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Effect of ethylenediamine tetra acetic acid additive on the nucleation kinetics and growth aspects of L-arginine phosphate single crystals

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Abstract Pure and Ethylenediaminetetraacetic acid (EDTA) doped L-arginine phosphate (LAP) single crystals were grown from the aqueous solution by temperature lowering method. The effect of EDTA additive on the solubility and metastable zone width of LAP solution has been investigated. Addition of EDTA has enhanced the metastable zone width of LAP and hence bulk crystals could be grown. The growth rate along the [100] direction increases with EDTA additive. Powder X-ray diffraction and FTIR studies reveal the absence of EDTA in the lattice of LAP. This reveals that the addition of EDTA to LAP doesn't influence the crystallinity. However, the transmittance and NLO properties significantly increase with EDTA additive and hence bulk LAP crystals are useful for laser fusion experiments.

Key words Solution growth, LAP, Semi-organic material, Nonlinear optics

1. Introduction

Semi-organic L-arginine phosphate (LAP) is a well-known non-linear optical crystal for its high nonlinearity, large laser damage threshold and wide transparency region [1-3]. It crystallizes in the monoclinic system with the space group $P2_1$ and has a perfect cleavage along (100) plane. In recent years, several attempts have been made to increase the nonlinear optical properties of LAP crystals by studying the growth kinetics and crystal properties [4]. Growth habit and surface topography of LAP single crystals depend on the supersaturation of the growth solution [5]. Growth of LAP crystals with special emphasis on methods to prevent the growth of microorganisms and colouration of the solution has already been reported [6, 7]. Additives are known to influence the growth kinetics and crystal properties. Ethylenediamine tetra acetic acid (EDTA), a well-known chelating agent has altered the growth kinetics and optical properties of many solution-grown crystals [8, 9]. The secondary nucleation and the growth rate of the crystals are also influenced by the addition of EDTA [10]. In this paper, we report the enhancement of metastable zone width of the LAP growth solution by the addition of EDTA, which is favorable for growing bulk crystals. Structural and spectral analyses have been carried out on the grown crystals.

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2. Experiment

2.1. Material synthesis and solubility studies

L-arginine phosphate (LAP) was synthesized from equimolar ratio of L-arginine (99 % Pure, Merck) and analar grade phosphoric acid.

$$(H_2N)NHCNH(CH_2)_3CH(NH_2)COOH + H_3PO_4 + H_2O \rightarrow [(H_2N)_2{}^+CNH(CH_2)_3CH(NH_3)^+COO^-H_2PO_4^-\cdot H_2O].$$

The purity of the salt was improved by successive recrystallization process. The recrystallised LAP salt was dissolved in low conductivity millipore water and the solution was prepared by adding 1 mol% of the chelating agent EDTA. The solubility of LAP and EDTA added LAP was studied for four different temperatures viz. 30, 35, 40 and 45°C. Recrystallised salt was dissolved in known quantity of water and kept in an airtight container maintained at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated by a gravimetric method. The same method was repeated for the solubility measurement of EDTA added LAP solution.

2.2 Metastable zone width measurements

Metastable zone width was measured by the conventional polythermal method. 250 ml of pure and EDTA added LAP solutions were used for the measurement. The experiments were carried out under identical conditions for both pure

and EDTA doped LAP solutions by keeping in an optically heated constant temperature bath with a control accuracy of ±0.01°C in a cryostat. Solutions were stirred for 4 h continuously. Constant cooling rates were adopted for both the solutions and the temperature at which the first nucleus was observed. The experiments were repeated for different saturation temperatures viz. 35, 40 and 45°C.

2.3. *Crystal growth and characterization*

Saturated solutions of LAP and EDTA added LAP were prepared at 45°C according to the solubility data. Optical quality seed crystals obtained by spontaneous nucleation were used for the growth run. The growth was initiated at 45°C followed by a cooling rate of 0.01°C/day throughout the growth period. Transparent bulk crystals were harvested after a typical growth period of 35 days. X-ray diffraction pattern was recorded for pure and EDTA added LAP crystals using Rich Seifert X-ray powder diffractometer. Finely powdered sample was scanned over the range 10~50 degree at a scan rate of 1 degree/minute. Fourier-transform infrared absorption spectra (FTIR) of LAP and EDTA added LAP were recorded in the range of 400~4000 cm^{-1} by KBr pellet technique using a Perkin-Elmer 783 spectrophotometer.

