Growth and Characterization of Methyl red Doped L-Arginine Phosphate Crystals for Laser Applications

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Abstract

L-Arginine Phosphate (LAP) is one of the potential materials for Non-linear optical property applications. Single crystals of LAP Crystals with very high degree of transparency were grown from aqueous solution by slow evaporation technique. The solubility of the pure and doped LAP crystals was measured at different temperatures in the double distilled water. The optical transparency of the grown crystals was studied by UV-visible spectroscopy and was found to increase in transmission in the doped crystals. The doping of Methyl Red was confirmed quantitatively by the atomic absorption spectroscopy and qualitatively by FT-IR spectroscopy. The mechanical properties were studied using Vickers microhardness tester. The dielectric studies were also reported for grown crystals. The thermo-gravimetric and differential thermal analysis was employed to know the thermal stability of the grown crystals. The Methyl Red doped LAP crystals have shown good thermal stability. The second harmonic generation efficiencies were studied.

Keywords: Solution growth, LAP, X-ray Diffraction, Optical Studies, Second Harmonic Generation
1. INTRODUCTION

Only a handful of materials are commonly available, despite considerable effort over the past twenty years, for frequency conversion, to extend the useful wavelength range of laboratory lasers [1]. LiNbO3, LiIO3, KTP, Barium borate, Urea, and KDP are the familiar materials used for non-linear applications. Primary limitations on size, damage thresholds and growth rate. In spite of their modest non-linearities, members of the KDP group materials remain the most widely used crystals for frequency conversion [2]. This is primarily due to the low cost and the relative ease with which large volumes of optically homogeneous material can be grown. Apart from these crystals, a new addition to this group is L-arginine phosphate. The attractive features of this material are its high damage threshold, large non-linearity and the facility with which large crystals of high optical quality can be grown.

Generally the organic crystals have been grown by solution growth like slow cooling and slow evaporation techniques and melt growth. The resultant crystals were multi faceted (report the morphology) and they were smaller in size. Instead, crystals of reasonable size and are grown along required direction are very essential for nonlinear optical application [3]. LAP was identified as a new organic NLO material and crystal structure of the material was solved by single crystal X-ray diffraction analysis. Moreover, single crystals of LAP were grown by slow solvent evaporation technique using mixed solvent of ethanol and acetone. Various functional groups present in the grown crystal were identified by FTIR spectroscopy. Thermal stability of the grown sample was studied by TG&DTA analysis. Mechanical properties of the grown crystal were analyzed by
micro hardness studies. The optical quality of the big crystal was even by optical transmission studies [4]. The dielectric constant and dielectric loss were measured as a function of frequency at 300K. The material shows high SHG efficiency than that of LAP and hence it could be applicable for nonlinear optical applications.

2. Experiment

2.1. Crystal growth

The experimental description of the employed solution growth technique can be found in the literature. The well insulated and resistively heated furnace construction in the present work resulted in a high thermal inertia and consequently increased temperature stability. The temperature of the furnace was controlled with an accuracy of ± 0.1°C. Glass beaker was used as a crucible and static crucible condition was employed during growth [5].

A micro tube mounted at one end of the seed rod was used as seed and can be rotated and translated in the range of 1 mm to 6 mm h⁻¹. Solubility of LAP in mixed solvent of ethanol and acetone was measured at 32°C for different volume ratio of the solvents. Figure 2 shows the solubility of LAP in the mixed solvent as a function of acetone measuring in volume ratio. It can be seen from the figure that the solubility of the material increases evidently while increasing the volume ratio of acetone. According to the solubility data, saturated solution of LAP was prepared by dissolving the purified source material in the pure and mixed solvents of ethanol and acetone at 32°C.

Then, the close to saturated answer was transferred to a crystallizer and coated by a perforated synthetic resin sheet for controlled evaporation.
at temperature. Transparent single crystals were harvested from the growth solution after achieved a reasonable size.

![Figure 2. Photograph of Methyl Red doped LAP Crystal](image)

### 2.2. X-ray diffraction analysis

X-ray diffraction spectrum was recorded on the grown LAP sample in a 2θ range from 10 to 70 using a JOEL JDX 8030 diffractometer with CuKα radiation of wavelength 1.5418 Å for identifying the growth orientation. The recorded XRD spectrum was shown in the Fig. 2 and exhibits the Powder XRD pattern of the pure and doped LAP crystals. The diffraction patterns of the pure and doped LAP crystals have been indexed by the least square fit method. It is seen that both the pure and doped crystals crystallize variations in the lattice parameters which are due to the incorporation of the dopant in the LAP crystal lattice.

![Figure 3. XRD of (a) Methyl Red doped LAP (b) Pure LAP Crystal](image)
2.3 FTIR Studies

The FTIR spectrum recorded in the range of 4000–400 cm\(^{-1}\) for LAP sample is shown in Figure 4. The various functional groups of the grown material were identified by FTIR spectroscopic analysis [5].

