Influence of Zinc on The Growth, Mechanical, Thermal and Dielectrical Properties of Ninhydrin Single Crystals for Non Linear Optical Application

A.Ponchitra, K. Balasubramanian and R. Jothi Mani

Abstract: Pure and zinc doped ninhydrin crystals were grown by conventional slow evaporation solution growth method. The powder XRD studies have been focused to determine crystal structure and various cell parameters of the grown crystals. The mechanical behavior such as work hardening coefficient values, yield strength and stiffness constant was calculated by using Vickers microhardness studies. The decomposition point of the harvested crystals was also observed by using TG/DTA analysis. The nonlinear optical behavior and its second harmonic generation efficiency have been tested by powder Kurtz and Perry powder technique.

Keywords: Organic crystal; XRD; TG/DTA; Dielectrical analysis; SHG;

1. INTRODUCTION

An extensive research is going on, some excellent materials for their great optical nonlinearities and those are very appropriate for potential applications in various fields like optical information processing, high density storage, telecommunication, and spectroscopy and so forth. In recent years organic, non-centrosymmetric space group crystals have widely used because they have good nonlinear properties due to the presence of delocalized pi-electron system [1]. Organic compounds such as, ninhydrin having good nonlinear optical coefficient and large band gap and it is useful in many industrial, biological applications. Ninhydrin is a light yellow colour solid it reacts with amino acids and produce purple violet colour it can be used in the field of chromatogram, food industry, microbiology and forensic science. Most of the non-centrosymmetric organic crystals have a high nonlinear optical susceptibility and good NLO efficiency but poor thermal and mechanical properties [2-11]. The pure inorganic crystals have good mechanical and thermal properties. It was expected that the doping process of some metal based inorganic element may influence the growth rate, physical property, mechanical strength, thermal property and nonlinear properties of the crystals and it is useful for many technological applications. In general transition metals possess a high melting and boiling point and it is useful in catalytic actions.

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Zinc nitrate is a colorless crystalline solid and it is soluble in both water and alcohol. It is used in the field of agriculture, rubber industry and water treatment industries. It is used as a synthesis of coordination polymers. An excellent, ranging of catalysts to pigments and strong oxidizing agent nature of zinc nitrate was forced for doping selection with the pure ninhydrin material. No researcher focused zinc nitrate to enhance various properties of ninhydrin crystals previously so which has been focused here to bring desired behavior in the sphere of dielectric, thermal and nonlinear optical properties.

2. EXPERIMENTAL METHODS

Single crystals of pure ninhydrin (NH) and 1 mole% zinc nitrate doped ninhydrin (Z1NH) crystals have been developed in distilled water by solution growth technique (Slow evaporation). The prepared solutions of both NH and zinc nitrate doped NH were stirred well for attaining homogeneity and then allowed for slow evaporation. The yellow colour good quality crystals were collected after 30 days. The grown crystals are depicted in figure.1.

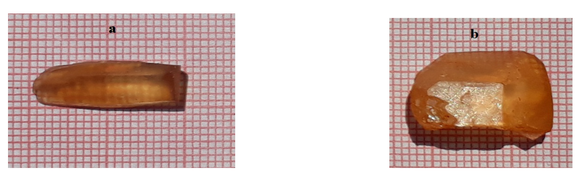

Fig. 1 *(a) NH (b) Z1NH crystals*

3. RESULTS AND DISCUSSION

3.1. Structural determination

The grown crystals have been subjected to X-ray diffraction analysis to find various structural parameters and it was found that both (NH and Z1NH) crystals crystallizes in the monoclinic crystal system with desirable space group ($P2_1$) for NLO applications [8-9]. The Calculated lattice parameter values for pure ninhydrin are (NH): a =11.3475 Å, b=6.0450 Å, c =5.7548 Å, V= 390.3477 Å^3 and 1 mole% zinc nitrate doped ninhydrin (Z1NH): a =11.3574 Å, b=6.0607 Å, c =5.7557 Å, V= 391.6866Å^3. The good crystalline behavior of the samples was predicted from the sharp peaks in the XRD pattern of powder samples (fig 2). The slight change in the intensity level of the peaks was due to the incorporation of zinc ions [10-11].

