Indian Journal of Engineering & Materials Sciences
Vol. 28, February 2021, pp. 82-88

Structural, mechanical, thermal, optical and antifungal properties of pure and nickel doped ninhydrin non liner single crystals

Anand Ponchitra[a,b], Kumarasamy Balasubramanian[a], Ramasamy. Jothi Mani[c] & Kathiresan Sakthipandi[d*]

[a]Department of Physics, The M.D.T. Hindu College, Pettai, Tirunelveli, Tamil Nadu 627 010, India
[b]Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, Tamil Nadu 627 012, India
[c]Department of Physics, Fatima College, Madurai, Tamil Nadu 625 018, India
[d]Department of Physics, SRM TRP Engineering College, Tiruchirappalli, Tamil Nadu 621 105, India

Received: 02 May 2020 ; Accepted: 18 May 2020

A conventional method was adopted to prepare pure ninhydrin (NH) and nickel doped ninhydrin (N1NH) single crystals. The present investigation focused on various properties of as grown NH and NINH crystals. Monoclinic crystal structure with P2$_1$ space group which is attractive phenomena were noticed in structural mode of grown NH and NINH crystals. Various vibrations of functional groups related to NH and nickel doped NINH crystals were assigned from Fourier-transform infrared peaks of good resolution. Energy-dispersive X-ray spectrum presents the percentage of carbon, oxygen and nickel occurs in the sample. The strength of the samples have deliberated with the help of Vicker's microhardness tester. The decomposition point of both NH and N1NH crystals has been measured by thermal analysis. The dielectric constant of both NH and N1NH crystals was also determined. Green emission which denotes second harmonic generation (SHG) process for the samples generally confirms the nonlinear optical (NLO) activity of the NH and N1NH crystals and it has been tested successfully based on the technique of Kurtz-Perry. The SHG efficiency values of NH and N1NH samples are comparable with KDP which has been used as reference sample as it is being used commercially. Basically, NH and NINH crystal samples were used for many medical applications. Therefore, the antifungal activity was also focused for investigation against two famous fungi like *Aspergillus niger, Aspergillus flavus*.

Keywords: Single crystals, Structural properties, Optical properties, Thermal analysis, Vicker's hardness, Dielectric studies, Antifungal activity

1 Introduction

Generally the material whose light intensity is very high in non linear media and produce laser light will be utile in optical switching, optical computing, high-speed optical modulators, high-density optical storage and ultra-fast optical switches applications[1-3]. Those materials will be transparent in optical regions and their phase matching should be interactive to withstand in laser damaging[4]. The above said features are almost fulfilled by organic materials so most of them are used in device fabrication of nonlinear optical (NLO) materials[5]. Ninhydrin is an important starting material in the organic synthesis of heterocyclic compound. Ninhydrin reacts with amino acids and it produce purple violet colour it can be used in the field of chromatogram, food industry, microbiology, protein science and forensic science[6-9]. Most of the organic crystals have high nonlinear efficiency but poor thermal and mechanical properties and which may be enlighten by doping proper inorganic metals.

Nickel nitrate is an inorganic crystalline salt which is taken as the dopant material. From the literature reports, it has been concluded that pure ninhydrin[6,7], 1 mole% copper nitrate and 1 mole% cadmium nitrate doped ninhydrin[8], 0.2 mole% copper chloride doped ninhydrin[9] and 1 mole% zinc nitrate doped ninhydrin crystals[10] having good linear and NLO property. To the best of our knowledge, no literature was found in 1 mole% nickel doped ninhydrin crystals. Hence, in this point of view, nickel nitrate was doped with pure ninhydrin sample to enhance the mechanical and thermal behaviors along with that structural analysis have been done to observe different parameters. Efficiency of the samples in generating second harmonic mode was also measured for further NLO applications along with determination of antifungal activities.

---

*Corresponding author (E-mail: sakthipandi@gmail.com)

2 Experiment section

2.1 Growth mechanism of crystals

Twice distilled water was used as a solvent in adopted method to prepare the crystals using pure ninhydrin ($C_9H_6O_4$) (Himedia AR Grade, India) and 1 mole% of nickel nitrate ($Ni (NO_3)_2.6H_2o$) (Himedia AR Grade, India). 5g of pure ninhydrin was dissolved and stirred using magnetic stirrer (4hrs) then kept for slow evaporation for pure ninhydrin crystallization process[6-10]. Again 1 mole% nickel nitrate was added with pure NH sample along with distilled water to make saturated solution. The same solution was stirred (4hrs) and allowed for evaporation slowly to get nickel doped crystals. The grown NH and N1NH crystals were harvested respectively after 36 and 60 days. The obtained crystals are transparent in yellow colour (Fig. 1). The pure ninhydrin and 1 mole% nickel doped grown crystals were marked as NH and NINH crystals respectively.