3. Results and Discussion

The solubility curves for LAP and EDTA doped LAP for different temperatures are shown in Fig. 1. The solubility is higher for EDTA added LAP solution. The metastable zone width for pure and EDTA added LAP

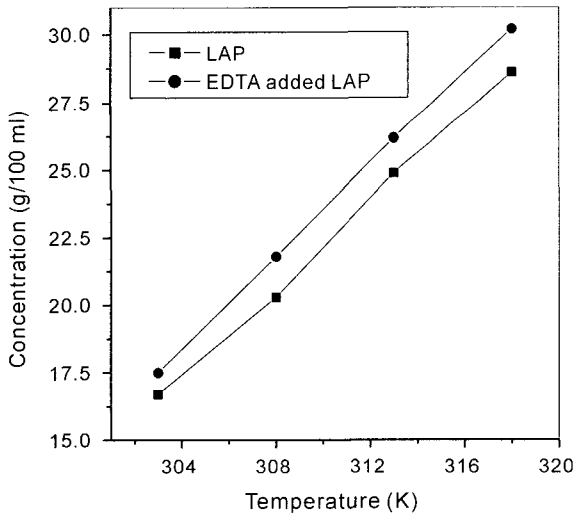

Fig. 1. Solubility of LAP and EDTA added LAP solutions.

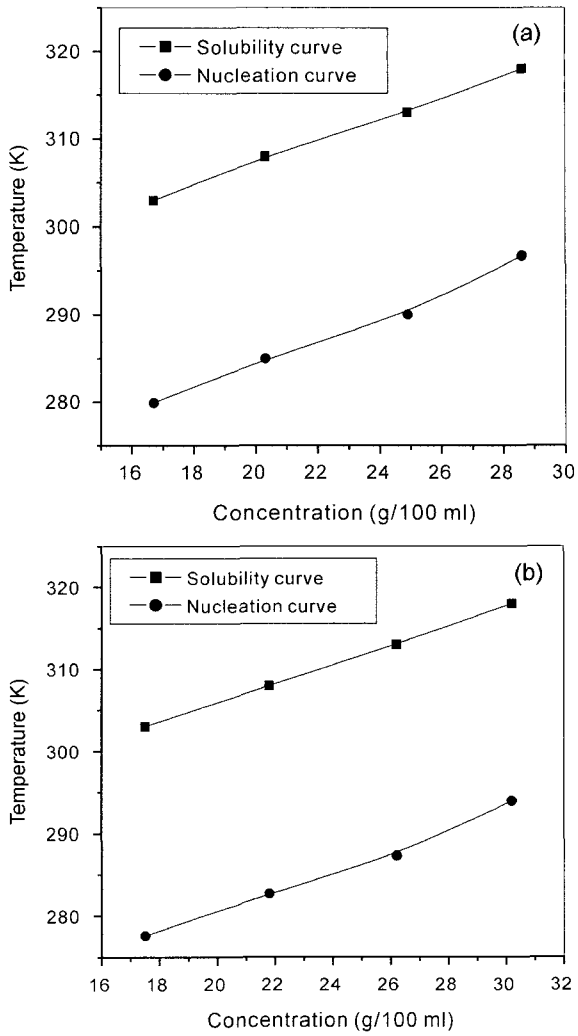

Fig. 2. Metastable zone width of (a) LAP and (b) EDTA added LAP solutions.

is shown in Fig. 2. It is observed that there is a slight decrease in the metastable zone width with increase of temperature. At a particular temperature, the zone width of EDTA added LAP is wider than pure LAP. This will be useful for the growth of bulk crystals with high transparency. The secondary nucleation is reduced in EDTA added LAP solution compared to pure LAP. EDTA suppresses the activities of metal ion impurities present in the solution and this in-turn enhances the metastable zone width limit and hence the growth of bulk crystals. As-grown crystals of pure and EDTA doped LAP are shown in Fig. 3. The grown crystals were colorless and free from microbial incorporation. Morphologies of LAP and EDTA added LAP crystals are shown in Fig. 4. The growth rate along [100] direction increased with the addition of EDTA. The growth habit reveals that {201} and $\{20\bar{1}\}$ faces are smooth (S) faces and all other faces are flat (F) faces. The polarity of PBC justifies the pres-

