

## Supporting Information

### Nucleation Kinetics, Growth, Mechanical, Thermal and Optical characterization of Sulphamic Acid single crystal<sup>†</sup>

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#### 1. Nucleation theory and details for calculation of thermodynamical parameters:

Nucleation process is an important phenomenon in case of liquid–solid phase transition. According to the classical theory of homogeneous nucleation<sup>1-3</sup> nucleation parameters (interfacial tension ( $\sigma$ ), free energy of formation ( $\Delta G$ ) of the critical nucleus and radius of the nucleus ( $r$ ) in equilibrium with its solution) can be calculated using the induction period. According to this theory the sum of the surface excess free energy ( $\Delta G_s$ ) and the volume excess free energy ( $\Delta G_v$ )<sup>4</sup> gives the overall excess Gibbs free energy ( $\Delta G$ ) between an embryo and solute in the solution, and is given by

$$\Delta G = \Delta G_s + \Delta G_v \quad (1)$$

where  $\Delta G_v$  is given as

$$\Delta G_v = -kT(\ln S)/v \quad (2)$$

The free energy required to form a spherical nucleus is given by

$$\Delta G = 4\pi r^2 \sigma + 4/3\pi r^3 \Delta G_v \quad (3)$$

The formation of clusters (with mean radius,  $r$ ) of solute molecules starts when it reaches a critical size ( $r = r_c$ ).<sup>5</sup> After this stage, ( $r > r_c$ ), the cluster becomes visible and is termed as nucleus, which eventually grows into crystal. If ( $r < r_c$ ), the cluster dissolves and does not yield to a crystal. At the critical state, the free energy of formation obeys the condition  $d(\Delta G)/dr = 0$ . Hence the radius of the critical nucleus is expressed as

$$r_c = -2\sigma / \Delta G_v \quad \text{or} \quad r_c = 2\sigma v / kT \ln S \quad (4)$$

The interfacial tension has been calculated using the experimentally measured induction period values by the relation

$$\ln \tau = -\ln B + 16\pi\sigma^3 v^2 N / 3R^3 T^3 (\ln S)^2 \quad (5)$$

The function  $\ln B$  weakly depends on temperature and hence there is a linear dependence between  $\ln \tau$  and  $(\ln S)^2$ . Bennema and Sohnel<sup>6-7</sup> have derived the expression for the linear dependence of interfacial tension ( $\sigma$ ) with respect to solubility is given by

$$\sigma = kT/a_0^2 (0.174 - 0.248 \ln(S)) \quad (6)$$

The critical free energy barrier is

$$\Delta G_c = 16\pi\sigma^3 / 3(\Delta G_v)^2 \quad (7)$$

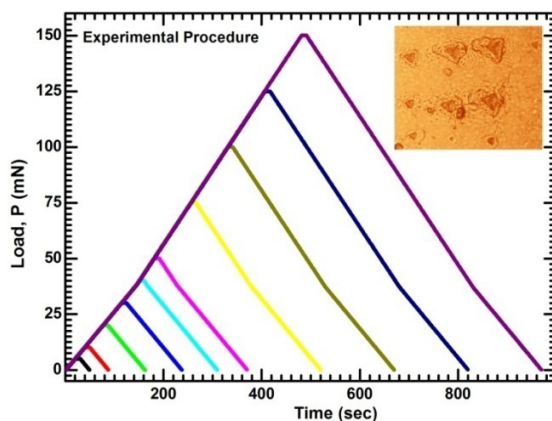
where  $v$  is the molar volume,  $R$  is the gas constant,  $\sigma$  is the interfacial tension,  $K$  is the Boltzmann's constant,  $T$  is Saturation temperature in Kelvin,  $a_0$  is the inter atomic distance,  $S$  is the supersaturation ( $S = C/C^*$ ) where  $C$  is actual concentration and  $C^*$  is the equilibrium concentration.