2.2 Characterization of pure and nickel doped ninhydrin crystals

Powder X-ray diffractometer (PANalytical X'pert Pro) was used for X-ray diffraction (XRD) measurement of NH and N1NH samples to find crystal system and respective lattice parameters at room temperature. Monochromatic beam of Cu Kα radiation (1.5406 Å) was imposed as a source on X-ray diffractometer. FTIR measurement was done Using Fourier-transform infrared spectrometer (Shimadzu IRAffinity – 1S Model) from 4000 to 400 cm^{-1} wave number. For FTIR spectra measurement, a pellet was prepared using KBr matrix. Energy-dispersive X-ray spectroscopy (EDAX) analysis was traced to identify the elemental composition presented in the grown crystals. In the present work, EDAX were performed using INCA Penta FET X3, Oxford instruments model. Scanning electron microscope (SEM; Genesis 1100, EmCraft, Korea) established through Department of Science and Technology - Fund for Improvement of Science and Technology scheme was used to characterize of NH and N1NH crystals. Microhardness measurement of NH and N1NH crystals was calculated by Shimadzu microhardness Tester (HM-200A Series). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was done using SIINT 6300 Japan made analyzer. The dielectric property was analyzed by LCR meter (Agilent 4284A model). The study of second harmonic generation efficiency was carried out using the Kurtz and Perry powder set-up. The Q switched Nd:YAG high energy laser (Quanta Ray model) with 1064 nm, pulse width 6 ns and 10 Hz repetition rate was used. The antifungal activity was measured using disc diffusion method and the glass wares were sterilized at 130°C for 2-3 hours. The test microbes were prepared using a Muller Hinton medium/potato dextrose agar medium which supports the growth of fungus. 40 µ/L molar concentrations of NH and N1NH crystals was taken to prepare solution then the solution was located on the petri plates which contain the media. The petri plates were incubated for 24 hours and the inhibition zones were noted.

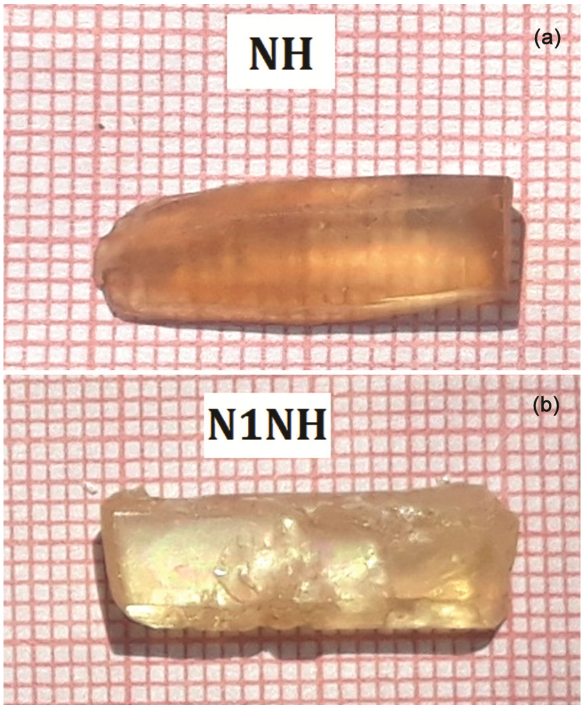

Fig. 1 — Schematic diagram of the grown (a) NH and (b) N1NH crystals.

3 Results and Discussion

3.1 Structural analysis

The powder XRD pattern (Fig. 2) of both NH and N1NH samples confirms the monoclinic crystal structure along with the desired space group of non-centrosymmetric ($P2_1$) position and the XRD data of both grown crystals are closely resembles the standard data (JCPDS Card No.31-1811). An important physical dimension of the crystal is referred by lattice constant or lattice parameter which was found to be a=11.3475Å, b=6.0450Å, c=5.7548Å, and V= 390.3477 Å^3 for NH crystal and for N1NH crystal they are a=11.3688 Å, b=6.0471 Å, c =5.7689 Å, V= 392.0092 Å^3. No changes in structure but very tiny variations in lattice constants are observed for N1NH sample. Due to the addition of 1 mole% nickel, a small increase in the crystal lattices (in all three axes) and also a small diversity in the intensity level of diffraction in the peaks were observed in the present investigation[6-10]. This observation implies that the dopant was well mixed with parent compound of NH crystal. Similar results for copper nitrate, cadmium nitrate, cupper chloride and zinc nitrate doped ninhydrin crystals were observed in the literature[8-10]. The lattice parameters for NH and cupper chloride doped ninhydrin crystals reported by Uma Devi *et al.*[7], (7) and Sreenivasan *et al.*[9], are a= 11.3387 Å, b= 6.0081 Å, & c= 5.7526 Å and a=11.28 Å, b=5.98 Å, & c=5.71 Å respectively. The lattice parameters for copper nitrate and cadmium nitrate doped ninhydrin crystals reported by Prasanyaa *et al.*[8], are a=11.42 Å, b=6.04 Å, c=5.96 Å and a=11.47 Å, b=6.02 Å, c=5.99 Å respectively. The lattice parameter values of zinc nitrate doped ninhydrin crystals reported by Ponchitra *et al.*[10], are a= 11.3574 Å, b= 6.0607 Å, and c= 5.7557 Å respectively.

