electrons and holes are emitted from the sample surface and it is the resulting photon emission spectrum that is studied in photoluminescence (PL). From the luminescence spectrum (Figure 4) of LVP, emission of green band at 490 nm may be assigned to an extremely rapid excited-state intramolecular proton transfer (ESIPT) with intramolecular hydrogen bonding between the phenolic group and nitrogen atom is observed [17].

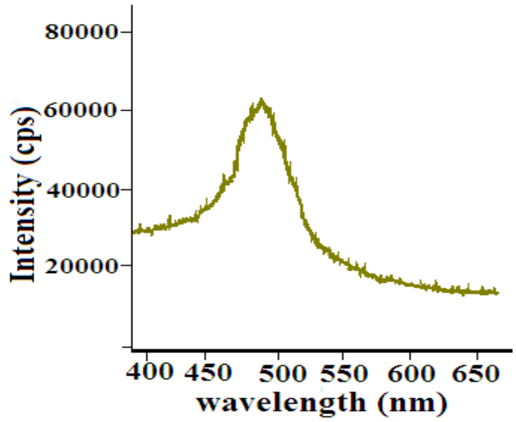

Figure 4. Photoluminescence spectrum of LVP crystal

Microhardness studies

Microhardness test is a general microprobe technique for measuring the bond strength, apart being a extent of bulk strength. Cut and polished unidirectional grown crystal was subjected to static indentation test at room temperature using Vicker's microhardness tester. Indentation was made on the sample plane with the load ranging from 25 to 150 g and the indentation time was kept constant as 10 seconds. The Vicker's microhardness of the material (HV) was determined by the relation [18]

$$Hv = 1.8544 \frac{p}{d^2} kg/mm^2 \quad (1)$$

where p is the applied load in kilogram and d is the average diagonal length of the indentation marks in millimeter and the result was plotted. From the figure 5, sample exhibits the formation of cracks above load 65 g due to the release of internal stress, the grown crystal exhibits the reverse indentation size effect (RISE) in which the hardness value increases with increase in load [19]. The measured hardness value is 66 kg/mm^2, which is systematically higher than other known organic NLO materials [20,21].

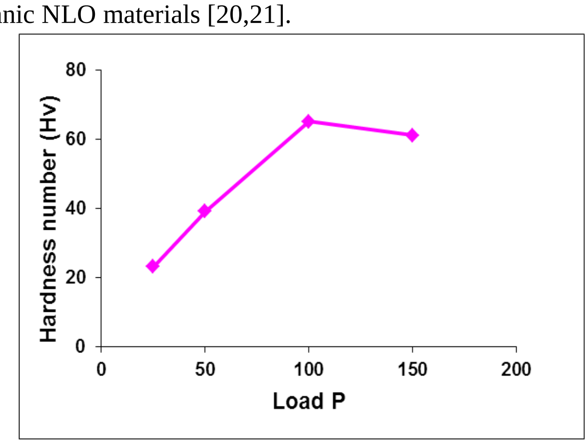

Figure 5. Plot of P vs Hv for LVP single crystal

Dielectric studies

The dielectric study on unidirectional LVP single crystal was carried out using the instrument, HIOKI 3532-50 LCR

HITESTER. A sample of dimension 2 x 2 x 1 mm^3 was silver coated on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample was noted for the applied frequency that varies from 500 Hz to 5 MHz. Figure 6, shows the plot of dielectric constant (εr) versus log frequency. The dielectric constant has higher values in the lower frequency region and then it decreases with the applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. The variation of dielectric loss with frequency is shown in figure 7. The characteristic of low dielectric loss with high frequency for a given sample suggests that the sample possess enhanced optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application [22].

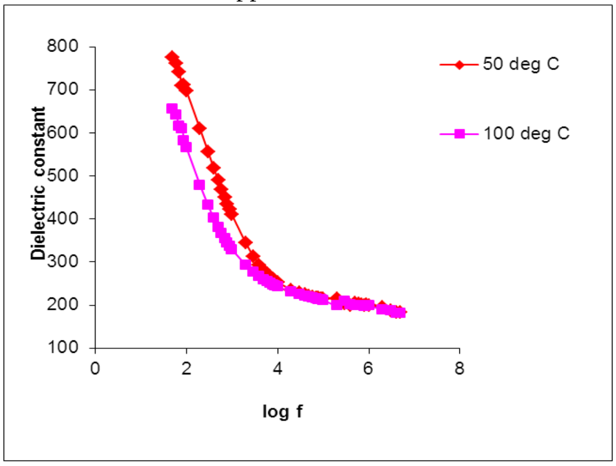

Figure 6. Dielectric constant of LVP single crystal

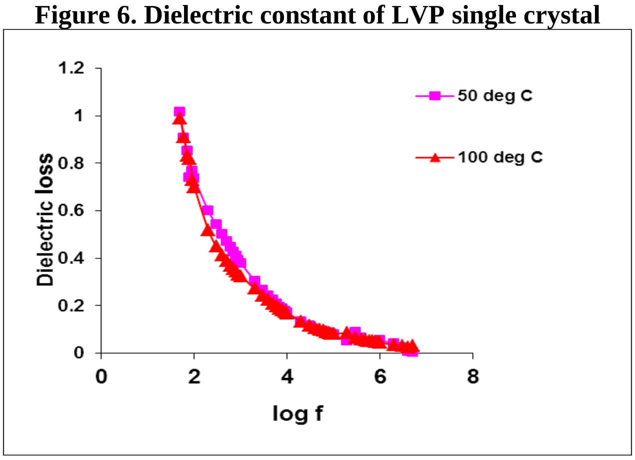

Figure 7. Dielectric loss of LVP single crystal

Conclusions

Good quality bulk single crystal of L-Valinium picrate was grown by Sankaranarayanan-Ramasamy unidirectional growth method. The structural analysis of this crystal is determined using the X-ray diffraction methods. From single crystal X-ray analysis, the material is found to be crystallized in the monoclinic system with a space group $P2_1$. Optical absorption studies on this sample shows minimum absorption in the region 500 and 1200 nm which is well suited for optical applications. The photoluminescence study indicates that the grown crystal has a green fluorescence emission. Mechanical hardness studies reveals that the Vicker's hardness number increases as the load increases and then decreases for higher loads. The dielectric studies showed that LVP has low dielectric loss with less power dissipation and hence this crystal can be used for optoelectronic device fabrications.

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