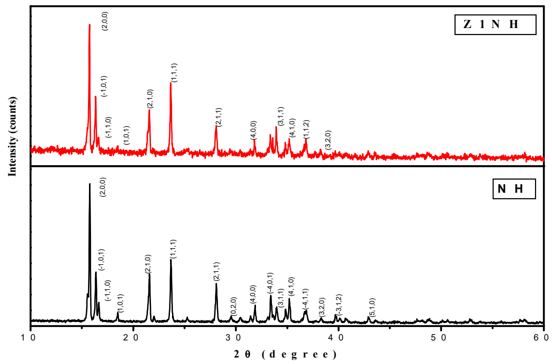

***Figure: 2**. Powder XRD patterns of NH and Z1NH crystals*

3.2. Hardness measurement

Microhardness measurement was carried out for undoped and zinc doped crystals using the Shimadzu microhardness Tester (HM-200A Series). Mechanical properties depend on the structure and nature of the bonding of the crystalline solids. From the studies various hardness parameters determined such as work hardneing coefficient, yield strength and stiffness constants etc. Vickers microhardness values were calculated from the relation $H_v = 1.8544\ (P/d^2)$ kg/mm^2. Where P is applied load (g) and d is the diagonal length (μm) of the indentation mark. From fig.3 the hardness number increases with increase in load and it reveals reverse indentation effect. The plots of log p versus log d have been made to find the values of the work hardening coefficient (n). The values of work hardening coefficient of undoped and zinc doped ninhydrin were 6.45 and 4.32 confirms the soft category belongings of the grown crystals and hence the formula $(\sigma_y) = (H_v/3)(0.1)^{n-2}$ were used to determine the strength of yielding nature.

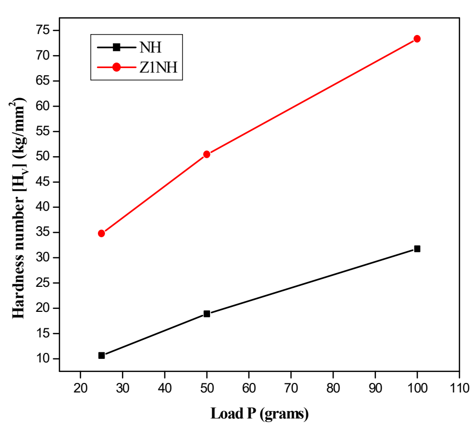

***Figure:3**. Variations of hardness with load for NH and Z1NH crystals*

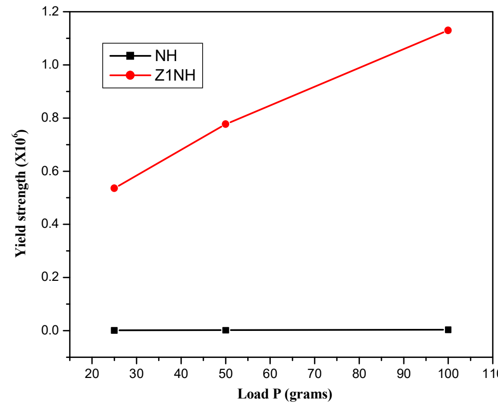

***Figure:4**. Plot of Yield strength versus load for* NH and Z1NH crystals

The variations of yield strength with load for the grown crystals are presented in the figures 4. It is observed that the values of yield energy of the grown crystals are increasing with the carried out load and for this reason the grown crystals have especially excessive mechanical energy [12-17]. The elastic stiffness constant of the prepared crystals for different loads were calculated using Wooster's empirical formula ($C_{11} = H_v^{7/4}$) to draw an idea about the tightness and the angle of bending between neighboring atoms. Increasing stiffness constant of the crystals with increase in load (figure 5) explains the strong binding force between the atoms and their pretty frangible [18].

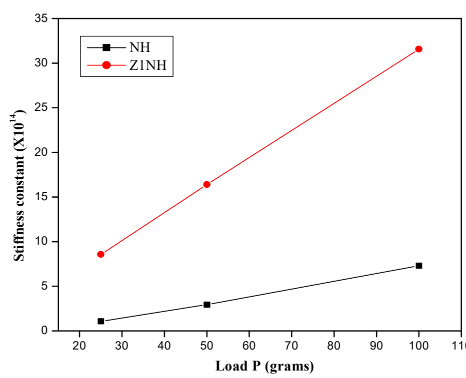

***Figure:5**. Plot of Stiffness constant with load for NH and Z1NH crystals*

3.3. TG/DTA analysis

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) was analysed using SIINT 6300 Japan made analyzer. The phase transition and the decomposition points of the grown crystals was analysed by using this study. From TGA curve fig 6 (a, b) the primary weight loss of the samples observed in the temperature range 110-160° C. The decomposition point for undoped and zinc doped ninhydrin was found to be 256.91° C and 262.51°C respectively. A decomposition point of Z1NH was found to be greater than NH sample.