The interfacial tension ( $\sigma$ ), volume free energy ( $\Delta G_v$ ), critical free energy ( $\Delta G_c$ ), and radius of the critical nucleus ( $r_c$ ) of SA were calculated at different supersaturation ratios and the details of which are included in Table 1.

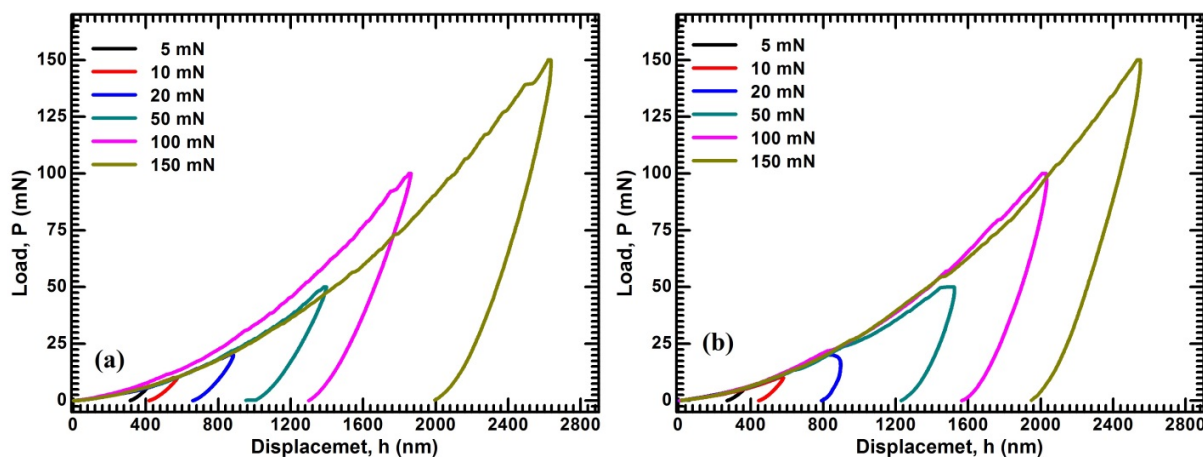
Saturation temperature (°C)	$S = C / C^*$	$(\sigma) * 10^{-4}$ (in $Jm^{-2}$ )	$\Delta G_v * 10^6$ (in $Jm^{-3}$ )	$(\Delta G^*) * 10^{-23}$ (in J)	$(r^*)$ (in nm)
<b>40</b>	1.1	3.008	-5.4847	1.512	0.1095
	1.2	2.586	- 10.4895	0.2627	0.0492
	1.3	2.198	- 15.0985	0.0779	0.029
	1.4	1.839	- 19.3622	0.0277	0.0189
<b>45</b>	1.1	3.056	- 5.5729	1.536	0.1095
	1.2	2.627	- 10.6582	0.2669	0.0492
	1.3	2.233	- 15.34032	0.0791	0.0290
	1.4	1.868	- 19.6735	0.0281	0.0189
<b>50</b>	1.1	3.104	- 5.6525	1.560	0.1095
	1.2	2.669	- 10.8269	0.2711	0.0492
	1.3	2.269	- 15.5815	0.0804	0.0290
	1.4	1.898	- 19.9840	0.0286	0.0189
<b>55</b>	1.1	3.152	-5.7400	1.585	0.1095
	1.2	2.710	-10.9945	0.0275	0.0492
	1.3	2.304	-15.8227	0.0816	0.0290
	1.4	1.927	-20.2933	0.0290	0.0189

**Table 1:** Interfacial tension ( $\sigma$ ), Volume free energy ( $\Delta G_v$ ), Critical free energy ( $\Delta G_c$ ) and Critical radius ( $r_c$ ).