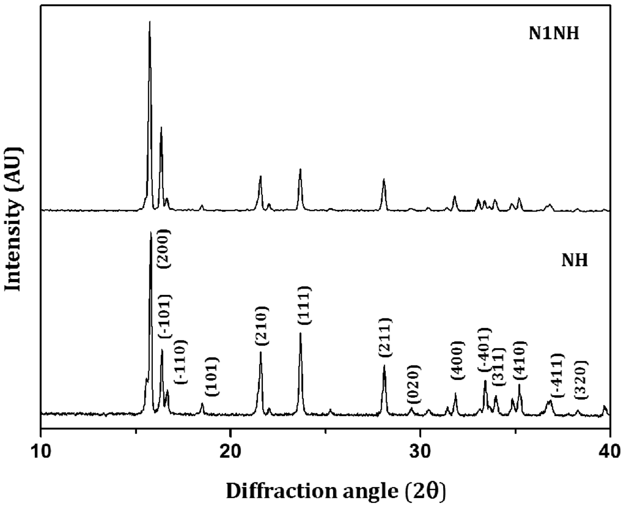

Fig. 2 — Powder XRD patterns of NH and N1NH crystals.

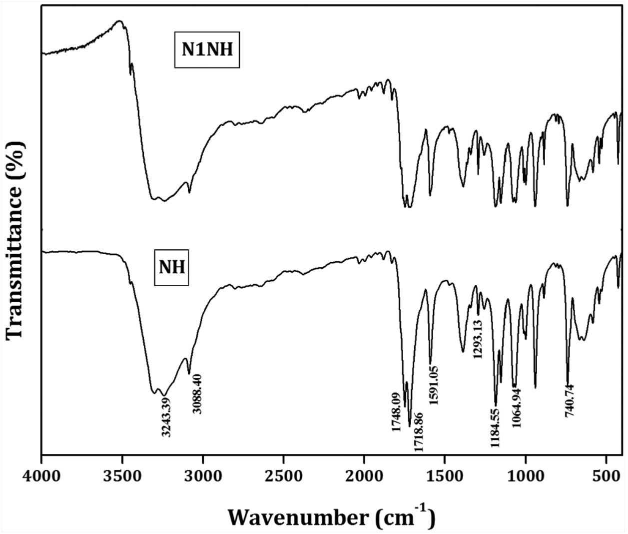

Fig. 3 — FTIR spectra of NH and N1NH crystals.

3.2 FTIR analysis

FTIR study is important in the investigation of molecular structure of crystals. FTIR spectra of NH and N1NH crystals were depicted in Fig. 3. The observed functional groups and corresponding band frequencies were represented in Table 1. The peak at 3243 cm^{-1} (for NH crystal) and 3238 cm^{-1} (for N1NH crystal) is occurred due to O-H vibration. The peaks at 3088 and 3086 cm^{-1} respectively for NH and N1NH crystal corresponds to aromatic C-H stretching. The recorded peak around 1748 and 1711 cm^{-1} is due to carbonyl (C=O) stretching for NH and N1NH crystals. The skeletal vibrations of aromatic rings are observed at 1591 cm^{-1}. The peaks around 1293, 1184, & 1064 cm^{-1} and 1291, 1185, & 1082 cm^{-1} in respectively NH and N1NH samples are due to in plane bending modes of aromatic C-H bonds. The out of plane aromatic C-H bond is observed near at

Table 1 — FTIR spectroscopy data for pure and nickel doped ninhydrin crystals along with the band assignments and comparison with the literature.