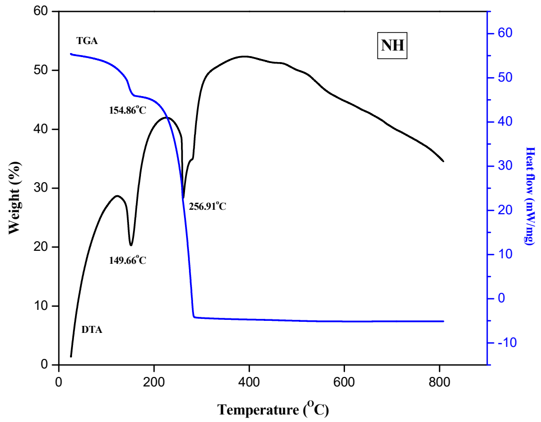

Fig.6(a). *TG-DTA curve of NH crystal*

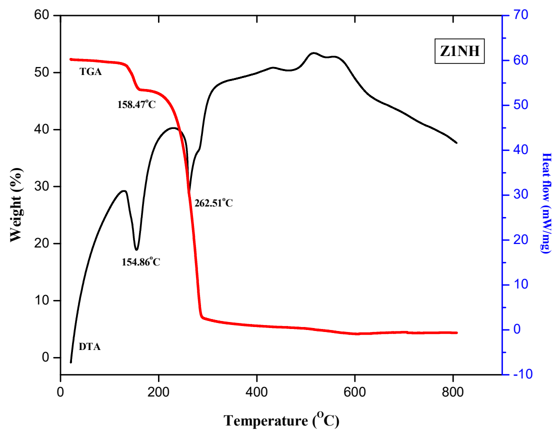

Fig.6(b) *TG-DTA curve of Z1NH crystal*

3.4. Dielectrical studies

The various electrical parameters like dielectric constant and loss and conductivity will give response of samples to an applied electric field which can be found by dielectric studies. The dielectric parameters depend on the applied frequency and temperature of the samples. Figures 7 (a) and (b) depicts increasing magnitude of both dielectric constant and loss of the samples with increase in temperature. AC conductivity (σ_{ac}) values have also been determined from dielectric constant and loss which was found to be increased while the temperature is increased (figure 7c) and which shows the enhancement of the conducting nature of the grown samples.

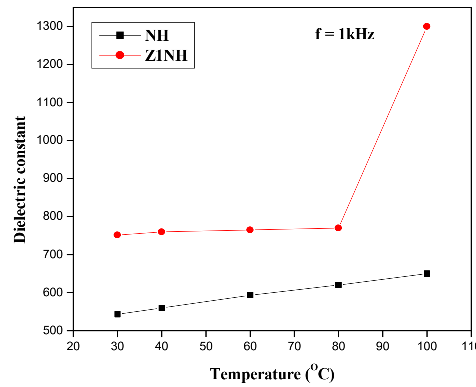

Fig.7(a). *Plot of dielectric constant versus temperature for* the NH and Z1NH crystals

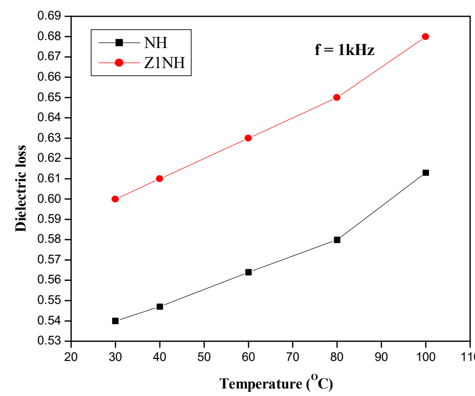

Fig.7(b) *Plot of dielectric loss versus temperature for the* NH and Z1NH crystals

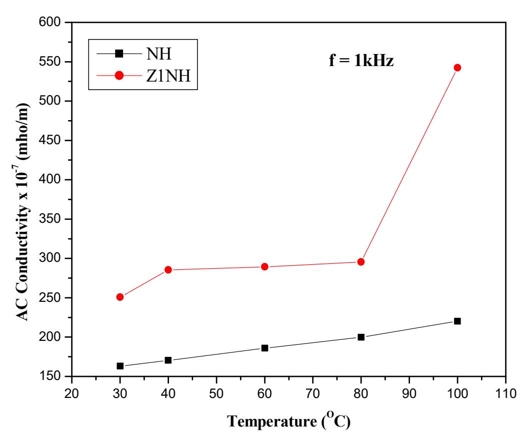

Fig. 7(c)*. Variation of AC conductivity with temperature at* 1kHz for the NH, Z1NH crystals

Plot of ln (σ_{ac}) with 1000/T helps to find required energy for the conduction of charge carriers in the sample generally known as the activation energy. So the same has been done and 0.04 eV and 0.03 eV are the respective values of the activation energy for NH and Z1NH samples. So the grown crystals needs very low energy to activate the charge carriers.