![Figure 4: FTIR Spectra of (a) Pure LAP (b) Methyl Red doped LAP Crystal](image)

N-H is one of the prominent functional groups of the primary aromatic amines, and its asymmetric stretching vibration is observed at 3448 cm\(^{-1}\) and the symmetric stretching vibration is observed at 3392 cm\(^{-1}\). The aromatic C–H stretching is observed at 3088 cm\(^{-1}\) and the aliphatic C-H stretching is observed at 2979, 2905 and 2812 cm\(^{-1}\). A strong peak observed around 1697 cm\(^{-1}\) is due to the out of plane bending of N-H vibration of the molecule. An absorption peak at 1605 cm\(^{-1}\) is due to carbonyl stretching (C=O) of the molecule. In plane bending of N-H stretching is observed at 1527 cm\(^{-1}\). The absorption peaks at 1482 and 1443 cm\(^{-1}\) are due to skeletal
vibrations of aromatic ring. Out-of-plane bending vibration modes of aromatic C–H bonds are observed at 1367, 1280, 1182, 1113 and 1012 cm\(^{-1}\). The absorption peaks observed below 1000 cm\(^{-1}\) illustrates in-plane-bending vibration modes of C–H bonds. From this spectroscopic investigation, the presence of all the fundamental functional groups of the grown sample was confirmed qualitatively. Moreover, no absorption peaks related to the solvent molecules or any other impurities were observed which confirms the absence of solvent trapping in the crystal lattice and also the purity of the grown sample.

2.4. Optical transmission studies

The UV-VIS-NIR transmission spectrum was recorded in the wavelength range of 300 to 1100 nm on the grown sample. The recorded transmittance spectrum was shown in Fig. 5. The attained highest percentage of transmission at 400 nm is 80% in the visible region. The sharp absorption onset at 300 nm and the high transmission values of the grown LAP single crystal at wavelength above 400 nm exhibit the optical quality, low concentration of grown in defects and suitability for second harmonic generation in the visible region[6]. The NLO crystal used for SHG applications should be transparent to the fundamental and second harmonic wavelengths. Therefore, the optical transparency study is more important. Polished thin samples of thickness 2mm were used to study the transmission over wavelength range 190-1000nm. All the crystals show a cut-off at around 285nm and have high transmission up to 1083nm (Fig.5).
Figure 5. Transmittance spectra of (a) Methyl Red LAP and (b) Pure LAP Crystal

The optical transparency is found to increase in Methyl Red doped crystals. Maximum transmission has been found to be for Methyl Red doped LAP crystal. For this crystal, the cut-off has been shifted somewhat at lower wavelength side. The increase in the transparency for the fundamental and second harmonic wavelengths makes the Methyl Red doped LAP crystals prominent for SHG applications. The electronic transitions associated within the units of LAP are responsible for the absorption in the near UV region. The π-orbital electron delocalization in LAP, which arises the mesomeric effect [7], is responsible for the nonlinear optical response and the absorption in the near UV region. In the present case, some positions of Zn have been replaced with Methyl Red. The strong coordination between Methyl Red and LAP weaken the coordination units with dye and prevents population of charge transfer excited states by light absorption besides increasing optical transparency with concentration of Methyl Red in LAP crystal [8].
2.5 Mechanical Property

Microhardness studies of any system have a direct correlation with the crystal structure and are very sensitive to the presence of any other phase or phase transition and lattice perfections are prevalent in the system [9]. The hardness of the material depends on the different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing [10]. Microhardness measurements are made using a Leitz microhardness tester fitted with a diamond pyramidal indentor. Single crystal of Methyl Red doped glycine zinc sulphate crystal is subjected to microhardness on (001) orientation. The applied load is varied from 1 to 100 g for a constant indentation period of 10s. The Vicker’s hardness number Hv is calculated using the relation

\[ H_v = 1.8544P/d^2 \text{ Kg/mm}^2 \]

where P is the indenter load in kg and d is the diagonal length of the impression in mm [Fig.6]

2.5.1 Hardness studies

Mechanical strength of these crystals has been determined using Vicker’s microhardness tester and this test, performed on the (100) and (010) planes of LAP and LAPS, showed that the cleavable (100) planes are harder in both crystals than the other planes; it coincides with the close packing of atoms in the cleavage plane. The pure LAP crystal was found to be harder than the mixed crystal [11] because, introduction of sulphate ion is believed to result in loosely packed lattice due to the reduced bond energy which is revealed from the solubilities of LAP and LAPS. The Vicker’s hardness number (VHN) for LAP and LAPS are given in Table 4.2 at a test load of 50 g.
Figure 6. Hardness studies of (a) Pure LAP and (b) Methyl Red doped LAP Crystal

2.6 Dielectric Studies

Dielectric properties are related with electro-optic property of the crystals [12]. The dielectric constant is the measure of how easily a material is polarized in an external electric field [13]. The dielectric study on Methyl Red doped EDMAB crystal is carried out using the instrument, LCR meter. Methyl Red doped EDMAB sample having silver coating on opposite faces is placed between the two copper electrodes and thus a parallel plate capacitor is formed [14]. The capacitance is measured in the frequency range of 100Hz to 5MHz. The dielectric constant is calculated using the relation \( \varepsilon_r = \frac{C_d}{A\varepsilon_0} \) and is shown in fig8. The dielectric studies were carried out using silver coated samples placed between the two copper electrodes which form a parallel plate capacitor [15].
The capacitance of the sample was noted for the applied frequency that varies from fifty cycles per second to five megacycle per second at completely different temperatures. Fig. 7 shows the plot of stuff constant ($\varepsilon_r$) versus applied frequency for various temperatures. The applied frequency is represented by logarithmic values in the plot.