S.No.	Wavenumber (cm^{-1})				Band assignment
	UmaDevi *et al.*[7]	Sreenivasan *et al.*[9]	NH	N1NH	
1	3238	3298	3243	3238	O-H vibration
2	3089	3087	3088	3086	Aromatic C-H stretching
3	1748	1747	1748	1747	carbonyl (C=O) stretching
4	1718	1717	1718	1711	carbonyl (C=O) stretching
5	1589	1592	1591	1591	The skeletal vibrations of aromatic rings
6	1291	1292	1293	1292	Plane bending of aromatic C-H bonding
7	740	741	740	740	Out of Plane aromatic C-H bonding

740 cm^{-1} for grown crystals[7-10]. The observation from the FTIR spectrum was tabulated in Table 1 for easy comparison along with available literature.

3.3 SEM and EDAX analysis

Spherical morphology phenomena of both NH and N1NH grown crystals are observed from SEM image. Fig. 4 shows that SEM and EDX spectrum of NH and N1NH crystal. The elemental weight percentage of carbon and oxygen in the grown NH crystals is 59.73, and 40.27 respectively. While, the weight percentage of carbon, oxygen and nickel in the grown N1NH crystals is 55.74, 44.08, and 0.18 respectively.

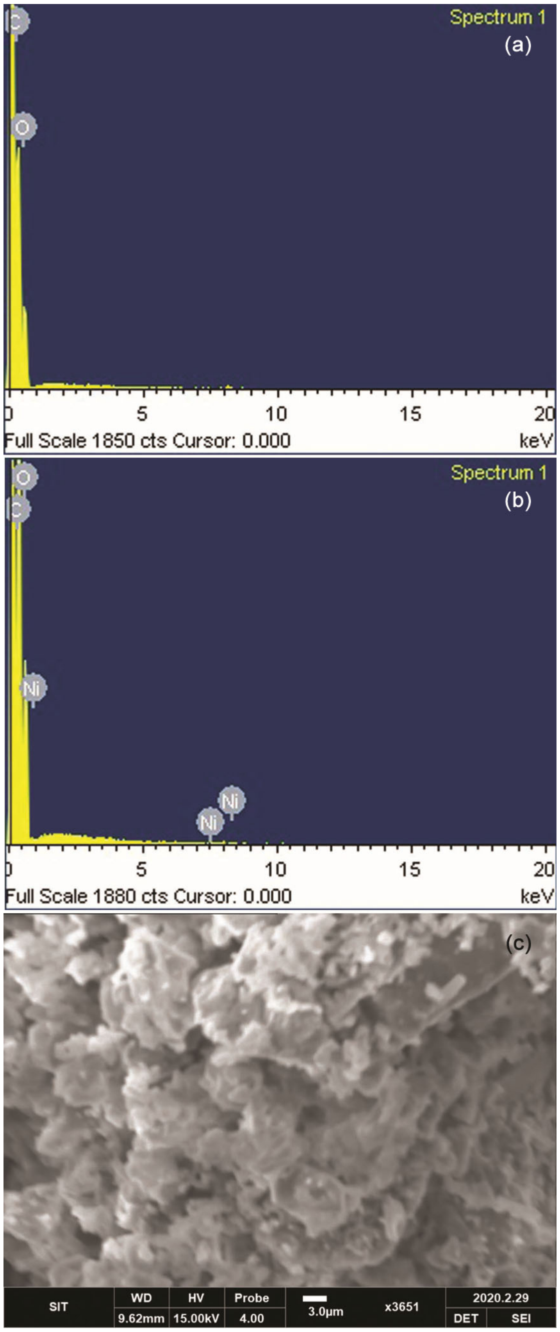

Fig. 4 — SEM image and EDAX spectra of NH and N1NH crystals.

3.4 Hardness measurement

Some important parameter like work hardneing coefficient, yielding strength and stiffness constants will give an idea about the mechanical wealth of materials and they were measured for the NH and N1NH crystals over the different loads (P) and the same was shown in Fig. 5. The hardness number (H_v) was computed using the formula $H_v = 1.8544P/d^2$ kg/mm^2 where P is the applied load and d is the diagonal length of indentation. The value of H_v increases while the load is increasing for both crystals (Fig. 5a). Enhanced hardness values for N1NH is due to presence of nickel into the lattice site of the crystals. The work hardening coefficient (n) was also found by plotting graph between logarithmic values of load and diagonal length and they are 6.45 (NH) and 3.63 (N1NH). Since the n values are greater than 2 both crystals comes under the roof of soft materials and hence they will allow the light to pass through easily. Yielding strength (σ_y) of the material was identified with the standard formula (σ_y) = $(H_v/3)(0.1)^{n-2}$. Figure 5(b) represents the variations of yield strength with load for the grown crystals. It is observed that the nickel doped ninhydrin crystal possess more yield energy than the undoped ninhydrin crystal due to better physical properties of nickel nitrate.