3.5. Nonlinear optical studies

The SHG efficiency was observed for the grown samples using Kurtz and Perry powder technique [19]. It was found that the SHG efficiency of NH, Z1NH crystals was found to be 1.28, 1.37 times greater than Potassium Dihydrogen Phosphate (KDP) respectively. The SHG efficiency of zinc doped ninhydrin was slightly improved due to the inclusion of zinc ions in the crystal lattice.

4. CONCLUSION

Pure and zinc doped ninhydrin crystals were successfully grown for second harmonic generation by solution growth method. A Monoclinic crystal system with noncentro symmetry space group of the crystals have been observed by single crystal XRD methods and various peak intensities were found with a few alterations due to dopant (zinc nitrate) were identified by PXRD techniques. Hardness values of the crystals were determined to find work hardening coefficient of the materials for categorization of material type and the measurements prove that the crystals belong to soft type. Energy changes with temperature and decomposition points of the samples were drawn by the TGA and DTA curves and found that the decomposition point of Z1NH is enhanced compared with NH and hence metal doped crystal withstands still to higher temperatures. Low values of dielectric parameters exhibits defect free and high quality nature of the samples and when the temperature increases the conductivity increases. The NLO efficiency of Z1NH sample was higher than that of NH sample.

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REFERENCES

[1] S. Gowri, T. Uma Devi, D. Sajan, S.R. Bheeter, N. Lawrence, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 89, (2012) 119-122.
[2] C.K. Lakshmana Perumal, A. Arulchakkaravarthi, N.P. Rajesh, P. Santhana Raghavan, Y.C. Huang, M. Ichimura, P. Ramasamy, Journal of Crystal Growth, 240, (2002) 212-217.
[3] R. Sankar, C.M. Raghavan, R.Jeyavel, Crystal Growth & Design, 7, (2007) 501-505.
[4] S. Manivannan, S. Dhanuskodi, Journal of Crystal Growth, 262, (2004) 473-478.
[5] K. Jaganathan, S.Kalainathan, T.Gnasekaran, N. Vijayan, G.Bhagavannarayana, Crystal Research and Technology, 42, (2007) 483-487.
[6] Ronald C. Medrud, Acta Crystallographica Section B, 25, (1969) 213- 220.
[7] T. Uma Devi, N. Lawrence, R. Ramesh Babu, S. Selvanayagam, Helen Stoeckli-Evans, K. Ramamurthi, Journal of Crystal Growth, 311, (2009) 3485-3490.
[8] T.Uma devi, N.Lawrence, R.Ramesh babu, K.Ramamurthi and G.Bhagavannarayana, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 71, (2009), 1667-1672.
[9] N. Vijayan, J. Philip, D. Haranath, Brijesh Rathi, G. Bhagavannarayana, S.K. Halder, N. Roy, M.S. Jayalakshmy, Sunil varma, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 122, (2014) 309-314.
[10] T. Prasanyaa, V. Jyaramakrishnan, M. Haris, Spectrochimica Acta Part A: Molecular and biomolecular Spectroscopy, 104, (2013) 110-113.
[11] R.S. Sreenivasan, N.Kangathara, G. Ezhamani, N.G. Renganathan and G. Anbalagan, Journal of spectroscopy, (2012), volume 2013, Article ID 386024, http://dx.doi.org/10.1155/2013/386024.
[12] P. Kanchana, A. Elakkina kumaran, Y. Hayakawa, C. Sekar, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 103, (2013) 187-192.
[13] P. Praveen kumar, V. Manivannan, S. Tamilselvan, S. Senthil, Victor Antony Raj, P. Sagayaraj, J.Madhavn, Optics Communications, 281, (2008) 2989-2995.
[14] R. Jothi Mani, P. Selvarajan, H. Alex Devadoss, D. Shanthi, Optik, 126, (2015) 213-218.
[15] T. Vela, P. Selvarajan, T.H. Freeda, K. Balasubramanian, Physica Scripta, 87, (2013) 045801.
[16] E.M. Onitsch, Mikroskopie, 2, (1947) 131-151.
[17] T.P. Srinivasan, S. Anandhi, R. Gopalakrishnan, Journal of crystal Growth, 318, (2011) 768.
[18] W.A. Wooster, Reports on Progress in Physics, 16, (1953) 62.
[19] S.K.Kurtz, T.T. Perry, J. Appl. Phys. 39, (1968) 3798-3813.