Bulk Growth, Nucleation Kinetics, Optical and Spectral studies of Organic Nonlinear Material: 4-Chloroaniline (pCA) Single Crystal

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Abstract

Organic nonlinear optical material 4-chloroaniline (pCA) single crystal was grown by slow cooling method. The material solubility was determined by gravimetric analysis and the metastable zonewidth was measured at various temperatures. Induction period values were evaluated for different supersaturation ratio at different temperatures. The interfacial energies were calculated by experimentally determined induction period values. The energy results were theoretically compared with the experimental values derived from the solubility data. The nucleation parameters such as gibb's free energy change, radius of the critical nuclei, number of molecules present in the nuclei and also nucleation rate were calculated. The unit cell parameters were determined by the X-ray diffraction analysis. pCA crystal transmission property was analyzed by UV-Vis-NIR spectrum. The various vibrational modes of different functional groups were identified and their wavenumbers were assigned from FT-Raman spectrum analysis. The nonlinear optical property of the grown crystal was measured by using Q-Switched Nd: YAG laser and the efficiency was compared to that of standard KDP.

Keywords: Single crystal, slow cooling, solubility, metastable zonewidth, nonlinear.

Introduction

Recently, organic nonlinear optical crystals are more attractive owing to their potentially high nonlinearities and rapid response in the electro-optic effect for various applications such as optical switching, frequency conversion, optical signal processing and electro-optical modulation compared to inorganic NLO crystals [**1**]. 4-chloroaniline is an organochlorine compound with molecular formula $C_6H_4NH_2Cl$. It is utilized as an intermediate in the industrial synthesis of pesticides, pigments and azo-dyes, as well as for the production of pharmaceuticals and cosmetic products [**2**]. Structural, spectral and quantum chemical studies of 4-Chloroanilinium perchlorate single crystal were studied [**3**]. Recently synthesis, growth and characterization studies of organic nonlinear optical material 4-chloroaniline single crystal were reported [**4**]. To the best of our knowledge, there are no reports available in the bulk growth part of pCA. Hence, in this paper we have reported the bulk growth, nucleation kinetics, optical and spectral characterization of pCA.

Methodology

Slow cooling method

To grow the bulk crystal, the supersaturated solution of pCA was kept in a constant temperature bath (CTB) at 38°C. The seed crystal of pCA was grown by the slow evaporation method. The seed crystal was suspended with the help of a nylon thread into the saturated solution. The temperature was reduced by 0.02°C/day. The single crystal of pCA was obtained after the growth period of 20 days. The harvested crystal is shown in **Fig. 1**.

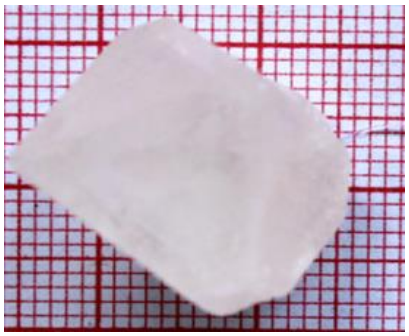

Fig. 1. Grown crystal of pCA.

Nucleation kinectics

Solubility, metastable zonewidth, induction period

The solubility is one of the essential parameters, which adopts the growth method and rate of the growth of crystals. The solubility of pCA was estimated at 30ºC, 32ºC, 34ºC, 36ºC and 38ºC by dissolving the solute in 20 ml of methanol in air-tight container maintained at a respective constant temperature with continuous stirring. After achievement of the supersaturation, using gravimetric analysis the equilibrium concentration of

the solute was measured [**5**]. The concentration versus temperature curve was plotted and it is observed that as the increase of temperature, increases the solubility of a pCA. It shows that pCA exhibits positive temperature coefficient (**Fig. 2**).

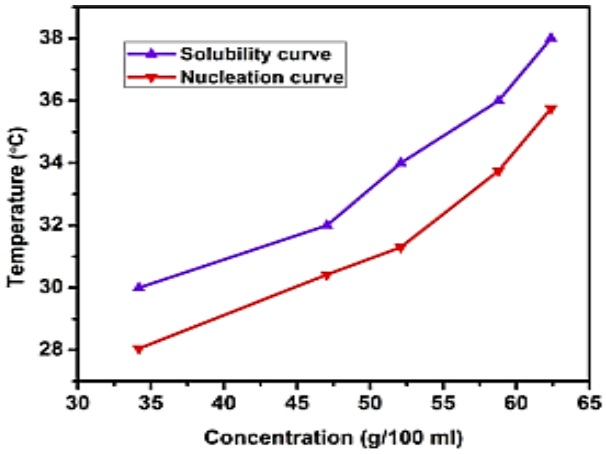

Fig. 2. Solubility & MSZW of pCA.