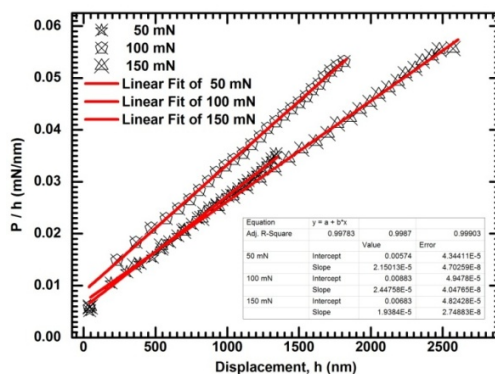
## 2. Details of Nanoindentation measurement and calculations:



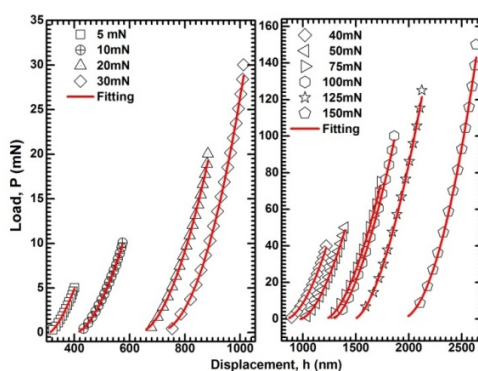
**Fig.1.** The load time sequence used in the experimental procedure with loading and unloading rate as 20.00 mN/min and a dwell time of 10 s at each peak load (Inset to figure shows optical image of a typical imprint made by berkovich nanoindenter on the sulphamic acid crystal)



**Fig.2.** A Typical load-displacement curve on the sulphamic acid crystal (a) along (100) and (b) along (011).



**Fig. 3.** The experimental data in the loading segments of the load displacement curves from Fig.1 were re-plotted in a P/h versus h scale.



**Fig. 4.** The experimental data in the unloading segments of the load displacement curves from Fig.2 were fitted with power equation.

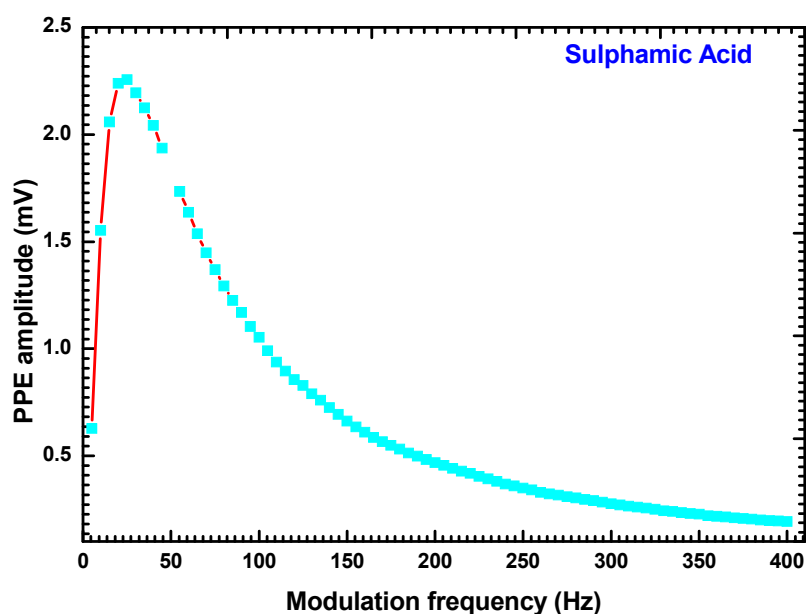
Load	A		m		$h_f$		Statistics	
	Value	Error	Value	Error	Value	Error	Reduced $\chi^2$	Adj. R-Square
5 mN	6.49E-03	2.72E-04	1.47	8.20E-03	309.02	0.31	7.96E-04	0.9996
10 mN	2.05E-03	1.07E-04	1.65	8.97E-03	406.06	0.60	2.91E-03	0.9997
20 mN	7.02E-04	8.66E-05	1.85	1.95E-02	631.59	1.88	3.61E-02	0.9989
30 mN	1.18E-04	1.96E-05	2.15	2.50E-02	694.13	2.84	7.33E-02	0.999
40 mN	1.14E-03	8.70E-05	1.75	1.13E-02	836.04	1.69	6.61E-02	0.9995
50 mN	1.78E-03	1.07E-04	1.69	8.82E-03	972.77	1.47	7.43E-02	0.9996
75 mN	1.51E-03	7.70E-05	1.72	7.22E-03	1206	1.49	1.13E-01	0.9998
100 mN	3.41E-03	1.29E-04	1.61	5.31E-03	1275.69	1.24	1.47E-01	0.9998
125 mN	2.32E-03	1.32E-04	1.68	7.82E-03	1478.52	1.99	4.14E-01	0.9997
150 mN	3.16E-04	4.71E-05	1.98	1.99E-02	1922.47	5.28	1.86E+00	0.9991

