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Nucleation, growth and characterization of L-tartaric acid—nicotinamide NLO crystals

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Abstract

The solubility, metastable zone width and nucleation parameters of organic nonlinear optical material L-tartaric acid–nicotinamide (LTN) have been determined. The crystals of LTN are grown by the slow cooling method. The grown crystals are morphologically interpreted. The crystalline powder of the grown crystals has been examined by X-ray diffraction and thermogravimetric analysis. The different modes of vibrations present in the crystal are identified by the Fourier infrared spectroscopy analysis. The powder SHG efficiency of LTN is comparable with that of KDP.

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1. Introduction

Because of the large nonlinearities and optical threshold of organic materials, a wide range of such materials has been found by many researchers. In general, most of the organic molecules designed for nonlinear optical (NLO) applications are the derivatives of an aromatic system substituted with donor and acceptor substituents [1–3]. On the search of new NLO materials with better mechanical properties, many researchers have focused on the small organic molecules having a large dipole moment and a chiral structure. These molecules are usually linked through the hydrogen bond [4]. L-Tartaric acid–Nicotinamide (LTN, $C_{20}H_{26}N_4O_{15}$) was found to be a new NLO material recently [5]. It crystallizes in the monoclinic system with the space group $P2_1$. The transmission range (280–1900 nm) and intense SHG signals from the crystal being better than KDP were reported [5]. However, its detailed

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crystal growth informations are not adequate. From the crystal growth point of view, the stability of the solution is related to the metastable zone width, and the higher the zone width greater will be the stability [6]. Therefore, the measurement of metastable zone width is inevitable.

Furthermore, there is no report on the nucleation kinetics of LTN as well. Indeed, the growth of large size crystals for device applications requires a better knowledge on the nucleation parameters. In the present investigation, the metastable zone width and the nucleation parameters such as the radius of critical nucleus and critical free energy change were evaluated numerically for aqueous LTN solutions with different supersaturations. Some characterizations like X-ray powder diffraction, Fourier transform infrared spectroscopy (FTIR), thermogravimetric (TG) analyses and powder SHG measurement were carried out.

2. Experimental

2.1. Synthesis

The starting materials L-tartaric acid (AR grad) and nicotinamide were commercially available (Aldrich). The required amount of nicotinamide was dissolved in excess of deionized water (resistivity of 18.2 MΩ-cm). The stoichiometric amount of L-tartaric acid was slowly added into the aqueous nicotinamide solution. The prepared solution was allowed to evaporate the excess water at a temperature of 50 °C for getting the dried salt of LTN. The synthesized material was further purified by repeated recrystallization. The deionized water with 18.2 MΩ-cm was also used as a solvent for nucleation experiments and crystal growth.

2.2. Nucleation

The nucleation experiments were carried out in a constant temperature bath with a control accuracy of ±0.01 °C provided with a cryostat for cooling below room temperature. Saturated LTN solution (100 ml) was used in all the experiments. Several trials were carried out to arrive at the optimized conditions. To measure the metastable zone width, the conventional poly thermal method was employed [7,8]. In this method, the equilibrium-saturated solution was cooled from overheated temperature under stirred condition till a first visible crystal was observed. Since the time taken for the formation of a visible crystal after the attainment of a critical nucleus is very small, the first crystal observed may be taken as the critical nucleus. In order to find the induction period for the LTN solution in different supersaturations, the conventional isothermal method was used. Here the saturated solution was cooled to the desired temperature and maintained at that temperature (30 °C) and the time taken for the formation of the first crystal was measured, which gave the induction period for a selected supersaturation.

2.3. Crystal growth

The solubility of LTN was estimated for the solvents of water, pure methanol, pure ethanol, methanol (50%) with water (50%), and ethanol (50%) with water (50%) by the gravimetric method. For the growth of LTN crystals, a known amount of LTN salt was saturated in 100 ml of water at 33 °C. A spontaneously grown good quality seed crystal was used to initiate the growth under the stoichiometric pH of 2.72. The solution temperature (33 °C) was then reduced initially by 0.2 °C per day in a constant temperature bath for two weeks.

2.4. Characterizations

X-ray diffraction was recorded for powdered LTN in the range of 20–60° where the monochromatic wavelength 1.5418 Å (CuK_α) was used. To find the thermal characteristics of LTN, TG and DTG analyses were carried out in the temperature range from ambient to 600 °C with a heating rate of 10 °C/min. The weight of the sample used in this study was 8.41 mg. For the spectroscopic study, FTIR spectrum was recorded in the range of 400–4400 cm^{-1} using the KBr pellet technique.