The polythermal method was used to measure the metastable zonewidth [**6**]. Based on the solubility data, the saturated solution of pCA was prepared in which a constant volume of 20 ml of solution was taken in a beaker. The solution contained in a beaker was kept in an optically heated crystallizer at the saturation temperature. The solution was preheated above the saturated temperature for homogenization. It was continuously stirred to ensure homogeneous solute concentration in the entire volume of the solution. After achievement of equilibrium state, the solution was cooled from the overheated temperature until the observation of first nuclei.The temperature of the first detectable size of the nuclei becomes visible is noticed by using condensing lens. The first detectable size of the nuclei is considered as critical nucleus.The difference between the saturation temperature and nucleation temperature is taken to be metastable zonewidth for the pCA (**Fig. 2**).

The induction period was assessed by isothermal method [**7**]. The induction period is defined as time interval taken for the formation of the critical nucleus. **Fig. 3** shows that the induction period as a function of the supersaturation. It is observed that the induction period decreases exponentially with increasing the supersaturation which provides that the nucleation rate increases exponentially. During that period, the formation of critical nuclei will be increased which will lead to spurious nucleation. In the present investigation, interfacial energy have been calculated on the basis of the classical theory of homogeneous nucleation [**8**].

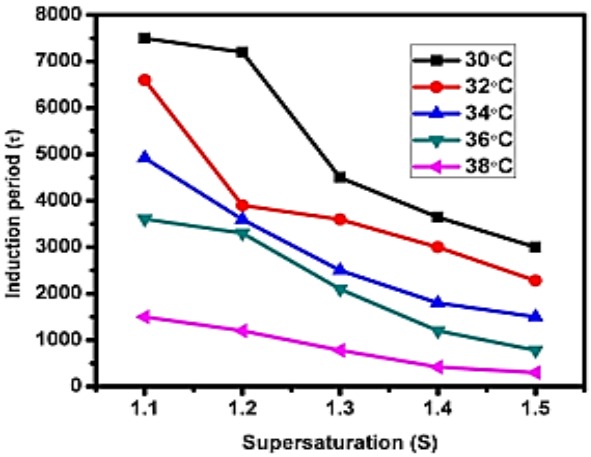

Fig. 3. Induction period of pCA.

The various nucleation parameters such as change in critical free energy of the nucleus (ΔG*), radius of critical nuclei (r*), nucleation rate (J) and the number of molecules present in critical nuclei (i*) have been computed using the interfacial tension values. The radius of critical nuclei decreases with increase in supersaturation and temperature [**9**]. **Table 1** represents the various nucleation parameters were calculated.

Table 1. Nucleation parameters of pCA.

T(°C)	γ (10^{-4}J m^{-2})	S	τ (s)	$\Delta G_v \times 10^6$ J/m^3	$\Delta G^* \times 10^{-21}$ (J)	r*(Å)	$J \times 10^{28}$ (nuclei/s/V)	i*
		1.1	7500	-0.6755	13.8619	21.4004	3.6384	69.5475
		1.2	7200	-1.2925	3.7864	11.1845	40.4501	9.9280
30	0.7228	1.3	4500	-1.8956	1.8290	7.7737	64.5842	3.3334
		1.4	3645	-2.3850	1.1119	6.0612	76.6592	1.5801
		1.5	3000	-2.8742	0.7656	5.0295	83.2768	0.9027
		1.1	6600	-0.6800	25.0402	26.0058	0.2614	124.8035
		1.2	3900	-1.3010	6.8407	13.5926	19.7010	17.8206
32	0.8842	1.3	3600	-1.8720	3.3041	9.4465	45.6302	5.9817
		1.4	3000	-2.4008	2.0088	7.3658	62.0642	2.8358
		1.5	2280	-2.8932	1.3832	6.1122	72.0074	1.6203
		1.1	4920	-0.6845	30.8552	27.8188	0.0689	152.7677
		1.2	3600	-1.3094	8.4314	14.5425	13.6804	21.8239
34	0.9521	1.3	2500	-1.8842	4.0717	10.1061	38.2663	7.3243
		1.4	1800	-2.4166	2.4753	7.8796	55.7663	3.4715
		1.5	1500	-2.9122	1.7045	6.5386	66.8913	1.9836
		1.1	3608	-0.6889	46.1530	31.7317	0.0020	226.7234
		1.2	3300	-1.3181	12.6055	16.5844	5.2089	32.3679
36	1.0930	1.3	2100	-1.8964	6.0894	11.5271	23.9931	10.8686
		1.4	1200	-2.4323	3.7017	8.9873	41.9916	5.1511
		1.5	780	-2.9311	2.5790	7.4577	55.0185	2.9432
		1.1	1500	-0.6933	51.4351	32.8458	0.0006	251.4524
		1.2	1200	-1.3266	14.0468	17.1656	3.7949	35.8916
38	1.1386	1.3	780	-1.9088	6.7846	11.9300	20.5954	12.0486
		1.4	420	-2.4474	4.1270	9.3045	38.2441	5.7160
		1.5	300	-2.9501	2.8403	7.7190	51.6076	3.2636

Results

Single crystal XRD analysis

The cell parameters attained by single crystal X-ray diffraction analysis are a = 7.38 Å, b = 8.64 Å, c = 9.24 Å, α = β = γ = 90°. It belongs to the orthorhombic crystal system with space group $Pb2_1$ and V = 590 $Å^3$. The calculated parameter values are in good agreement with the reported values [**10**].