**Table 2:** Values obtained after non linear fitting of the experimental data (Fig.4) with power equation.

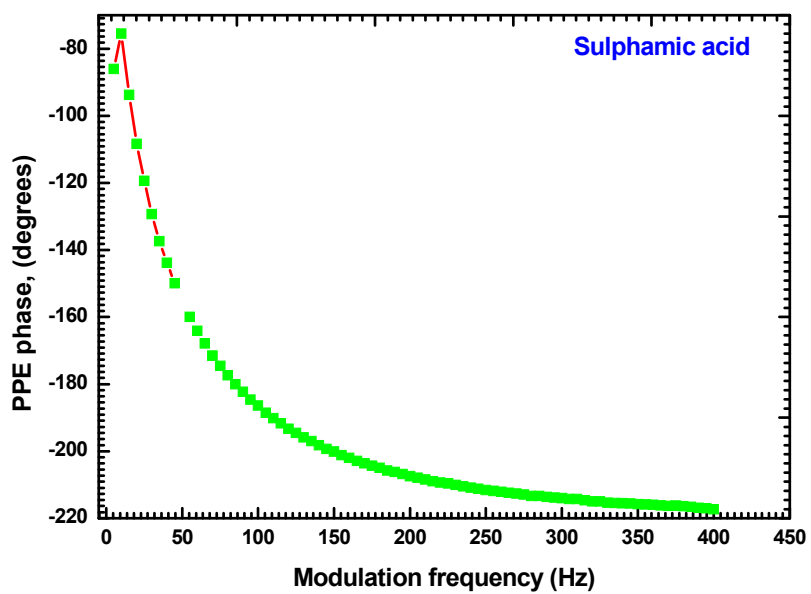
Peak load, $P_{\max}$ (mN)	Displacement, $h_{\max}$ (nm)	Initially unloading stiffness, $S$ ( $\text{mN} \times \text{nm}^{-1}$ )	Contact depth, $h_c$ (nm)	Hardness, $H$ (MPa)
5.033	399.880	0.079432	352.3584	1654.59
10.054	574.784	0.094821	495.2602	1673.04
20.056	882.866	0.142442	777.2649	1355.00
30.023	1012.274	0.191575	894.7362	1530.73
40.079	1219.231	0.172784	1045.261	1497.27
50.070	1396.351	0.195386	1204.154	1409.44
75.053	1732.566	0.236566	1494.62	1371.32
100.059	1863.000	0.268281	1583.277	1629.21
125.043	2124.024	0.317343	1828.5	1526.52
150.08	2635.615	0.391261	2347.93	1111.19

