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Effect of Ni^{2+}- ions on the Structural, Optical and Mechanical Properties of Ninhydrin Crystals

A.Ponchitra[1], K.Balasubramanian[2]
1(Department of Physics, Sadakathullah Appa college, Tirunelveli, India)
2(PG & Research Department of Physics, The M.D.T.Hindu college, Tirunelveli, India)

Abstract: *Single crystals of pure and nickel doped ninhydrin were grown by slow evaporation method. Structural characterizations of the grown crystals were carried out by powder crystal X-ray diffraction method. The functional groups were identified by Fourier transform infrared spectroscopy. The percentage of transmittance of the crystal was recorded using the UV-Visible Spectrophotometer. The presence of nickel in the doped crystal was confirmed by Energy Dispersive X-ray analysis. The mechanical strength of the crystal was found out using Vickers micro hardness test. The second harmonic generation efficiency was measured by powder Kurtz method.*
Keywords: *FTIR analysis, Mechanical properties, Organic crystals, SHG test, X-ray diffraction.*

I. Introduction

The search for new organic materials with high optical nonlinearity is an important area due to their practical applications such as optical communication, optical computing, laser remote sensing and so forth [1]. Ninhydrin is one of such organic materials, with high melting point and it is a compound with two hydroxyl groups attached to the same carbon atom. It is used to detect ammonia or primary and secondary amines and fingerprints. It is an important analytical tool in various fields including soil biology, chemistry, agriculture, medicine and so on [2]. R.C. Medrud reported the crystal structure of ninhydrin [3]. Uma devi et al., reported the growth and characterization of pure ninhydrin and urea with ninhydrin [4, 5]. T. Prasanyaa et al., reported the antimicrobial activity and second harmonic studies on organic non - centrosymmetric pure and doped (cu^{2+}, cd^{2+} ions) ninhydrin single crystals [6]. Some transition metal ions influence in the habit modification, growth kinetics and the large size single crystals by doping. In the present work, we report the growth of pure and nickel nitrate doped ninhydrin single crystals.

II. Experimental Method

Commercially available organic chemical ninhydrin (AR grade) were used for the crystallization. The crystallization process was carried out by adding ninhydrin in 100 ml of distilled water at room temperature with constant stirring. To grow single crystals of Ni^{2+}: ninhydrin two mole% of nickel nitrate was added to the saturated solution of ninhydrin. Transparent seeds of pure and doped crystals are obtained by nucleation. Then it was selected for further growth. In a span of 45 days, well developed single crystals of pure and nickel nitrate doped ninhydrin (fig. 1 a, b) have been harvested.

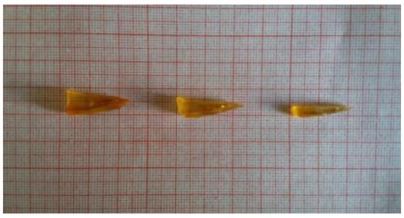
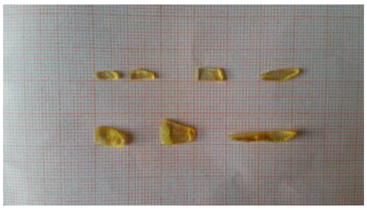

Fig. 1(a) Pure ninhydrin **(b)** Nickel nitrate (2 mole%) doped ninhydrin

III. Results And Discussion

3.1. X-ray diffraction analysis:

A small portion of the single crystals of pure and nickel nitrate doped ninhydrin was crushed and subjected to powder X-ray diffraction analysis. The narrow, sharp and high intensity peaks reveal that the grown crystals were of high degree of crystallinity. The calculated lattice parameter values for pure ninhydrin a =11.3475 Å, b = 6.0450 Å, c = 5.7548 Å, V=390.3477 $Å^3$ and nickel nitrate doped ninhydrin was a =11.3700 Å, b =6.0341 Å, c =5.7503 Å, V=390.0948 $Å^3$. The changes in lattice parameters are due to incorporation of metal ions in the lattice of ninhydrin crystal. The presence of dopants in the crystal may produce lattice strain which leads to change in bond lengths, unit cell parameters and intensity of peaks [6]. The XRD pattern reveals (Fig. 2) that the nickel ions have entered the crystal lattice of pure ninhydrin.