UV-Vis-NIR studies

The UV-Vis-NIR transmission spectrum was carried for the crystal between the wavelength range of 200 nm and 1200 nm using SHIMADZU 1061 UV-VIS-NIR SPECTROPHOTOMETER.The pCA crystal has a cut-off wavelength of 325 nm (**Fig. 4**) which indicates that it can be employed for NLO applications over the entire visible and IR region.

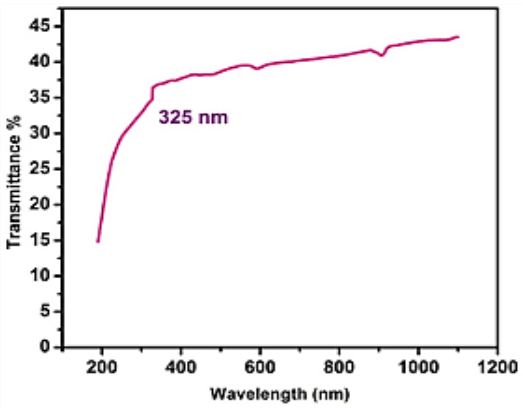

Fig. 4. Transmittance spectrum of pCA.

FT-Raman analysis

FT-Raman spectrum of pCA crystal was observed using the BRUKER RFS 27 spectrum between the regions of 4000 to 500 cm^{-1} at room temperature. **Fig. 5** shows the FT-Raman spectrum of pCA. The peak at 3382 cm^{-1} was due to N-H Stretching. C-H stretching appears at 3059 and 2976 cm^{-1}. The peak N-H in-plane bending occurs to 1608 cm^{-1}. The peaks represent the aromatic C-H stretching at 1087 and 1006 cm^{-1}. The p-disubstituted benzenes normally occurred at 800–860 cm^{-1}. In the present investigation the peak occurs at 815 cm^{-1}. C-Cl stretching shows that 632 cm^{-1} [**11**].

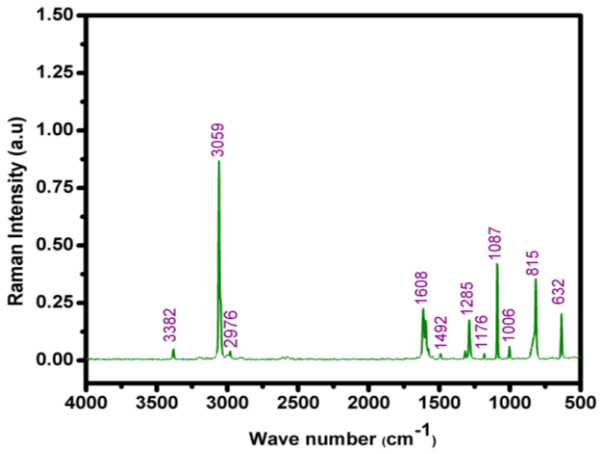

Fig. 5. FT-Raman spectrum of pCA.

SHG test

The SHG conversion efficiency was measured by Kurtz and Perry powder technique [**12**]. The fine powder of pCA was filled between two glass plates and the laser beam of wavelength 1064 nm with 10 ns pulse width was allowed to incident on it. The green light emission at the wavelength of 532 nm was detected by the photomultiplier tube. This confirms that the frequency of output light was double that of the incident light.

Conclusion

An organic single crystal of pCA was successfully grown into a bulk single crystal by slow cooling method by optimizing the growth parameters. Solubility of pCA increases with increase in temperature, thus pCA possess positive temperature co-efficient. The metastable zonewidth of the pCA has narrow zonewidth and it determines minimum growth period to achieve the bulk growth of the single crystal. The induction period decreases with the increase of supersaturation ratio. The interfacial energy has been experimentally determined by induction period values. The change in critical Gibb's free energy of the nucleus(ΔG^*), radius of the critical nuclei (r^*), number of molecules present in the critical nuclei (i^*) and nucleation rate (J) were experimentally determined by using classical homogeneous nucleation theory. Single crystal XRD analysis provides the cell parameter values, confirming the fact that the structure of the grown crystal belongs to orthorhombic crystal system. The optical properties reveals that pCA possess a cut-off wavelength in visible region around 325 nm. The various functional groups were present in the compound was identified by FT-Raman spectral analysis. The SHG efficiency is greater than that of KDP.

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