**Table 3:** Best-fit results for the unloading segments of measured load-displacement curves

### 3. Curves obtained from photopyroelectric (PPE) technique for calculation of thermal parameters



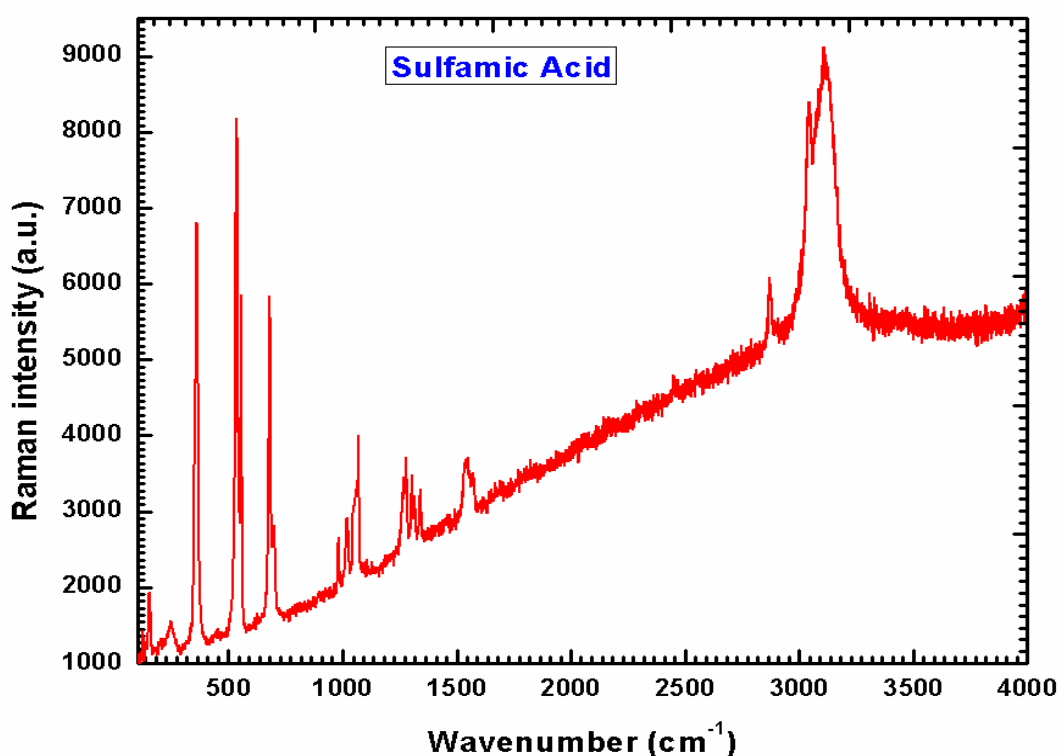
**Fig. 5a.** Frequency dependent PPE amplitude of SA single crystal.



**Fig. 5b.** Frequency dependent PPE phase of SA single crystal.

#### 4. FT-Raman Analysis

To confirm the formation of the functional groups of the compound, the FT-Raman spectrum of the grown SA single crystal was recorded in the wavelength ranging from 100-4000  $\text{cm}^{-1}$  using Renishaw inVia Raman microscope as shown in Fig. 20. The absorption peaks obtained at 3200  $\text{cm}^{-1}$  represents degenerated  $\text{NH}_3^+$  stretch, 3140 represents symmetric  $\text{NH}_3^+$  stretch, 1542  $\text{cm}^{-1}$  represents degenerated  $\text{NH}_3^+$  deformation, 1312  $\text{cm}^{-1}$  represents degenerated  $\text{SO}_3^-$  stretch, 1262  $\text{cm}^{-1}$  represents symmetric  $\text{SO}_3^-$  stretch, 1064  $\text{cm}^{-1}$  represents symmetric  $\text{SO}_3^-$  deformation, 1015 and 1000  $\text{cm}^{-1}$  represents degenerated  $\text{NH}_3^+$  rock, 682  $\text{cm}^{-1}$  representing N-S stretch, 540 and 526  $\text{cm}^{-1}$  represents degenerated  $\text{SO}_3^-$  deformation in FT-Raman spectra vibration in the grown single crystal.<sup>8</sup> The presence of these bands in the spectrum confirms the formation of SA single crystal.



**Fig.6.** FT-Raman spectrum of SA single crystal.



## References

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