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Growth and characterization of high proficient second order nonlinear optical material: L-Valinium Picrate

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ABSTRACT

High-quality translucent solitary crystals of L-Valinium Picrate (LVAP) were lucratively grown by a conventional solution growth method and unidirectional growth technique of Sankaranarayanan–Ramasamy. The as grown organic LVAP crystal belongs to monoclinic crystal system with noncentrosymmetric space group $P2_1$. The seed crystal acquired by conventional solution growth method was slash along the (0 1 0) direction and consequently employed for unidirectional growth. A bulky extent single crystal was fully fledged by slow cooling procedure with facilitate of solubility data. The unit cell parameters were resolved from single crystal X-ray diffraction studies. The grown crystals by both conventional solution growth (SEST) and SR methods were subjected to assorted characterization processes such as HRXRD, UV–Vis, dielectric, Hardness and Laser damage threshold studies to investigate the properties. The etching and high resolution X-ray diffraction studies designate that the unidirectional grown LVAP crystal encompass good crystalline excellence and lesser amount of imperfections. The UV–Visible study reveals the ocular excellence of the SR grown LVAP crystal is superior to SEST grown crystal. The laser damage threshold of SEST and SR grown LVAP crystals has been examined and SR grown LVAP crystal boast higher damage threshold than the conventional method grown crystal. Microhardness measurements at dissimilar temperatures show that crystals fully fledged by SR method contain elevated mechanical steadiness than the crystals grown by SEST method. Dielectric dispersion is soaring in SR grown crystal compared to SEST grown LVAP crystal. The piezoelectric nature and the relative Second Harmonic Generation (for various particle sizes) of the material were also studied.

1. Introduction

Engineering of novel nonlinear materials, configurations and devices with improved figures of merit has comported over the past two decades as a main vigour to coerce nonlinear optics from the laboratory to authentic applications. Due to their latent applications in photonic strategy, the nonlinear optical properties of molecules and their hyperpolarizabilities have turn into an significant region of widespread research, and a many of experimental [1,2] and hypothetical efforts [3,4] are purposeful on bulk NLO properties as well as their reliance on the first order hyperpolarizabilities of molecules. The inspiration for these crams ranges from the testing of ab initio calculations of molecular properties to the progress of materials appropriate for NLO contrivance applications. Organic molecules with manifest nonlinear optical bustle normally consist of a π-electron conjugated moiety surrogated by an electron contributor cluster on one end of the conjugated arrangement and an electron acceptor cluster on the other end, creating a "push–pull" conjugated structure [5,6]. The conjugated π-electron moiety offers alleyway for the redeployment of electronic charge transversely the whole span of conjugation beneath the perturbation of exterior electric field. The donor and acceptor groups present the ground state charge irregularity of the molecule, which is requisite for second order nonlinearity. The astonishing physical properties of this attractive group of compounds are ruled by lofty amount of electronic charge delocalization along the charge transport axis as well as by the squat band gaps [7]. Earlier report discussed a few donor–acceptor complexes showing high second order nonlinearity [8,9]. In furtherance work on charge transfer complexes, we focus on L-Valinium Picrate ($C_5H_{12}NO_2^+ \cdot C_6H_2N_3O_7^-$) which consists valinium as the cation and the picrate as the anion. The title amalgam is a potential NLO material in which L-Valine performs as donor and the picric acid as electron acceptor which offers the

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ground state charge asymmetry of the molecule. In general, the slow evaporation solution technique (SEST) has been extensively used to develop numerous categories of crystal at room temperature. Crystals of dissimilar morphology with countless growth segment boundaries are grown by SEST method and the disarticulation can instigate from the growth sector boundaries [10]. Hence, the growth of large extent crystals with reduced amount of imperfection is an exigent chore for crystal growers. The SR method fascinated the researchers by its exclusive advantages contrast to the conventional slow evaporation (SEST) method. Unidirectional growth by SR method provides superior mechanical steadiness, superior crystalline perfection, less density of dislocations and good ocular excellence with 100% solute–crystal translation efficiency [11]. Therefore, the SR method grown crystals are exposed to be better than the conventional solution grown crystals [12]. Hence, we spotlight the foremost instant on the growth of bulk size single crystals of the title compound by SR method in the present swot. We also described the growth characteristics, defects and various properties of conventional solution and unidirectional (SR) methods fully fledged L-Valinium Picrate (LVAP).

