Synthesis, Growth and Nucleation Kinetics of Potassium Hydrogen Oxalate Hydrate Single Crystal ($C_4H_3KO_8 2H_2O$) - A Third Order Nonlinear Material

Ajisha D.S[1], R. Ezhil Vizhi[2]*

Materials Research Laboratory, SAS, VIT, Vellore 632014, India

*Corresponding author: E-mail: rezhilvizhi@vit.ac.in

DOI: 10.5185/amp.2019.0001
www.vbripress.com/amp

Abstract

Slow evaporation method was used to develop the metal organic compound of potassium hydrogen oxalate hydrate. The crystal system and lattice constant of the developed compound were analyzed with the help of single crystal X-ray diffraction technique. For diverse temperature, the nucleation curve and solubility of the compound were calculated experimentally. The solubility curve showed that the compound exhibit a positive temperature gradient of solubility. Various parameters for growth kinetics such as free energy change, induction period, nucleation rate were evaluated experimentally. The semiconductor laser of wavelength 532 nm was utilized in the Z-scan method to determine different nonlinear parameters like third-order refractive index, susceptibility and absorption coefficient. Copyright © VBRI Press.

Keywords: Solubility, nucleation, Z-scan, nonlinear susceptibility, critical nucleus.

Introduction

The technology of today is changing rapidly due to the development of new materials. To a larger extent, this technological growth depends on the improvement of crystal growth techniques. For fundamental research and device fabrication, large crystals with structural flawlessness are necessary. Moreover, in device fabrication such as solid-state laser, transducer and also in computer industries, good quality crystals are highly essential [**1, 2**]. The selection of material in various field depends on its various physical properties such as laser damage threshold conversion efficiency, phase matching, transparency etc. [**3, 4**]. In inorganic NLO crystal, the hydrogen bonds often have dominant NLO contributions to overall nonlinearity [**5**]. Now researchers are more concentrated on the nonlinear material because of their extensive series of applications in the electronic and optical industry. Because of advanced properties of second and third order nonlinearity, these compounds are highly demanded in frequency conversion, optical limiting and optical switching [**6**].

Dicarboxylic acids and their metal complexes are very interesting because of their wide range of applications. Among this many of the oxalate compound exhibit good nonlinear properties [**7**]. The solution supersaturation, nucleation rate and other optimizing growth condition of growing good quality crystals were understanding with the help of nucleation kinetics. It provides essential data concerning the procedure of crystal growth and that can be utilized for the development of massive crystals [**8**]. In the present investigation, third-order nonlinear single crystal of potassium hydrogen oxalate hydrate (KHOH) was grown and its various nucleation parameters were calculated experimentally.

Experimental method

Potassium hydrogen oxalate hydrate single crystal was synthesized at room temperature by dissolving 1:1 stoichiometric ratio of oxalic acid and potassium hydroxide in Millipore water. For getting homogeneous solution it was constantly stirred for five to six hours and was transferred to Petri dish after filtering by means of Whatman filter paper. Without disturbing the solution, the Petri dish was enclosed with a polythene sheet to manage the evaporation rate of the solution and high-quality crystals were collected after 20 days as appeared in **Fig. 1**.

Fig. 1. KHOH single crystal.

Result and discussion

Single crystal X-ray diffraction

Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer was used for analyzing the structure of KHOH crystal. This analysis verified the material's triclinic crystal system with space group P-1. For the grown KHOH crystal the lattice constant were observed as a = 6.389Å, b = 7.055Å, c = 10.6 Å, α = 93.92°, = 101.51°, γ = 100.08° and 461 A^3 be the volume of the unit cell.

