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Enhanced Mechanical, Thermal, Photoluminescence, NLO and Antifungal Activities of Magnesium Doped Ninhydrin Crystals

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A normal way of slow evaporation method had been used to preparing pure ninhydrin (PN) and magnesium doped ninhydrin (M1N) single crystals. The research describes the various characterizations of the developed PN and M1N crystals. Monoclinic crystal structure with non centrosymmetric $P2_1$ space group were marked in the developed crystals. Additionally, to find out the various functional groups of the grown PN and M1N crystals Fourier's transformation infra-red studies had been used for this research. Vicker's microhardness tester had been used to identify the strength of the developed crystals. In energy dispersive x-ray analysis the presence of carbon, oxygen and magnesium into the crystal lattice was observed. In connection with this by using thermal analysis the decomposition point of the developed crystals were marked. The photoluminescence study was used to identify the excitation and emission peaks of the grown samples. Conclusively, by powder Kurtz-Perry method the second harmonic generation efficiency had been verified in a greater aspect of this research. The antifungal activity of the PN and M1N crystals was observed against two fungi such as *Aspergillus flavus, Aspergillus niger.*

Keywords: Single Crystals, Structural properties, Thermal analysis, Hardness and Antifungal activity

1 Introduction

In present days, there had been a study described on the synthesis and growth process of non-linear optical (NLO) materials due to the necessity of applications in various scientific areas like optical communication, high-speed optical modulators, high-density optical storage, ultra-fast optical switches and medical diagnostics *etc*[1-3]. The second harmonic generation materials were widely used because of its significant properties like good optical transparency, withstand the high laser intensity, allow phase matching interactions *etc*[4, 5]. Organic materials with aromatic ring compounds keeps delocalized π-electron system and thus, the materials had low mobility, more laser damage threshold, large band gap and more nonlinear optical coefficient. Ninhydrin (indane-1, 2, 3-trione) is basically an indanone class compound, and it is a light yellow colour solid that and it contains two hydroxyl groups they are attached with the same carbon atoms. Ninhydrin reacts with some amino acids it creates violet colour and it was useful in chromatogram field, soil biology, protein analysis and chemistry *etc.*[6-17]. Most of the organic crystals have good nonlinear property but poor mechanical and thermal properties and which may be enhanced using some inorganic compound like divalent and trivalent metals. Magnesium nitrate is an inorganic salt which is taken as the dopant metal. To concentrate in the literature point of view, it was observed that ninhydrin single crystals were developed in 1969 by R.C. Medrud[12]. T. Uma Devi *et al*., stated that the structure and characterization of ninhydrin crystals using slow evaporation method[13]. Copper and cadmium doped ninhydrin crystals also reported in earlier literature and it having good mechanical and NLO properties[16, 17]. Until now, none of the research was focused in 1 mole% magnesium doped ninhydrin crystals. Hence, in this point of view, pure ninhydrin (PN) and magnesium doped ninhydrin (M1N) single crystals were developed by the slow evaporation method. The characterizations of the developed single crystals had been taken and so the structural, mechanical, thermal, photoluminescence, nonlinear optical and antifungal properties were described in this study.

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2 Experimental

2.1 Crystal growth

The method of slow evaporation had been used for preparing the pure ninhydrin (PN) as well as 1 mole% magnesium doped ninhydrin (M1N) crystals using the solute salt namely, ninhydrin ($C_9H_6O_4$) (Himedia AR Grade, India) and magnesium nitrate ($Mg(NO_3)_2.6H_2o$) (Himedia AR Grade, India) and double distilled water had been used as a solvent [6-10]**.** 5 gram of pure ninhydrin was dissolved in 250-300 ml of double distilled water and mixed well using magnetic stirrer machine for 4-5 hrs to get a saturated solution of pure ninhydrin. The saturated solution was filtered using whatmann filter paper and it was placed in a dust free room. Well defined yellow colored crystals were collected after 36-55 days. For the growth process of 1 mole% magnesium nitrate doped ninhydrin crystals, take saturated amount of PN solution and add 1 mole% magnesium nitrate salt. The solution was mixed well using stirrer machine for 4-5 hrs. The saturated solution of M1N was filtered and it was placed in a dust free room. After 45-55 days yellow colored crystals were harvested. The obtained crystals are transparent in yellow colour (Figs. 1(a-b)). The undoped ninhydrin and 1 mole% magnesium doped developed crystals were named as PN and M1N crystals respectively.