2. Experimental

2.1. Growth of LVAP seed by SEST

The premeditated quantity of picric acid was liquefied in combined solvent of acetone and water (1:1). Further, L-Valine was gradually appended to the solution by stirring. The equipped solution was allowed to arid at room temperature. The Yellowish materials were obtained by slow evaporation solution growth technique (Fig. 1). The limpidness of the amalgamated material was further enhanced by consecutive recrystallization process.

2.2. Solubility and metastable stable zone width measurements

Metastable zone width is a vital parameter for the augmentation of bulk size crystals from solution since it is the direct gauge of the stability of the solution in its supersaturated region. The solubility of LVAP in acetone and water (1:1) was measured as a function of temperature in the range 30–55 °C. The solubility was ascertained by dissolving the three epoch's recrystallized solute in deionized water in an airtight container maintained at a constant temperature with continuous stirring. The solution was continually stirred for 2 h using a magnetic stirrer for homogenization. The symmetry concentration of the solute was analyzed gravimetrically after attaining the saturation. The solubility curve was thus obtained. Drenched solution of LVAP has been prepared in harmony with the currently ascertained solubility curve for the nucleation experiments. The studies were performed in a constant temperature bath controlled to an exactness of ±0.01 °C, endow with a cryostat for cooling beneath room temperature. Metastable zone width of LVAP was deliberate using the polythermal method [13]. The acquired solubility and nucleation curve for LVAP is shown in Fig. 2. It is seen from the figure that the LVAP has a constructive gradient of solubility. It also shows that LVAP has good solubility in the assorted solvent of acetone and water (1:1) and the solubility augments almost linearly with temperature. The metastable zone width decreases with increasing temperature.

2.3. Growth from slow cooling technique

The decontaminated Seed crystals (gratis from macro defects) obtained by spontaneous nucleation from the saturated solution of LVAP was used for vastness growth. The bulk growth of LVAP single crystals were carried out by low temperature solution growth technique by slow cooling method. According to the solubility data of LVAP in equimolar concentration of solute (acetone + deionized water), the saturated solution of LVAP at 40 °C was prepared from recrystallised material. The solution was sifted to eradicate any other insoluble impurities. We carefully ensured that the prepared solution was glowing within the metastable zone width region. The low temperature solution growth technique by slow cooling was carried out by using constant temperature bath controlled at an accuracy of ±0.01 °C. Transparent and good quality seed crystals of size $19 \times 3 \times 18$ mm^3 obtained from slow evaporation technique were selected for the growth of bulk LVAP single crystals by slow cooling method. The solution was maintained at 40 °C in constant temperature bath for 2 days before seeding. The cooling rate of 0.05 °C/day was employed throughout the growth period till 36 °C was reached. Optically translucent crystal of size $22 \times 4 \times 23$ mm^3 was harvested in a period of 80 days (Fig. 3) after completion of the growth run.

2.4. SR method of crystal growth

According to the solubility data of LVAP in deionized water, the saturated solution of LVAP was prepared. The equipped solution was within the metastable zone width region. Single crystal XRD studies and Morphology (morphology) from Fig. 4, the (0 1 0) plane was selected in the present study to enforce the orientation in the growing crystal. The seed crystal was vigilantly located at the base of 1 feet length and 20 mm diameter ampoule. The saturated solution of LVAP was vigilantly sieved and decanted into the ampoule. The top ring heater temperature was put at 38 °C to augment the evaporation rate. The temperature around the growth region is preserved at 36 °C. The residency of ring heater at the top of the drenched solution also controls the forged nucleation near the surface region of the solution throughout the intact growth period. Due to the translucent nature of the solution and the experimental set-up, real time close-up examination exposed solution-crystal interface, which was found to be flat. Highly translucent crystal growth was seen in under optimized condition. We found that the seed crystal commenced to grow after 7 days. The growth pace for (0 1 0) plane of LVAP crystals was 2 mm/day which has cautiously observed. The extremely high excellence crystal of diameter 20 mm and 77 mm length has grown in a period of 28 days

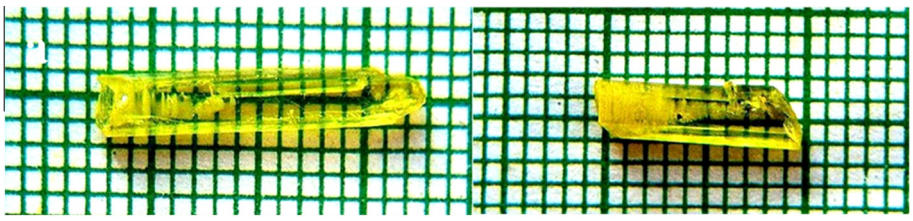

Fig. 1. Photographs of as grown single crystal of LVAP by SEST method.