By using Wooster's formula $C_{11} = H_v^{7/4}$, the stiffness constant was found. Plastic resistance, bending and tightness in bonds of nearby atoms could be measured by stiffness constant (C_{11}). From Fig. 5(c), it was examined that the stiffness constant is increases while the load is increasing for the NH and N1NH crystals so generally binding forces are quit strong for both. High values of C_{11} for the grown N1NH crystal compare to NH manifest that the binding forces among the ions of nickel added crystal are little pretty frangible and which may due to incorporation of the nickel ions[11-13]. 62% of variation observed in the N1NH crystals. From the results, the nickel doped ninhydrin mechanical stability enhances compared with undoped ninhydrin. In the previous literature, the work hardening coefficient value for pure ninhydrin, copper, cadmium and zinc doped ninhydrin was greater than 2, 1.0, 1.06 and 4.32 respectively. From the report it was noticed that

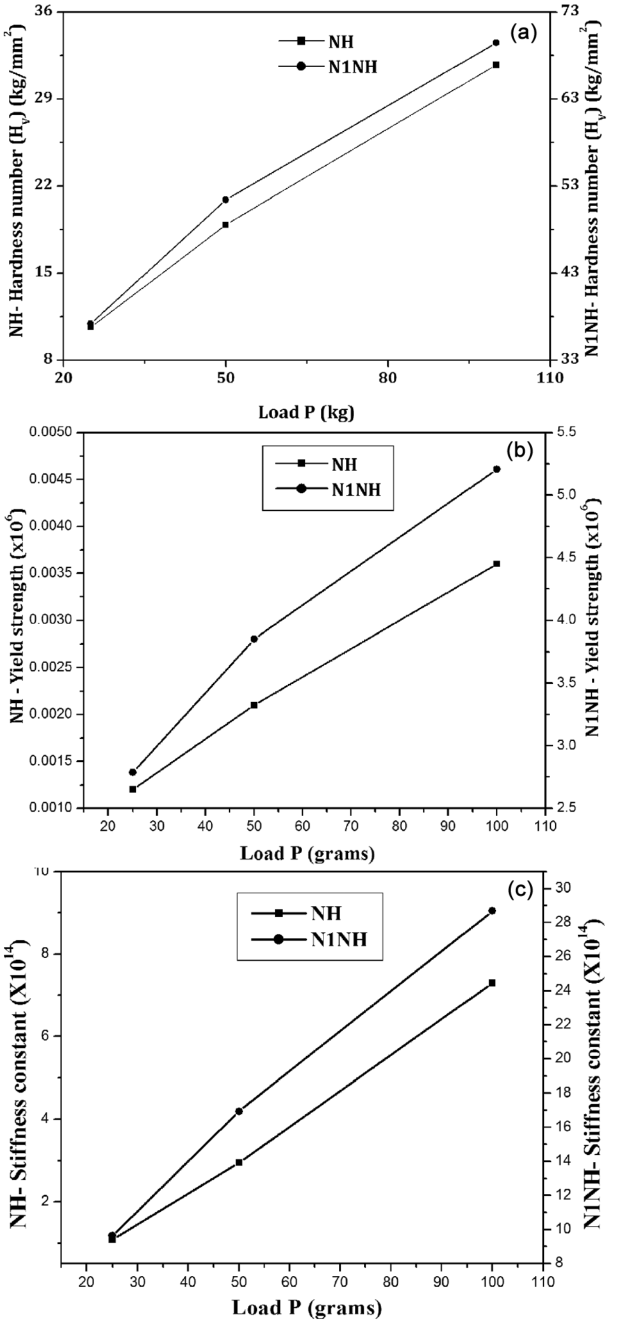

Fig. 5 — Variations of (a) hardness, (b) yield strength and (c) stiffness constant with load for NH and N1NH crystal.

ninhydrin is soft material, copper and cadmium doped ninhydrin was hard material, zinc doped ninhydrin is soft materials[8,10]. Therefore, it can be used in the device fabrication processing and many optical applications[9].

3.5 TG/DTA analysis

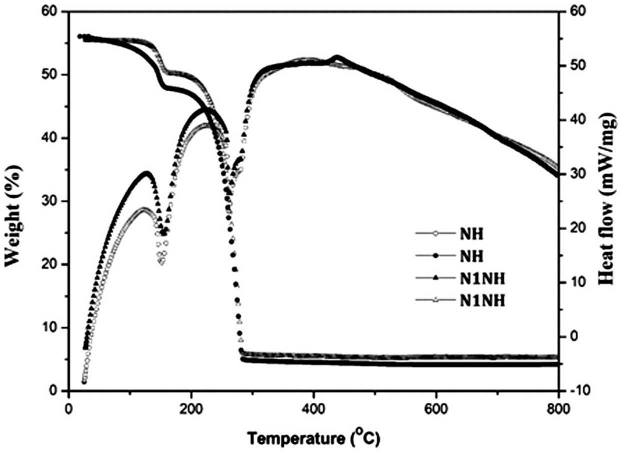

Fig. 6 — TG-DTA curve of NH and N1NH crystal.