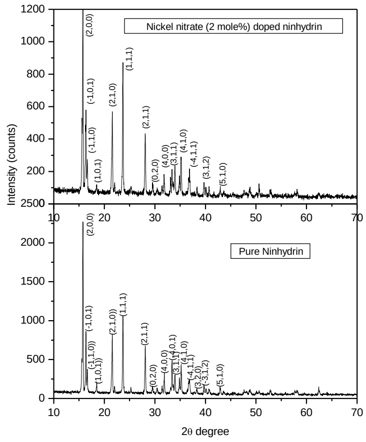

Fig.2. The powder XRD pattern of grown crystals

3.2. FTIR Analysis:

Fourier infrared spectrum was recorded using KBr pellet technique in the range 400-4000 cm^{-1} and the recorded FTIR spectrum is shown in figure 3. Vibrational spectroscopy provides an important tool to understand the chemical bonding. The peaks at 3452.98 cm^{-1}, 3302.83 cm^{-1} are all due to O-H symmetric stretching. The wave number 3088.40 cm^{-1}, 3087.73 cm^{-1} belongs to the aromatic C-H stretching for pure and nickel doped ninhydrin. The recorded peak at 1748.09 cm^{-1}, 1718.86 cm^{-1} is due to carbonyl (C=O) stretching [6]. The skeletal vibrations of aromatic rings are observed at 1591.05 cm^{-1}, 1590.64 cm^{-1} in both pure and doped ninhydrin. The peaks at 1293.13 cm^{-1} , 1256.28 cm^{-1}, 1184.55 cm^{-1}, 1152.37 cm^{-1}, 1012.45 $cm^{-1}$are all due to in plane bending modes of aromatic C-H bonds. The out of plane aromatic C-H bond is observed at 740.74 cm^{-1}, 740.13 cm^{-1}.

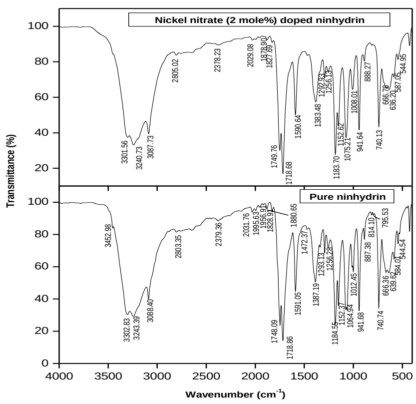

Fig.3. FTIR spectra of grown crystals

3.3. UV-Visible analysis:

The UV-Visible spectrum gives information about the structure of the molecule that the absorption of UV and visible light involves in the promotion of electrons in σ and π orbital from the ground state to higher energy state. The UV transmission spectrum of grown samples is shown in figure 4. The determination of UV transparency and cutoff wavelength is very important since these crystals are mainly used in optical application. The lower cutoff wavelength is found to be 303 nm and upper cutoff wavelength is 430 nm. Between 430 and 1100 nm, there is no absorption of wavelength which is clearly indicates that grown crystals can be used as window material in optical instruments. The small peak at 339 nm is due to n- π* transition [6]. The band gap was found to be 2.8 eV.

Department of Physics, St. John's College, Palayamkottai-627 002, Tamilnadu, India. DOI 10.9790/4861-1700203105108

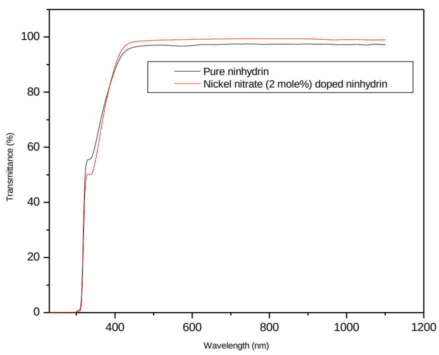

Fig. 4. The UV-Visible transmittance spectrum of grown crystals.