Solubility and metastable zone width

The solubility curve and metastable zone width are important for the successful development, optimization and improve the crystallization process. The solubility of the compound was measured with the assistance of steady temperature water bath for diverse temperatures beginning from 30°C up to 50°C. At a fastidious temperature, the solubility was measured by dissolving the required amount of finely powdered sample in 20 ml of water in a beaker with uninterrupted stirring. After achieving the supersaturation, the amount of solute was measured by gravimetric analysis. The material's solubility was increased with temperature expansion, indicating the positive temperature coefficient of solubility. The conventional polythermal method [**9**] was adopted for the analysis of the metastable zone width. As per the solubility information, saturated solution of 20 ml was synthesized at 30°C with constant stirring. After getting a homogenous solution it was cooled below the room temperature by switching on the condenser switch in the water bath. The first detectable size nuclei called critical nucleus was observed at 13°C, that was the nucleation temperature at 30°C. The similar method was used upto 50°C with a steep rise of 5°C. The dissimilarity in temperature between solubility and nucleation curve provides information about the metastable zone width of the grown crystal KHOH [**10**], represented in **Fig. 2**.

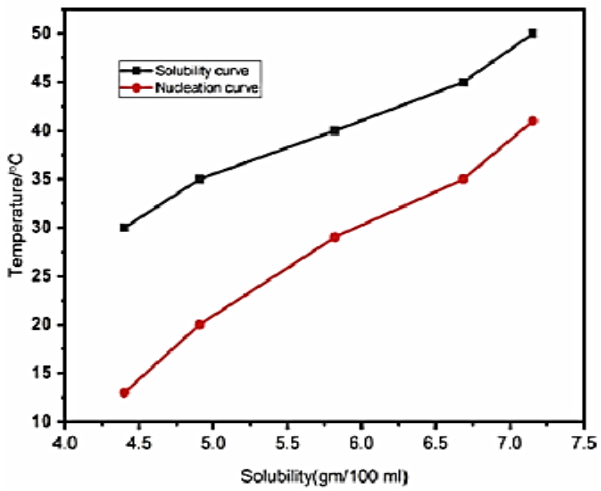

Fig. 2. KHOH- Metastable zone width.

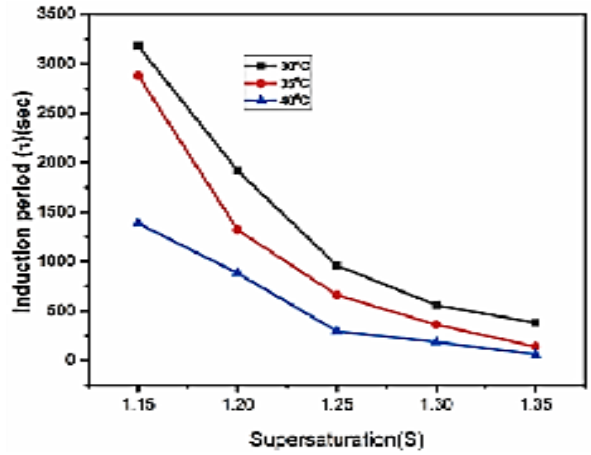

Fig. 3. KHOH-Induction period.

Nucleation kinetics

Nucleation kinetics plays a vital role in crystal growth. The various nucleation parameters were calculated based on the estimated time for the formation of first measurable spot of nuclei in the supersaturated solution termed as induction period [**11**], for various supersaturation level (S = 1.15, 1.2, 1.25, 1.3 and 1.35) and temperature between 30°C to 40°C with a interval of 5^0C. The deviation of induction period with temperature and supersaturation was shown in **Fig 3**. The graph revealed that the induction period diminishes with increment in temperature and supersaturation level due to the increase in the concentration of solute in the solvent. Standard equations [**12**] were used for calculating various parameters for growth kinetics like Gibb's free energy (ΔGV), radius of critical nuclei(r*), critical free energy change (ΔG*), no of molecules present in the critical nuclei (i*) and rate of nucleation and calculated values are mentioned in **Table 1**. Due to the variation in entropy and anisotropic nature of the crystalline solids, interfacial energy of KHOH crystal was increasing with the rise in temperature as shown in **Fig 4**. Experimentally calculated interfacial energy was analyzed with the theoretical values [**13**] and tabulated in **Table 2**. Both values are well matched with the method given by Sanwal *et al.*

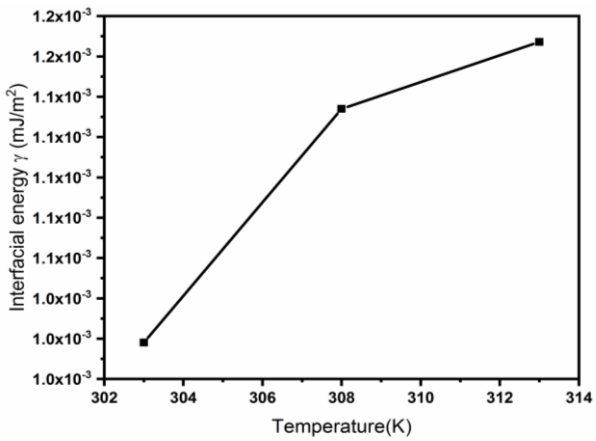

Fig. 4. Interfacial energy of KHOH.