3. Results and discussion

3.1. Nucleation kinetics of LTN crystals

To calculate the interfacial tension, energy of formation and critical radius of the nuclei, the following theoretical consideration can be used [9]. The kinetics of nucleation depends on the thermodynamic driving force, which in turn depends on the supersaturation, temperature and impurities present in the system. The induction period, a measure of the nucleation rate, is determined experimentally for LTN solution at different supersaturations. Though experiments are conducted under controlled conditions, crystal nucleation normally occurs earlier than expected, there being a less time lag than the theory would predict under the same conditions. According to the classical theory of homogeneous formation of spherical nucleus

$$\ln \tau = -\ln B + 16\pi\gamma^3 V^2 N_A / 3R^3 T^3 (\ln S)^2, \tag{1}$$

where V is the molar crystal volume, N_A is Avogadro's number, R is the gas constant and S is the relative supersaturation ($S = C/C^*$), where C is the actual concentration and C^* is the equilibrium concentration. The function, $\ln B$; weakly depends on temperature and hence there is a linear dependence between $\ln \tau$ and $(\ln S)^{-2}$ at constant temperature. The above equation suggests that a straight line for $\ln \tau$ and $(\ln S)^{-2}$ with the slope given by

$$m = 16\pi\gamma^3 V^2 N_A / 3R^3 T^3. \tag{2}$$

The interfacial tension of the solid relative to this solution has been calculated from the slope of the line as

$$\gamma = RT[3m/16\pi V^2 N_A]^{1/3}. \tag{3}$$

The energy of formation of a critical nucleus has been evaluated from the experimental data as

$$\Delta G = RTm/(\ln S)^2. \tag{4}$$

The radius of the nucleus in equilibrium with its solution has been computed as

$$r = 2\gamma V / RT \ln S. \tag{5}$$

The solubility diagrams for methanol, ethanol, methanol (50%) with water (50%) and ethanol (50%) with water (50%) at different temperatures of 30, 35, 40, 45 and 50 °C are shown in Fig. 1. LTN possesses positive solubility coefficient in the solvents since its solubility increases with the temperature. The solubility of LTN in water is higher than that in methanol and ethanol and their mixed solvents. The difference in strengths of polarity of the solvents and the interactions of solute–solute and solute–solvent are the reasonable parameters for the difference in solubilities.

The value of the metstable zone width depends not only on the temperature but also on the type of the crystal and its physicochemical properties [10]. The metastable zone width of LTN aqueous solution as a function of temperature is shown in Fig. 2. It is found that the width of the solutions decreases with increase of temperature. The metastable zone width of LTN solution was about 7.92 °C at lower temperature and 5.50 °C at the higher temperature.

The crucial parameter involved in between a growing crystal and the surrounding mother liquor is the interfacial tension. This complex parameter has been determined by conducting the nucleation experiments on the stirred saturated solution of LTN. The interfacial tension (γ) was obtained from the slope value of $\ln \tau$ and $(\ln S)^{-2}$ curve

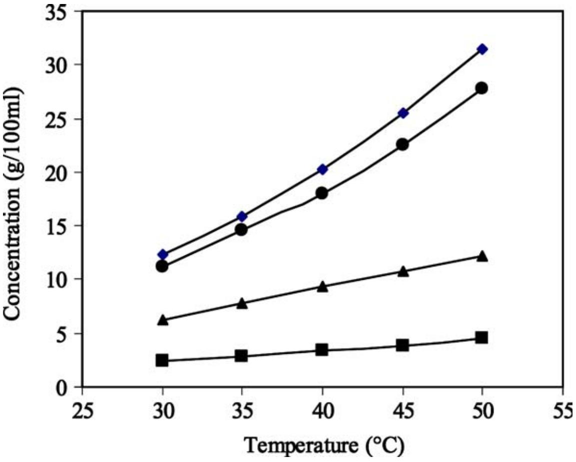

Fig. 1. Solubility curves of LTN in different solvents. ◆—methanol, ●—ethanol, ▲—methanol + water(1:1), ■—ethanol + water(1:1)

