

Scholars Research Library

Archives of Applied Science Research, 2016, 8 (11):12-18 (http://scholarsresearchlibrary.com/archive.html)



# Growth and characterization of succinic acid doped zinc sulphate single crystals

# T.Lidiaarockia Thai<sup>1</sup>, S Ajitha<sup>2</sup>, R Krishna Priya<sup>3</sup> and S Mary Delphine<sup>2</sup>

<sup>1</sup>Nanotechnology Research Facility, College of Engineering and Petroleum, Kuwait University, PO Box 5969, Safat 13060 Kuwait <sup>2</sup>Department of Physics, Holy Cross College, Nagercoil <sup>3</sup>Department of Physics, Pioneer Kumaraswamy college, Nagercoil

# ABSTRACT

Single crystals of pure and succinic acid doped zinc sulphate crystals were grown from aqueous solution using low temperature solution growth technique at room temperature. The grown crystals have been characterized by powder X-ray diffraction to confirm the crystalline nature of the crystals, UV-Vis-NIR spectra have been recorded in the wavelength range of 190-1100 nm. The Vicker's micro hardness measurements were carried out.

Keywords: Succinic acid, Zinc sulphate heptahydrate, X-ray diffraction, Vis-NIR spectra and Microhardness.

# **INTRODUCTION**

Semi-organic nonlinear optical (NLO) materials have excellent nonlinear and fluorescent properties. They are significantly used in tele communication, optical computing, optical data storage, light emitting diodes, optical information processing etc.[1,2]. Synthesizing inorganic heptahydrate sulphate crystals of the formula (RSO<sub>4</sub> 7H<sub>2</sub>O, R=Zn/Mg) have been of more interest due to a variety of applications in the fields of medicine, agriculture, etc. [3] They are orthorhombic in crystal structure and fall under the space group category of P2<sub>1</sub>P2<sub>1</sub>P2<sub>1</sub>. Due to the presence of several hydrogen bonds they have tetra molecular unit cell.Organic NLO crystals have high nonlinearity compared to inorganic crystals and possess higher second order and third order nonlinear coefficients, yet often have poor transparency, short optical band gap, laser damage threshold, thermal & mechanical properties[4-7]. To rectify this, a novel group of materials called semi-organic or metal-organic class of crystals are grown by solution growth technique by combining organic and inorganic molecules to form semi organic compounds which has the advantage of being grown easily into reasonably large crystals[8].In the present work, succinic acid (SA), (CH<sub>2</sub>)<sub>2</sub>(COOH)<sub>2</sub>,was doped in 0.01, 0.03, 0.05, 0.07 & 0.09 mol% concentrations with zinc sulphatehepta hydrate (ZSH), ZnSO<sub>4</sub>.7H<sub>2</sub>O.

## EXPERIMENTAL

# **Crystal growth**

Solutions were prepared in the appropriate proportions of 1:0.01, 1:0.03, 1:0.05, 1:0.07 and 1:0.09 mole concentrations of ZSH:SA using Sigma Aldrich chemicals namely,  $ZnSO_4$ .7H<sub>2</sub>O and  $(CH_2COOH)_2$  The solution was prepared by adding the accurately weighed ZSH and SA in double distilled water, heated upto 45°C to enable dissolution and left stirring to reach saturation and homogeneity. The solution is then covered with polythene cover with holes impinged to facilitate slow evaporation and left in a dust free environment at room temperature for crystallization. Good quality crystals were formed within a span of 5 to 20days.

#### **Characterization studies**

The defect free fully grown pure ZSH crystals and crystals of all the SA doping concentrations 0.01, 0.03, 0.05, 0.07 and 0.09 mol% with ZSHwere harvested. All these five differently doped ZSH + SA and pure ZSH crystals were categorically characterized, structurally by powder XRD analysis (PXRD) using an X-ray diffractometer, Model

RICH, SEIFERT, XRD 3000 P with monochromatic nickel filtered CuK $\alpha$  ( $\lambda = 0.15406$  nm) radiation, over a range of 10 to 70 at the rate of 1°/min. The optical absorption and transmission studies were carried out in the range of 190 to 1100 nm using VARIAN CARY 5E UV-Vis-NIR spectrophotometer. Vickers diamond pyramidal indentor fitted to MVCCD-1000 Video Digital microhardness tester was used to determine the Vickers Hardness number H<sub>v</sub> for the pure ZSH and all the five different SA doped ZSH crystals (ZSHSA).