Table 1. Various parameters for nucleation kinetics.

(K)	γ x10^{-4} [J/m^2]	S	τ (sec)	ΔGv x10^6 [J/m^3]	ΔG* x10^{-21} [J]	r* [Å]	Jx10^{28} [nuclei / s/V]	i*
303	1.02	1.15	3180	-1.27	10.99	16.05	7.24	37.58
		1.2	1920	-1.65	6.46	12.31	21.37	16.93
		1.25	960	-2.02	4.31	10.06	35.69	9.23
		1.3	560	-2.38	3.12	8.55	47.46	5.68
		1.35	380	-2.72	2.38	7.48	56.58	3.8
308	1.13	1.15	2880	-1.29	14.69	17.59	3.16	49.45
		1.2	1320	-1.68	8.63	13.49	13.13	22.27
		1.25	662	-2.06	5.76	11.02	25.78	12.15
		1.3	361	-2.42	4.17	9.37	37.51	7.47
		1.35	139	-2.77	3.19	8.19	47.26	4.99
313	1.17	1.15	1386	-1.31	15.52	17.82	2.76	51.38
		1.2	882	-1.71	9.12	13.66	12.12	23.15
		1.25	296	-2.09	6.09	11.16	24.45	12.62
		1.3	186	-2.46	4.4	9.49	36.1	7.77
		1.35	60	-2.81	3.37	8.30	45.9	5.19

Table 2. Interfacial energy values at various temperature.

Temperature (K)	Experimental value (Present work) [x10^{-3}J/m^2]	Theoretical value		
		Christoffersen [x10^{-3}J/m^2]	Nielson and Sohnel [x10^{-3}J/m^2]	Sangwal [x10^{-3} J/m^2]
303	1.018	0.255	0.301	1.015
308	1.113	0.259	0.306	1.032
313	1.167	0.263	0.311	1.048

Third-order nonlinear optical studies

Essential third order properties, for example, nonlinear refractive index (n_2), absorption coefficient ($\boldsymbol{\beta}$), susceptibility ($\chi^{(3)}$) of the material was precisely estimated by Z-scan method. Open and closed aperture experiments were used in the Z-scan method to analyze the above-mentioned material parameters [**14**]. The experiment was carried out with continuous laser of wavelength 532nm with the help of 103 mm focal length lens.1 mm thickness material was located along the axis of the Gaussian beam. The intensity of the transmitted beam was determined as a function of the sample location from –z to +z through the focus at z = 0. In the first part of the experiment the sample display greatest transmittance at the center (focus) that confirms the material's saturation absorption with positive absorption coefficient confirm the occurrence of multi photon assimilation in the material as shown in **Fig. 5(a)**. The maximum pre focal transmittance followed by minimum post focal transmittance in the second part of the experiment (closed aperture) represented in **Fig. 5(b)** demonstrates the sample's negative nonlinearity because of the self-defocusing effect [**15**]. This happens because of the local temperature variation of the refractive index. The standard equations [**16**] were utilized for computing various parameters of the higher order (third) nonlinearity. For KHOH crystal the calculated value of the nonlinear absorption coefficient was observed to be 4.68×10^{-4} cm/W and 1.47×10^{-10} cm^2/W be the refractive index. 1.31×10^{-5} esu be the measured susceptibility ($\chi^{(3)}$)of KHOH.