The phase transition and the decomposition points of the grown NH and N1NH crystals were observed. The TGA and DTA curves of NH and N1NH crystals are depicted in Fig. 6. From TGA curve, the primary weight loss of the NH and N1NH samples observed at the temperature range of 110-163° C. The first endothermic peaks were noted at 149.66° C for NH and 156.86° C for N1NH crystals. The decomposition point for NH and N1NH crystals was found at 256.91°C and 264.11°C respectively. The decomposing tip of N1NH sample is higher than the pure ninhydrin (NH) due to increase in bond energy with the presence of few amount of nickel. Similarly the decomposition temperature of copper nitrate (249.81°C), cadmium nitrate (254.31°C) and zinc nitrate doped ninhydrin (262.51°C) crystals are also increases and it was observed in the literature[8,10].

3.6 Dielectric measurement

Generally dielectric properties are more concern with storage and dissipation of electric and magnetic energy. Some dielectric parameters like dielectric constant and dielectric loss were determined for the grown crystals with various frequencies using LCR meter to explain various electrical phenomena of optically active materials in nonlinear mode. The dielectric constant (ε_r) is determined by measuring the capacitance (C) with the help of following formula $\varepsilon_r = Cd/\varepsilon_o A$ where d is the thickness, ε_o is the permittivity of free space and A is area[14]. Figure 7 implies behavior of dielectric parameters of NH and N1NH crystals at room temperature. It was clear that dielectric constant is higher around lower frequency and lower for higher frequency region due to contribution of various polarizations that depends on frequencies. The values of dielectric constant are 906 and 1096 for NH and N1NH crystals respectively. The higher value of nickel doped N1NH crystals may be due to the excitation of dipole orientation and polarization occurred in doping process and some significant loss of polarization made coincidence in values of dielectric constant at higher frequencies. Similar results for cupper chloride and zinc nitrate doped ninhydrin crystals were observed in the literature[9,10]. The inherent dissipation of electromagnetic energy can be quantified through the values of dielectric loss and which was also found to be decrease while frequency is increases for both crystals from Fig. 7(b). Grain boundaries of nickel doped N1NH crystals played energetic role in enlighten the dielectric loss values around low frequencies but less dielectric loss at high frequencies designates about minimum defects of crystals and hence both crystals could be better materials in device fabrication for microelectronics industry[14-18].

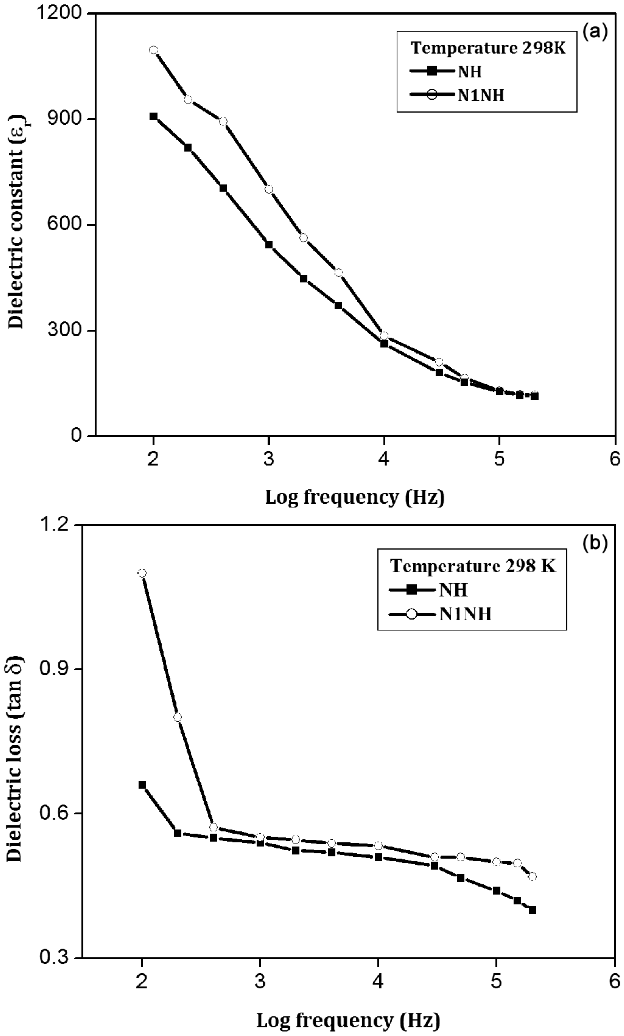

Fig. 7 — Variation of (a) dielectric constant and (b) dielectric loss with frequency for room temperature.