#### **RESULTS AND DISCUSSION**

### Powder X-ray diffraction analysis

The sharp well-defined peaks of the PXRD results, for the pure ZSH and ZSHSA, proclaims the crystalline nature of the crystals. The lattice parameters of the unit cell of the grown pure ZSH and the doped ZSHSA crystals were found out by matching the PXRD data with the standard JCPDS data and tabulated in Table 1. The PXRD patterns obtained for the pure ZSH and doped ZSHSA crystalline samples are shown collectively in Figure 1. The PXRD data reveals that the grown pure ZSH and ZSHSA crystals are orthorhombic. The peak intensity decreases with the dopant concentration which is consistent with Shou-Yi Kuo*et al*[9], it is represented in Figure 2. This may be attributed to the decline in crystallinity with dopant concentration, and as the dopant concentration increases beyond 0.05 mol% of SA, the lattice parameters values too have a jump and hence there is an increase in particle size for both 0.07 and 0.09 mol % ZSHSA which is substantiated by a significant fall in thePXRD peak intensity of the respective crystals. The variation of the lattice parameter with respect to the doping concentration of SA is graphically represented in the Figure 3. According to Shou-Yi Kuo*et al*, this gradual reduction in the PXRD peak intensity may be due to the stresses created in the lattice due to the ion size mismatch prevalent between the zinc and the dopant ions and the exclusion of dopant ions at the grain boundaries at higher doping concentrations.

 Table 1: Unit cell parameters of pure ZSH and doped ZSHSA crystals.

Crystal Data	Pure ZSH	ZSH + 0.01 mol% SA	ZSH + 0.03mol % SA	ZSH + 0.05mol % SA	ZSH + 0.07mol % SA	ZSH + 0.09mol % SA
a (in Å )	12.83865	12.78814	12.7807	12.75315	12.79478	12.77966
b (in Å )	11.98457	12.02043	12.01595	11.91562	12.08422	12.01428
c (in Å )	5.73798	5.71455	5.71631	5.67498	5.73884	5.70752
Volume V (in Å <sup>3</sup> )	882.87831	878.43458	877.8666	862.37955	887.31038	876.32357



Figure 1:PXRD patterns of pure ZSH and doped ZSHSA crystals.



Figure 3: Variation of lattice constants of pure and SA doped ZSH unit cell with dopant concentration.

#### Ultraviolet – visible – near infrared spectral analysis

The absorption spectrum is the consequence of the electronic transition of the molecules of the crystal. The optical absorption spectrum for the pure ZSH and five differently doped ZSHSA crystals are recorded in the wavelength range of 190 - 1100 nm. The absorption coefficient  $\alpha$  is calculated from the following formula,

$$\alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right)$$

where T is the transmittance and d is the thickness of the crystal. For direct band gap materials the absorption coefficient obeys the formula for high photon energies [17],

$$\alpha = \frac{A(hv - E_g)^{\frac{1}{2}}}{hv}$$

where  $E_g$  is the energy band gap of the crystal and A is a constant. The optical band gap of the crystal is the X – intercept while extrapolating the linear portion of the curve to the abscissa *hv* axis plotted against the ordinate (*ahv*)<sup>2</sup>

axis[18]. Figure 4 shows the absorbance spectrum and Figure 5 shows the transmittance spectrum of pure ZSH and the doped ZSHSA crystals. The UV cutoff wavelength for all the crystals are calculated from their individual absorbance spectrums and the Energy gap E<sub>a</sub>, from their respective transmittance spectrums and tabulated in Table 2.The UV cutoff wavelength is found to be 209.7 nm for the pure ZSH crystal and a gradual blue shift in the absorption edge is observed with the increase in SA dopant concentration. This confirms the possibility of ZSHSA crystals to serve as optical materials in the UV-Vis range. Henceforth, the transparency and energy gap of the ZSHSA crystals increases with doping concentration, which is reported by R.K. Choubey et al. [10], P. Sen et al. [11] Kazuo Niwa et al. [12] and KD Girase et al. [13]. This blue shift may be attributed to the fact that the SA doping reduces the number of localized excitons and the grown ZSHSA crystal approaches the stoichiometric composition [11]. The variation of the UV- $\lambda_{cutoff}$  and  $E_{s}$  with the SA dopant concentration of the pure ZSH and doped ZSHSA crystals is graphically represented in Figure 6. The E<sub>g</sub> values as reported by Farhana et al.[14, 15] and M.SenthilPandian et al.[16] for Triglycine Sulphate crystal doped with KBr of 5.4 – 5.48 eV is of close proximity to the E values of pure Zinc Sulphate crystals of 5.92 eV. The good transmittance in the entire visible range indicates the high probability of application in the second harmonic generation devices. The increase in the transmission percentage of the ZSHSA crystals with doping concentration from Figure 5, indicates the presence of lesser defects compared to the pure ZSH crystals [19]. Hence the scattering centers are minimized which in turn promotes the intensity output of the doped ZSHSA crystals.