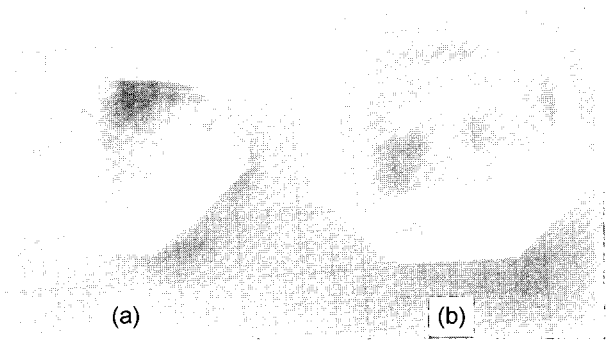

Fig. 3. As grown crystals of (a) LAP and (b) EDTA doped LAP.

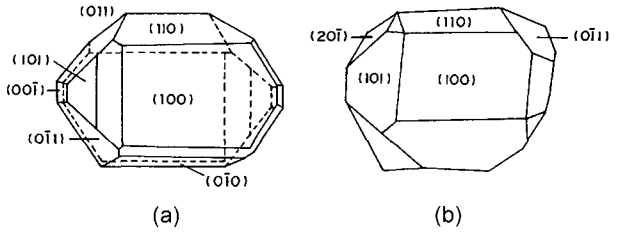

Fig. 4. Morphology of (a) LAP and (b) EDTA added LAP crystals.

ence of $\{0\bar{1}0\}$ face and the absence of $\{010\}$ face.

X-ray diffraction pattern of the grown crystals is shown in Fig. 5. There is no significant variation in the lattice parameter values. The lattice parameters of LAP and EDTA added LAP crystals are respectively, a = 10.859 Å, b = 7.888 Å, c = 7.404 Å, V = 627.5 Å^3 and a = 10.783 Å, b = 7.911 Å, c = 7.261 Å, V = 612.9 Å^3. This confirms that the addition of EDTA to LAP doesn't influence the crystallinity. To analyze the incorporation of EDTA into the lattice of LAP, FTIR spectra were taken for both the crystals as shown in Fig. 6. The FTIR spectrum of LAP shows a broad envelope lying in between 2500 and 3500 cm^{-1} arising out of symmetric and asymmetric modes of NH_2 group. Symmetric and asymmetric modes of CH_2 are positioned just below 3000 cm^{-1}. C-N stretch and N-H bending modes have produced a close array of peaks around 1600 cm^{-1}. The peaks at 1690 cm^{-1} may be assigned to C=O stretch of carboxyl group. C-H bending modes occur at 1409 and 1358 cm^{-1}. C-COO$^-$ group shows its characteristic peaks at 1200 cm^{-1}. The peak due to torsional N-H oscillation is observed at 509 cm^{-1}. In EDTA doped LAP, there is no peak corresponding to EDTA, which confirms the absence of EDTA in the crystal lattice of LAP. The EDTA doped LAP crystals possess higher transmittance compared to pure crystals as shown in Fig. 7.