3.4. EDAX Analysis

The EDAX has been performed to identify the elements present in the crystals [7]. The EDAX spectrum of nickel nitrate doped ninhydrin is shown in fig.5. From the analysis it is found that 0.19 weight% of nickel is incorporated into the interstitial sites of the ninhydrin crystals.

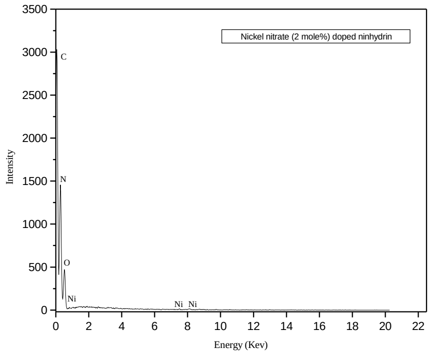

Fig.5. EDAX spectrum of Nickel nitrate doped ninhydrin samples

3.5. Microhardness studies

Hardness is one of the important mechanical properties to determine the plastic nature and strength of a material. The hardness number was calculated using 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. The plot between hardness number and load is shown in fig 6. A rise in the hardness value was observed for pure and nickel doped ninhydrin crystals. By plotting log p versus log d, the value of the work hardening coefficient n was found to be greater than two for pure and nickel nitrate doped ninhydrin crystal. Onitsch states that the values 1.0<n<1.6 for hard materials and n>1.6 for soft materials [8]. Hence, it is concluded that pure and nickel nitrate doped ninhydrin crystals are also soft materials.

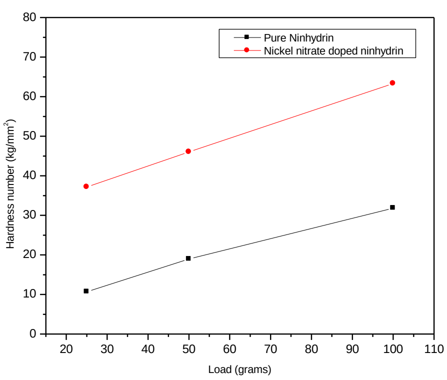

Fig.6. Plot of hardness vs load for pure and nickel doped ninhydrin crystals.

3.7. Nonlinear optical studies:

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The study of nonlinear optical conversion efficiency was carried out using the modified experimental setup of Kurtz and Perry [9, 10]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm, with input energy 0.701 Joule with a repetition rate of 10 Hz was used. The grown single crystal of ninhydrin was powdered with a uniform particle size and then packed in a micro-capillary tube of uniform bore and exposed to collect the intensity of 532 nm component and to eliminate the fundamental frequency. It was found that the efficiency of nickel doped ninhydrin crystal is 1.56 times greater than KDP, where as the efficiency of pure ninhydrin is 1.28 times greater than KDP. The SHG efficiency of nickel doped ninhydrin was slightly enhanced due to the incorporation of metal ions in the crystal lattice.

IV. Conclusion

Pure and nickel nitrate doped ninhydrin crystal were successfully grown using slow evaporation method. The powder XRD studies show that there is a small variation in lattice parameter values because of the contribution of metal dopants. FTIR spectrum gives the various functional groups present in the structure. Optical transmission studies confirm that transparency of doped crystals is greater than pure ninhydrin in the entire visible region and the band gap energy is 2.8 eV. Micro harness measurements imply that the pure and doped ninhydrin comes under the soft materials category. The SHG efficiency of the pure and nickel nitrate doped ninhydrin samples was found to be 1.28 and 1.56 times that of KDP.

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