![Dielectric Constant vs Log Frequency](image)

**Figure 7. Dielectric Studies of Methyl Red doped LAP Crystal**

### 2.7 Thermal Studies

Thermal characteristics of the material were investigated by TG & DTA analysis. For the TG analysis, the known gram of material was heated from ambient temperature to 300°C at a heating rate of 20°C/min in air atmosphere. Figure 8 illustrates the TG and DTA curves for the grown Methyl Red doped LAP
sample. The TG curve shows very small (2.5%) weight loss up to 164.23°C. Hence the material is thermally stable up to 127°C and above this temperature the material loses its weight gradually [16-18]. As can be seen from the DTA curve in the figure, the material undergoes an endothermic transition at 65.31°C where the melting begins.

The TG curve shows no weight loss throughout the primary 2 endoergic peaks that confirms the phase change of the fabric from solid to liquid (melting) and therefore the weight of the material starts to losses after 128°C is not due to self-degradation of LAP but merely its evaporation after melting. The endothermic peak at 235.23°C indicates a phase change from liquid to vapor state as evidenced from the huge loss of weight in TG curve.

![Figure 8. TGA &DTA curves of the Methyl Red doped LAP crystal](image)
2.8. SHG efficiency

The SHG conversion efficiency was measured by using a Kurtz and Perry method [19-22]. In the setup Q-switched mode locked Nd: YAG laser with fundamental output at 1064 nm, repetition rate 10Hz, pulse energy 3.1mJ was used. The output at second harmonic wavelength 532nm was monitored. Powder samples were filled in quartz capillary and kept in the path of laser beam [23]. The output was collected in perpendicular direction, detected by photomultiplier tube and measured with digital storage oscilloscope.

Laser damage threshold was measured for the well polished samples prepared from the grown LAP single crystal using a Nd: YAG laser operating at 1064 nm wavelength. The pulse width and the repetition rate of the laser pulses are 65 ns and 10 KHz respectively [24]. The average damage threshold obtained for the doped LAP sample was \(32 \text{ J/cm}^2\). Similar study on the KDP single crystal grown in our laboratory by conventional slow solvent evaporation technique shows a damage threshold of 6 J/cm2. This result illustrates that the grown doped LAP crystal has nearly five times higher laser damage threshold than that of KDP.

3. RESULTS AND DISCUSSION

In general, the growth rate of a growing crystal can largely be influenced by the size and rate of diffusion of molecules or growth units. In solution growth, the rate of diffusion of molecules or growth units are mainly depends on the solute-solvent interactions which can be effectively tuned by means of providing mixed solvents instead of single solvent. Due to the different vapour pressures of the constituent solvents as well as their interaction with solute molecules, the diffusion of growth
units can very well be modified or controlled. Also, the vital growth parameters such as induction period and the nucleation rate can be varied by means of altering the chemical environment around the growing surface. Based on these aspects, an attempt has been made to grow large size Methyl Red doped LAP crystals from mixed solvent containing ethanol and acetone, in which Methyl Red doped LAP has low solubility in ethanol and high solubility in acetone. Moreover, both the solvents are miscible and have different vapour pressures. This led us to investigate the controlling of supersaturation thereby nucleation of LAP, since changing the solubility as well as the interaction between the solute and the solvent has profound effect on these vital growth parameters.

It was observed that the solubility of Methyl Red doped LAP was increased with the increasing of acetone volume ratio in the mixed solvents. The results indicates that the effective interaction between the solute and solvent is higher when the dipole moment of the solvent increases. The obtained large size LAP single crystal from the mixed solvent having 25% of acetone-volume ratio indicated an optimized growth condition. Moreover, the growth rate of LAP crystal along the a-axis seems to be much higher than that along b- and c- axes.

4. CONCLUSION

The experimental description of the employed solution growth technique can be found in the literature. The well insulated and resistively heated furnace construction in the present work resulted in a high thermal inertia and consequently increased temperature stability. The temperature of the furnace was
controlled with an accuracy of ± 0.1°C. Glass beaker was used as a crucible and static crucible condition was employed during growth. Then, the close to saturated resolution was transferred to a crystallizer and lined by a perforated polythene sheet for controlled evaporation at temperature. Transparent single crystals were harvested from the growth solution after achieved a reasonable size.

References