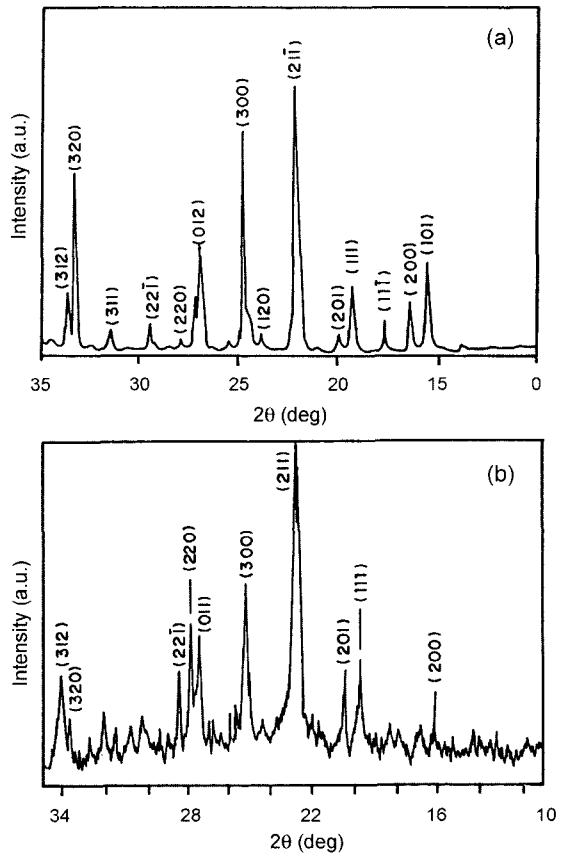

Fig. 5. X-Ray diffraction patterns for (a) LAP and (b) EDTA added LAP crystals.

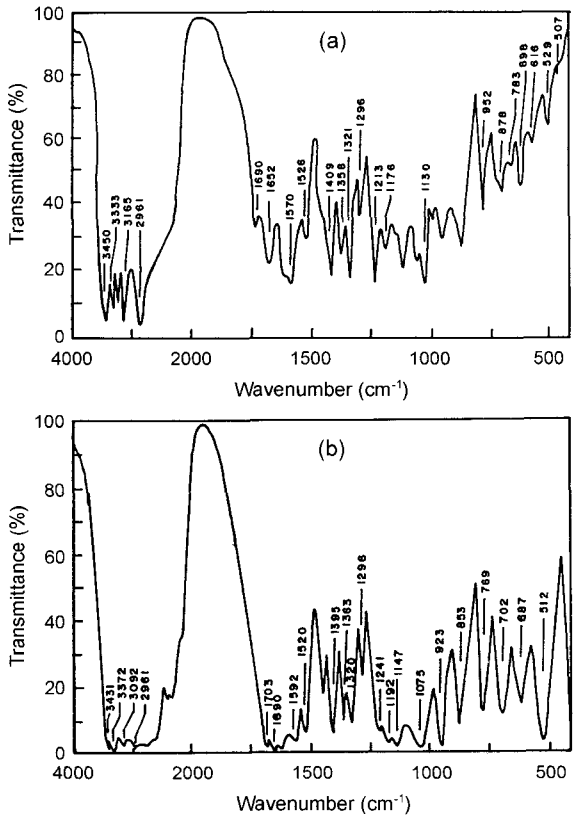

Fig. 6. FTIR Spectra of (a) LAP and (b) EDTA added LAP crystals.

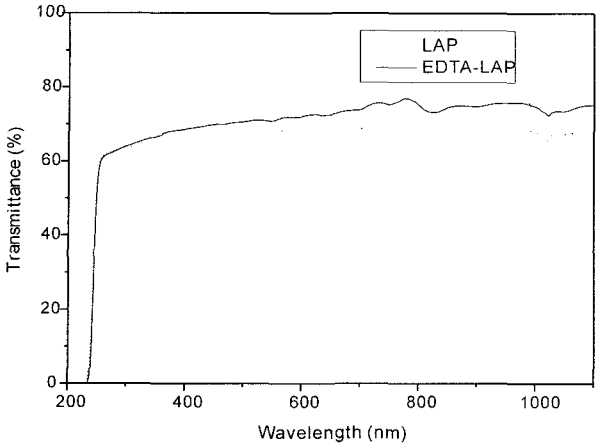

Fig. 7. Transmission spectra of pure and EDTA doped LAP crystals.

4. Conclusions

Effect of EDTA additive on the growth aspects of LAP crystals has been studied. The growth rate along the [100] direction is significantly increased by EDTA additive. EDTA suppresses the activity of the metal ion impurities present in the LAP solution by forming metal complex and hence the metastable zone width is increased. XRD and FTIR analyses confirm that the additive is not incorporated into the crystal lattice. EDTA additive is effective for the growth of bulk LAP crystals with higher transmittance.

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