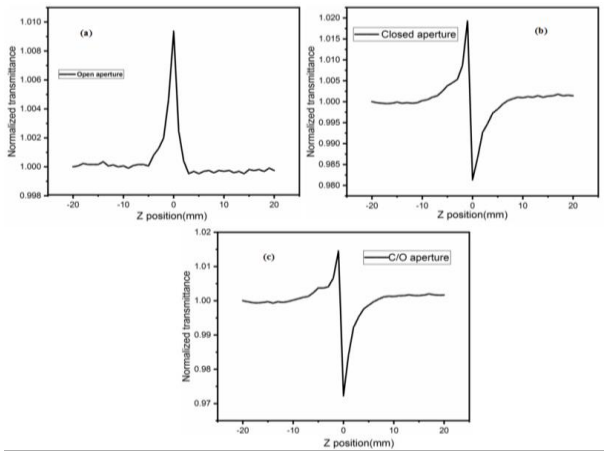

Fig. 5. (a) Open and (b) Closed aperture curve. (c) Closed and open aperture ratio.

Conclusion

Good quality potassium hydrogen oxalate hydrate single crystal was developed with the help of slow evaporation process. The triclinic crystal system of the material was confirmed with the help of single crystal X-ray diffraction. Solubility curve shows that KHOH crystal has a positive solubility gradient temperature. Induction period and nucleation temperature were determined experimentally which in turn used for measuring diverse parameters for the growth kinetics. The various nucleation parameters were calculated and tabulated. The induction period was noticed to decrease with increment in temperature and supersaturation level due to more solute concentration, however interfacial energy of KHOH increments with rising temperature. Various third order parameters were measured with the help of the Z-scan method. The negative nonlinearity of the compound confirms the application of the compound in various optoelectronic application.

Acknowledgments

Authors are grateful to VIT Vellore for the outstanding laboratory facility and Dr. G. Vinitha VIT Chennai for the measurement of third-order characteristics.

References

1. Yadav, H.; Sinha, N.; Kumar, B.; *Mater. Res. Bull.*, **2015**, *64*, 194.
2. Selvaraj, A.; Stalin, J.P.; Devarajan, P.A.; *Optik (Munich, Ger.)*, **2016**, *127*, 110.
3. Prasad, P.N.; Williams, D.J. (Eds.); Introduction to nonlinear optical effects in molecules and polymers. Wiley, New York, **1991**.
4. Senthil, A.; Ramasamy, P.; *J. Cryst. Growth*, **2010**, *312*, 276.
5. Xue, D.; Zhang, S.; *Chem. Phys. Lett.*, **1999**, 301, 449.

6. Bhat, H.L.; *Bull. Mater. Sci*., **1994**, *17*, 1233.
7. Chandran, S.; Paulraj, R.; Ramasamy, P.; *J. Cryst. Growth*, **2017**, *468*, 68.
8. Sun, G.H.; Zhang, G.H.; Wang, X.Q.; Sun, Z.H.; Xu, D.; *Mater. Chem. Phys.*, **2010**, *122*, 524.
9. Zaitseva, N.P.; Rashkovich, L.N.; Bogatyreva, S.V.; *J. Cryst. Growth*, **1995**, *148*, 276.
10. Nývlt, J.; Rychlý, R.; Gottfried, J.; Wurzelová, J.; *J. Cryst. Growth*, **1970**, *6*, 151.
11. N. Zhang.; M. Jiang, D.; Yuan, D.; Xu, X.; Tao, *Chin. Phys. Lett.*, **1989**, *6*, 280.
12. Krishnan, P.; Gayathri, K.; Sivakumar, N.; Gunasekaran, S.; Anbalagan, G.; *J. Cryst. Growth*, **2014**, *396*, 85
13. Vijayalakshmi, M.; Vizhi, R.E.; Babu, D.R.; *Cryst. Res. Technol.*, **2015**, *50*, 15.
14. Medhekar, S.; Kumar, R.; Mukherjee, S.; Choubey, R.K.; *AIP Conf. Proc.* **2013**, *1512*, 470.
15. Kalaiyarasi, S.; Zahid, I.M.; Devi, S.R; Kumar, R.M.; *J. Cryst. Growth*, **2017**, *460*, 105.
16. Bharathi, M.D.; Ahila, G.; Mohana, J.; Chakkaravarthi, G.; Anbalagan, G.; *Mater. Chem. Phys.*, **2017**, *192*, 215.