2.2 Characterization of pure and magnesium doped ninhydrin crystals

The XRD measurement were carried out on PN and M1N samples at room temperature using Powder X-ray diffracto meter (PAN alytical Xpert-PRO) into monochromatic beam of Cu Kα radiation (1.5406 Å). X-ray diffraction analysis had been tested to know about the system of crystals with lattice parameters. Fourier-transform infrared spectroscopy (FTIR) measurement had been marked using Shimadazu IR Affinity – 1S Model in the wave number level of 4000 to 400cm^{-1}. 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 developed crystals. In the present work, EDAX were performed using INCA Penta FET X3, Oxford instruments model. Microhardness measurement of PN and M1N crystals was calculated by Shimadzu microhardness Tester (HM-200A Series). Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) had been completed by using SIINT 6300 Japan made product. The photoluminescence (PL) measurement was tested for the developed samples used in a Varian Cary Eclipse Photoluminescence spectrometer. The study of second harmonic generation efficiency was calculated using the Kurtz and Perry powder technique. To analysis this, A Q switched high energy Nd:YAG (Quanta Ray model) laser beam of wavelength 1064 nm with input power 1.5 -3 mJ and pulse width 6 ns with a repetition rate of 10 Hz had been used. The developed PN and M1N single crystals were powdered with uniform particle size 100-150 µm and it was filled in a micro capillary tube. It exposes for collecting the intensity of 532 nm. The study of antimicrobial activity was observed using disc diffusion method. The glass wares that were accustomed in the analysis in which that was sterilized at 130°C for 2-3 hours in the beginning level. The test microbes got ready to use a Muller Hinton medium/potato dextrose agar medium and support the development of fungus. The crushed samples of the developed crystals had been dissolved in distilled water. Additionally, the solution had been taken of molar concentration was 40µ/L. The solution was placed on the Petri plates and it contains the media. The petri plates were incubated for 23-24 hours and the inhibition zones were marked.

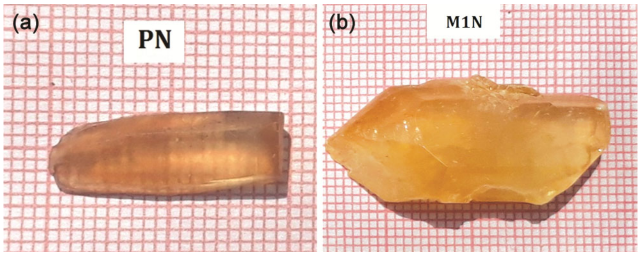

Fig. 1 — a) As grown Ninhydrin crystal, b) magnesium doped Ninhydrin crystal

3 Results and discussion

3.1 Structural Analysis

The powder XRD pattern (Fig. 2) of both PN and M1N crystals finalizes the monoclinic crystal structure and space group ($P2_1$). The XRD data of PN and M1N crystals were almost closely agreed with the standard JCPDS data (JCPDS Card No.31-1811). The lattice parameter was found to be a=11.3475Å, b=6.0450Å, c=5.7548Å and V= 390.3477 Å^3 for PN crystal and for M1N crystal such as, a=11.3286 Å, b=6.0130 Å, c =5.7329 Å and V= 386.1793 Å^3. From the studies, there is no change in crystal structure but very small variations in lattice constants are observed for M1N crystal sample. In this research, a small change in the crystal lattice axes and small range variation in the intensity level of diffraction peaks had been monitored due to the addition of 1 mole% magnesium[12-16]. This study implies that the dopant was well mixed with mother compound of PN crystal. Medrud and Uma devi *et al.,* stated that the lattice parameters of pure ninhydrin was a=11.24 Å, b=6.06 Å, & c=5.77 Å and a=11.3387 Å, b=6.0081 Å, & c=5.7526 Å respectively[12-13]. Prasanyaa *et al*., analyzed that the lattice parameters for copper nitrate and cadmium nitrate doped ninhydrin crystals are a=11.42 Å, b=6.04 Å, c=5.96 Å, a=11.47 Å, b=6.02 Å and c=5.99 Å respectively [16]. From measured from the present investigation and the earlier reported literature, it confirms that there were no modifications in the structure and space group of the crystal but very minute variations in lattice constants.