3.7 Nonlinear optical studies

The powdered sample of NH and N1NH were exposed to high intense laser light[19]. From the studies, it was found that the SHG efficiency of NH and N1NH samples are 1.28 and 1.47 respectively and both are comparable to potassium dihydrogen phosphate (KDP). The SHG efficiency of nickel doped ninhydrin is enhanced due to the incorporation of nickel ions and their effective electron-phonon interaction in the crystal lattice[7-10].

3.8 Antifungal activity

The antifungal study was done against two fungus species such as *Aspergillus niger*, *Aspergillus flavus*. The images of this test for pure NH and nickel doped N1NH presented in Fig. 8. Standard Nystatin, NH and

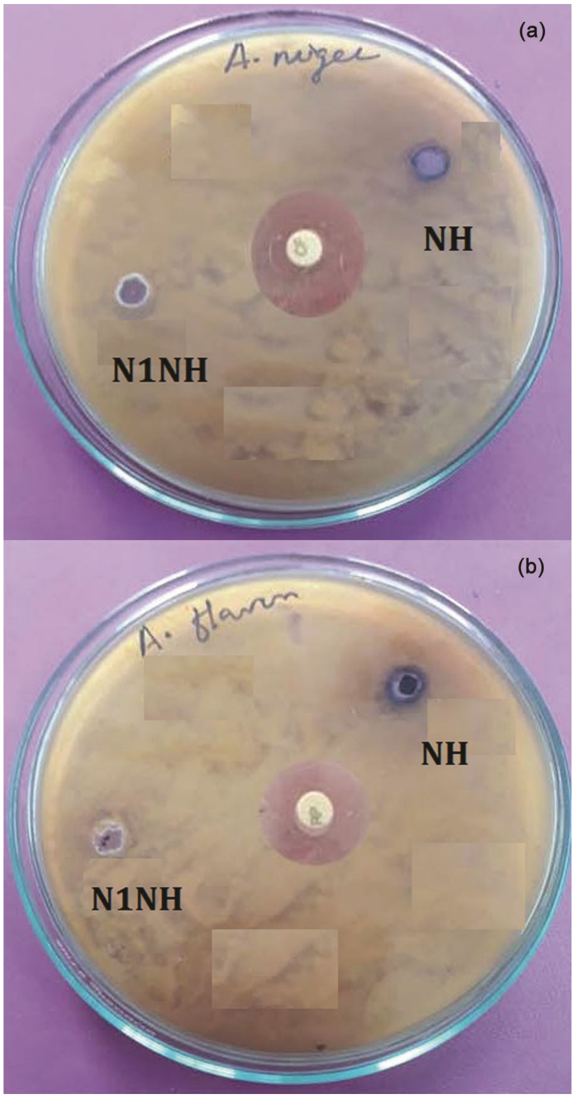

Fig. 8 — Antifungal activity of NH and N1NH against *Aspergillus niger, Aspergillus flavus*.

N1NH zone of inhibition is 21, 7 and 9 mm for *Aspergillus niger*. Standard Nystatin, NH, N1NH zone of inhibition is 18, 6 and 7 mm for *Aspergillus flavus*. From the studies inhibitory excellence against the fungus is good for N1NH sample than pure NH sample due to fusion of few nickel ions and their toxic effect around cell membranes of the microbes. The nickel drills into the cell membrane and enhances the inhibition rate due to its cytotoxic behavior[20]. Similar results for copper nitrate doped ninhydrin crystals (measurement of inhibiting zone is 11 mm for *Aspergillus flavus,* 12 mm for *Aspergillus niger*) and for cadmium nitrate doped ninhydrin crystals (inhibition area is 12 mm for *Aspergillus flavus*, 15 mm for *Aspergillus niger)* were observed in the literature[8]. This study confirms the co-existence of antifungal activity in NH and N1NH single crystals which can be used in many agriculture, medicine and forensic applications[17].