Figure 4: The absorbance spectrum of pure ZSH and doped ZSHSA crystals.



Figure 5: Transmittance spectrum of pure ZSH and doped ZSHSA crystals.

**Table 2:** UV- $\lambda_{cut off}$  and  $E_{g}$  of pure ZSH and doped ZSHSA crystals

Concentration of SA with ZSH (mol %)	UV cutoff wavelength (nm)	Band energy gap E <sub>g</sub> (eV)
0.00	209.7	5.916
0.01	208.5	5.948
0.03	199.5	6.218
0.05	199.3	6.225
0.07	198.9	6.236
0.09	198.5	6.249



Figure 6: Variation of UV- $\lambda$ cutoff and Eg with SA dopant concentration.

# Vickers Micro hardness studies

Hardness of the material is a measure of the resistance against local plastic deformation. The plastic deformation can be made by variety of testing methods such as indentation, bending, scretching or cutting. Bond strength of the crystals are closely related to the mechanical hardness of the crystals [20 - 22]. A MVCCD-1000 Video Digital microhardness tester is used for testing mounted with a diamond pyramidal indenter. Static Indentation test was performed with a varying load P of 25 g, 50gg and 100 g while the indenter is maintained in contact with the polished crystal surface for 10 s for all measurements. The load was restricted to 100 g as at higher loads the crystal developed cracks. The Vickers hardness number  $H_v$  is calculated using the following formula,

$$H_v = 1.8544 \frac{P}{d^2} {\binom{Kg}{mm^2}}$$

where P is the applied load in Kg and d is the diagonal length of the indentation in mm and 1.8455 is a constant of geometrical factor for the diamond pyramid indenter. The H<sub>v</sub> values for all the loads applied to each one of the pure ZSH and the doped ZSHSA crystals are tabulated in Table 3. A graphical representation of the load versus H<sub>v</sub> for all the pure ZSH and doped ZSHSA are shown in Figure 7. The microhardness number increases with increase in the load. The microhardness of the solution grown crystals are largely affected by the entrapment of solution particles into the crystal[23]. For ideal crystalline materials the hardness is independent of the applied load. But in practice, we observe a dependence of hardness on applied load which is in agreement with the Indentation size effect [24 – 27]. The relationship between the load P and the diagonal length d of the indenter is given by Meyer's law,

Load P	Vickers hardness number $ m H_v$ for different SA dopant concentration with ZSH (Kg / mm²)							
(g)	Pure	0.01 mol %	0.03 mol %	0.05 mol %	0.07 mol %	0.09 mol %		
25	17.50588	40.03315	44.37177	62.91679	41.29888	62.91679		
50	30.93596	50.48946	59.37561	78.32109	48.82306	78.32109		
100	35.87709	65.65714	85.3325	83.9875	68.37194	79.46262		

 $P = ad^n$ 

## $\log P = \log a + n \log d$

where a is the material constant and n is the Meyer's index also called the work hardening coefficient and calculated from the slope of the plot of log(d) versus log(P)[16]. The value of the n for harder materials lies between 1 and 1.6 and if n value is larger than 1.6 they are categorized as softer materials. Figure 8 shows graphically the variation of the work hardening coefficient n with the SA dopant concentration of ZSH crystals. As all the pure ZSH and doped ZSHSA crystals have values greater than 1.6 they all belong to the soft material category[28].

#### CONCLUSION

Optically transparent good quality crystals of pure ZSH and five differently doped ZSHSA crystals were grown by slow evaporation solution growth method. The lattice parameter values of ZSHSA were in good agreement with pure ZSH crystals. The slight variation in the lattice constants may be recognized to the inclusion of the dopant molecules

in the pure ZSH crystal lattice. The optical studies reveal that the energy gap of the pure ZSH is less than the doped ZSHSA crystals. The work hardening coefficient of the crystals suggest that the pure and the doped crystals belong to the soft material category. The mechanical stability of the doped crystals are much harder than the pure ZSH crystals.