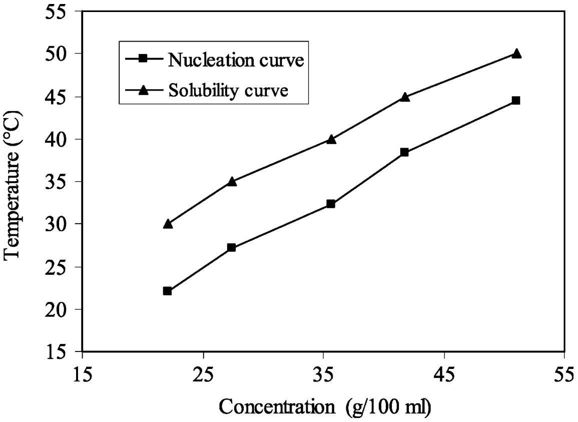

Fig. 2. Metastable zone width of LTN at different temperatures in the aqueous solution.

using Eq. (3) and it was estimated as 1.28 mJ/m^2 for LTN. To study the effect of supersaturation, induction period experiments were conducted for various supersaturations at a particular temperature (30 °C). It was observed that the induction period decreases with increase in supersaturation. The energy of formation (ΔG) and radius (r) of the critical nucleus were found to be 3.016 kJ/mol and 2.429 nm, respectively, at lower supersaturation level.

3.2. Crystal growth

It is observed from the growth of LTN crystal that the growth rate along the b-axis was found to be much larger than that of a- and c-axes, which shows that the {0 0 1} habit faces grow predominantly. Also the growth was faster in the positive b-axis than the negative b-axis. The other planes (0 1 0), $(1\,0\,\bar{2})$ and their family planes were found in the grown crystals. During the growth of LTN crystals, some secondary nucleation originated from the nucleation steps at the edge of seed was formed parallel to the fast growth b-axis due to the impurity adsorption and more solute accumulated in the seeded area. In addition, the (0 0 1) was found to be cleavage plane. The LTN crystal is cut by a wet thread method. In this method, the crystal is fixed on a movable platform though which a wet thread is rolling so as to cut the crystal at a specific orientation. A good quality LTN single crystal is ground with zero grade silicon carbide (SiC) paper and then lapped with SiC powder and finally polished with fine grit alumina powder. The LTN crystal is shown in Fig. 3.

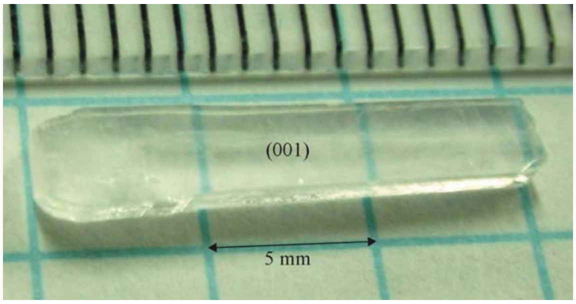

Fig. 3. Photograph of the polished LTN crystal (4 × 16 × 4 mm^3).

3.3. Characterizations

3.3.1. X-ray powder diffraction study

The X-ray powder diffraction pattern of LTN crystal is shown in Fig. 4. From the diffraction pattern of LTN, the lattice parameters were calculated by using 2θ values of the high intensity peaks corresponding to the hkl planes using the monoclinic crystallographic equation. The lattice parameter values of the crystal are shown in Table 1. The calculated lattice parameter values of LTN are consistent with the reported values [5].

3.3.2. Thermal analysis

From the thermogravimetric curve recorded from room temperature to 600 °C for LTN, it is found that the LTN is stable at least up to 140.78 °C. The weight loss was about 0.2144% and is due to the water molecule in LTN. At 201.16 °C, the material lost its weight by 2.638%. Above this temperature, the material lost its weight abruptly due to the decomposition of amino molecules associated with LTN. The material was fully decomposed at about 250 °C and finally LTN becomes volatile in nature.

3.3.3. FTIR spectroscopic analysis and powder SHG measurement

The FTIR spectrum of LTN was recorded in the region 400 and 4400 cm^{-1} as shown in Fig. 5. The

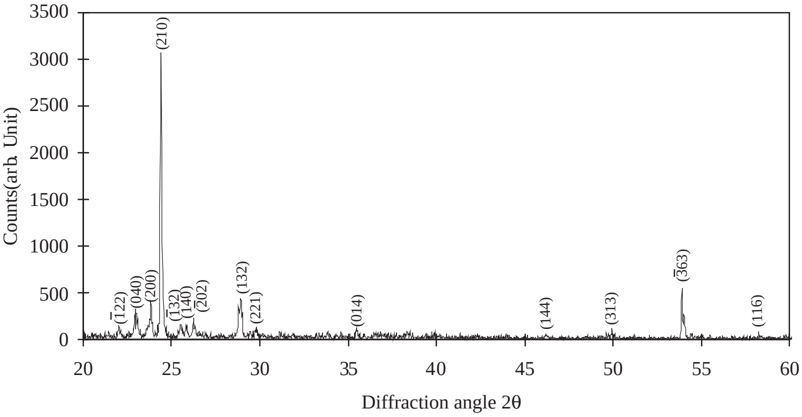

Fig. 4. X-ray powder diffraction pattern of LTN.