4 Conclusions

The pure ninhydrin and nickel doped ninhydrin single crystals were grown by conventional method. The powder XRD studies show that both crystals possess the monoclinic crystal structure with non-centrosymmetric space group ($P2_1$). The functional groups of the pure ninhydrin and nickel doped ninhydrin crystals were found from FTIR spectrum. The EDX analysis provides the elemental composition of pure ninhydrin and nickel doped ninhydrin single crystals. Micro hardness measurements imply that the pure and nickel doped ninhydrin comes under the soft materials category and it is noticed that the nickel improved the hardness which indicates the importance of doping in mechanical stability of optical applications. The thermal studies show that decomposition temperature is higher for nickel doped ninhydrin crystal sample than pure ninhydrin crystal sample. Thus, the doping metals could enhance the thermal property of organic materials. The low value of dielectric parameter is essential application for the microelectronics industry and the same observed in pure ninhydrin and nickel doped ninhydrin crystal. The second harmonic generation efficiency of the samples is comparable with materials and nickel ion enhanced the efficiency of second harmonic production in pure ninhydrin crystal. The antifungal activity of nickel doped ninhydrin is slightly higher than the undoped ninhydrin. Hence it can be used in many food sciences, medicinal and agricultural applications. From the above results we confirms the nickel doped ninhydrin single crystals gives better nonlinear optical efficiency and recommended to many industrial and optical communication applications.

Acknowledgment

The authors (A. Ponchitra and K. Balasubramanian) are thankful to the Management of The M.D.T Hindu College, Tirunelveli for providing opportunity to access the DST-FIST Sponsored Instrumentation Laboratory and Research facilities of the Physics Department and also thankful to Manonmaniam Sundaranar University, Tirunelveli for their research support.

References

1 Prasad P N & Williams D J, *Introduction to nonlinear optical effects in molecules and polymers* (John Wiley & Sons, New York, USA), 1991.
2 Marcy H O, Warren L F, Webb M S, Ebbers C A, Velsko S P, Kennedy G C & Catella G C, *Applied Opts*, 31 (1992) 5051.
3 Wang X Q, Xu D, Yuan D R, Tian Y P, Yu W T, Sun S Y, Yang Z H, Fang Q, Lu M K, Yan Y X, Meng F Q, Guo S Y, Zhang G H & Jiang M H, *Mater Res Bull*, 34 (1999) 2003.
4 Franken P A, Hill A E, Peters C W & Weinreich G, *Phys Rev Lett*, 7 (1961) 118.
5 Lakshmana Perumal C K, Arulchakkaravarthi A, Rajesh N P, Santhana Raghavan P, Huang Y C, Ichimura M & Ramasamy P, *J Cryst Growth*, 240 (2002) 212.
6 Medrud R C, *Acta Cryst Section B,* 25 (1969) 213.
7 Uma Devi T, Lawrence N, Ramesh babu R, Ramamurthi K & Bhagavannarayana G, *Spectrochim Acta A,* 71 (2009) 1667.
8 Prasanyaa T, Jyaramakrishnan V & Haris M, *Spectrochim Acta A*, 104 (2013) 110.
9 Sreenivasan R.S, Kangathara N, Ezhamani G, Renganathan N G & Anbalagan G, *J Spectrosc*, 2013 (2012) 1.
10 Ponchitra A, Balasubramanian K & Jothi Mani R, *Int J Sci Technol Res*, 8 (2019) 3773.
11 Onitsch E M, *Mikroskopie,* 2 (1947) 131.
12 Wooster W A, *Rep Prog Phys,* 16 (1953) 62.
13 Siva V, Asath Bahadur S, Shameem A, Athimoolam S, Udayalakshmi K & Vinitha G, *J Mol Struct,* 1191 (2019) 110.
14 Rajesh Kanna R, Sakthipandi K, Senthil Kumar A, Dhineshbabu N R, Seeni Mohamed Aliar Maraikkayar S M, Sabah Afroze A, Rajshree Jotania B & Sivabharathy M, *Ceram Int*, 46 (2020) 13695.
15 Kathiravan P, Balakrishnan T, Srinath C, Ramamurthi K & Thamotharan S, *Karbala Int J Moder Sci,* 2 (2016) 226.
16 Sangeetha K, Ramesh Babu R, Bhagvannarayana G & Ramamurthi K, *Spectrochim Acta A*, 79 (2011) 1017.
17 Peramaiyan G, Pandi P, Bhagvannarayana G & Mohan Kumar R, *Spectrochim Acta A*, 99 (2012) 27.
18 Ganesh V, Shkir Mohd, Alfaify S & Mahmoud Sayed, *Optik,* 127 (2016) 5479.
19 Kurtz S K and Perry T T, *J Appl Phys,* 39 (1968) 3798.
20 Revathi V & Karthik K, *Chem Data Collect,* 21 (2019) 100229.