Figure 7: Variation of Load versus Vickers hardness number Hv



Figure 8: Variation of work hardening coefficient n with SA dopant concentration of ZSH.

## REFERENCES

- Williams J (edn) (1983) Nonlinear Optical Properties Organic and Polymeric Materials. American Chemical Society Symposium Series 233, American Chemical Society, Washington DC.
- [2.] Chemla DS, Zuss J (edn) (1987) Nonlinear Optical Properties of Organic molecule and Crystals, vol 1 and 2, Academic press, New York.
- [3.] M. Ema, A. Gebrewold, B.T. Altura and B.M. Altura, Report, Department of Physiology, StaeUniversity of New York, Health Science Centre, Brooklyn, USA (1998).
- [4.] LedouxSmZyss J, Nonlinear Organic Molecules and Materials for Optoelectronic Devices. Int J Nonlinear Opt Phys 3: (1994) 287-316.
- [5.] Mostad A. Natarajan S, Crystal and molecular structure of DL-methionine nitrate Z Kristallogr 210(1995) 114-117.
- [6.] Shen YR The principles of nonlinear optics, Wiley, New York. (1984)
- [7.] Marcy HO, Warren LF, Webb MS, Ebbers CA, Velsko SP, Catella GC (1992) Second-harmonic generation in zinc tris (thiourea) sulfate. Appl Opt 31:5051-5060.
- [8.] Ruiz B. Jazbinsek M. Gunter P (2008) Crystal growth of DAST. Cryst Growth Des 8:4173-4184.
- [9.] Shou-Yi Kuo, Wei-Chun Chen, Fang-I Lai, Chin-Pao Cheng, Hao-Chung Kuo, Shing-Chung Wang and Wen-Feng Hsieh, Journal of Crystal Growth 287 (2006) 78 – 84.
- [10.] R.K.Choubey, P.Sen, P.K.Sen, R.Bhatt, S.Kar, V.Shukla and K.S.Bartwal, Optical Materials 28 (2006) 467 472.
- [11.] P.Sen, P.K.Sen, R.Bhatt, S.Kar, V.Shukla and K.S.Bartwal, Soild State Communications. 129 (2004) 747.
- [12.] Kazuo Niwa, Yasunori Furukawa, ShunjiTakekawa and Kenji Kitamura, Journal of Crystal Gowth 208 (2000) 493.
- [13.] K.D.Girase, H.M.Patil, D.K.Sawant and D.S.Bhavsar, Scholars Research Library, Archives of App. Sci. Research, (2011) 3(3):128 – 134.
- [14.] FarhanaKhanum and JibanPodder, Journal of Crystallization Process and Technology, (2011) 1, 49 54.

- [15.] FarhanaKhanum and JibanPodder, Journal of Crystallization Process and Technology, (2011) 1, 26 31.
- [16.] M.SenthilPandian, N. Balamurugan, V.Ganesh, P.V.RajaShekar, K.Krishan Rao and P.Ramasamy, Materials Letters 62 (2008) 3820 – 3832.
- [17.] Bhagavanarayana G, Parthiban S and Subbiah M, Cryst. Growth Des., (2008) 8 (2), 446-451.
- [18.] Ashour A, El-Kadry N and Mahmoud SA, Thin Solid Films, (1995), 269 : 117 120.
- [19.] M. SenthilPandian, P. Ramasamy and Binay Kumar, Materials Research Bulletin, (2012) 47, 6, 1587 1597.
- [20.] K. Li, D. Xue, Phys. Scr. T(2010)139, 014073.
- [21.] K. Li, D. Xue, Chin. Sci. Bull. 54 (2009) 131.
- [22.] K. Li, X. Wang, F. Zhang, D. Xue, Phys. Rev. Lett.(2008) 100, 235504
- [23.] M. SenthilPandian, Unit Chareon, In: P. Ramasamy, PrapunManyum, M. Lenin, N. Balamurugan (Eds.), J. Cryst. Growth 312 (2010) 397.
- [24.] B.Venkatesan, N. Kanniah, P.Ramaswamy, Journal of Material Science letters 5, 987 (1986).
- [25.] K.Sangwal, Mater. Chem. Phys. 63, 145 (2000).
- [26.] B.W, Mott, Microindentation Hardness Testing, Butterworths, London (1956).
- [27.] D.Tabor, The Hardness of materials, Oxford University Press, Oxford (1951).
- [28.] V. Krishnakumar, M. Rajaboopathi and R. Nagalakshmi, Advanced Materials Letters, (2011) 2(2), 163-169.