Table 1
Lattice parameters of LTN

Lattice parameters	Present study (Å)	Previous study (Å) [5]
a	7.650	7.654
b	15.499	15.498
c	10.489	10.506

fundamental modes have been qualitatively assigned. The bands observed in the region arise from the vibration of protons in the hydrogen bonds, the internal vibration of the nicotinamide cation, and the vibration of L-tartaric acid anions. Many bonds of the title material are changed from their position from the nicotinamide molecule due to self association with intermolecular interactions through hydrogen bonds. Nicotinamide takes up a proton through its ring nitrogen from L-tartaric acid. The title material consists of molecules of nicotinamide, tartaric acid and water. In the case of amide group, NH_2 symmetric stretching and NH_2 asymmetric stretching were observed at 3307 and 3277 cm^{-1}, respectively. The group C–O was assigned to 1641 cm^{-1}. In the case of tartaric acid, the bands corresponding to symmetric stretching type of vibration of COO^- group were observed at 1481, 1454 and 1357 cm^{-1}. The asymmetric stretching vibration frequencies of ionized carboxylic group of tartaric acid were attributed to 1641, 1579 and 1564 cm^{-1}. The frequencies of the protonated amino group were observed between 3307 and 3188 cm^{-1}. For water molecules, the frequencies of normal modes are 3730, 1595 and 3756 cm^{-1} according to Herzberg [11]. In the case of LTN, the symmetric and asymmetric stretching of water give rise to absorption bands at 3487 and 3730 cm^{-1}, respectively.

In order to find out the powder second harmonic efficiency, Kurtz and Perry powder technique was used [12]. The wavelength of 1064 nm, 40 ns laser pulses with spot radius of 1 mm emitted from *Q*-switched Nd^{3+}: YAG laser (Model: DCR-3G SPECTRAPHYSICS) was used as fundamental and it was converted into the output wavelength of 533 nm by sandwiched LTN crystalline powder between the quartz slides. The SHG developed by this crystalline powder was confirmed from the emission of the green light as output. It is observed that the powder SHG efficiency of LTN is 1.3 times larger than that of KDP used as a reference.

4. Conclusion

In this study, the solubility of LTN in different temperatures for various solvents was found out. Among theses solvents, water was found to be a good solvent for crystal growth. The metastable zone width of an aqueous LTN solution was found for different temperatures. According to the classical theory of homogeneous formation of spherical nucleus, the nucleation parameters were calculated. The interfacial tension of LTN was

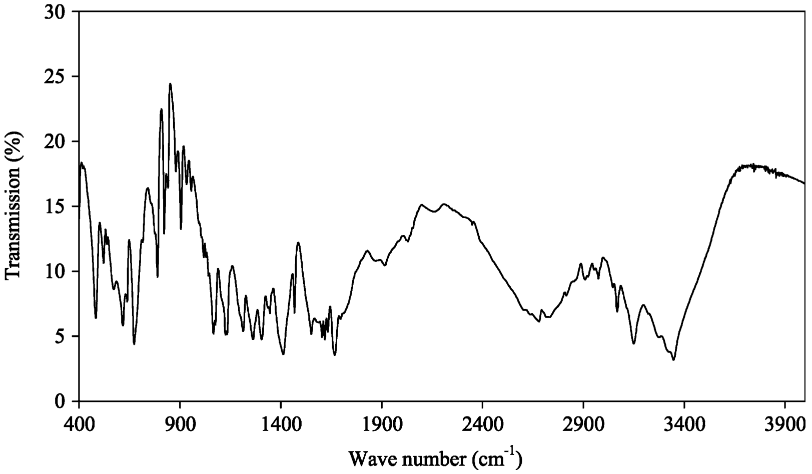

Fig. 5. FTIR spectrum of LTN.

estimated as 1.28 mJ/m^2. The Gibb's free energy and the critical radius of LTN were also determined. LTN crystals were grown by the slow cooling method from an aqueous solution. From the X-ray powder diffraction study, the lattice parameters were determined using the simulated *hkl* and experimentally observed '*d*' values. From the TG curve, the weight loss of the material during heating was obtained. Finally, the different modes of vibrations and their frequencies were assigned qualitatively from the FTIR spectrum. The powder SHG efficiency of LTN was comparable with that of KDP.

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