3.2 FTIR Analysis

FTIR study was used to analysis the molecular structure of crystals. Figure 3 shows the FTIR spectra of PN and M1N crystals. Table 1 focuses the tested functional groups and its corresponding frequencies of the developed crystals. The peaks at 3243 and 3299 cm^{-1} respectively for PN and M1N crystal corresponds to O-H vibration. The recorded peaks around 3088 and 3082 cm^{-1} due to aromatic C-H stretching for PN as well as M1N crystals. The peaks at 1748 and 1746 cm^{-1} was due to carbonyl (C=O) stretching for PN and M1N samples. Due to the skeletal vibrations of aromatic rings the peaks was at 1591 cm^{-1}. It around 1293, 1184, & 1064 cm^{-1} and 1291, 1185, & 1082 cm^{-1} in respectively PN and M1N samples are due to in plane bending modes of aromatic C-H bonds. The out of plane aromatic C-H bond was noted near at 740 cm^{-1} for developed crystals[11-17]. The vibration due to the presence magnesium was observed at range of 641.68, 606.54, 543.85 and 425.92 cm^{-1} respectively for M1N samples. The subsequent FTIR spectrum observation was listed in Table 1 for easy comparison along with available source of literature.

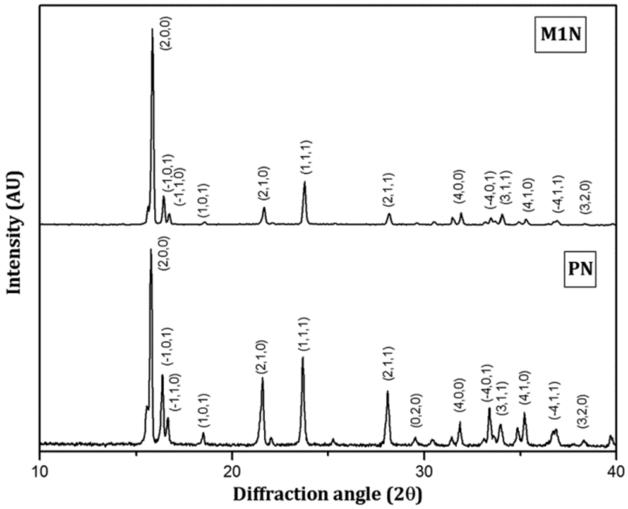

Fig. 2 — Powder XRD patterns of PN and M1N crystals

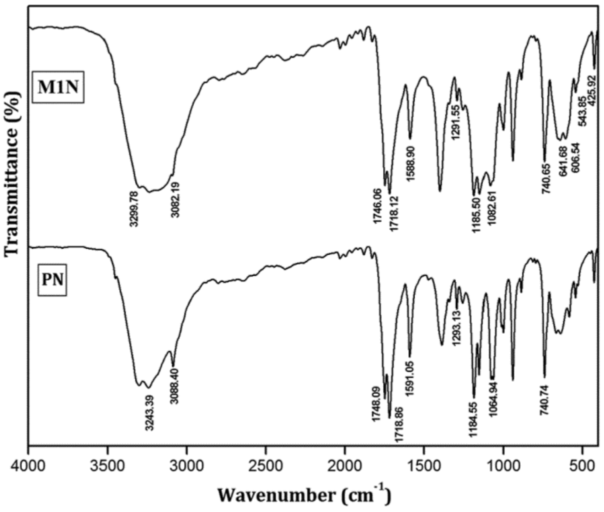

Fig. 3 — FTIR spectra of PN and M1N crystals

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

S.No.	Wavenumber (cm^{-1})				Band assignment
	T. Uma Devi et al. (13)	R.S. Sreeni-vasan et al. (17)	Present work (PN)	Present work (M1N)	
1	3238	3298	3243	3299.78	O-H vibration
2	3089	3087	3088	3082.19	Aromatic C-H stretching
3	1748	1747	1748	1746.06	carbonyl (C=O) stretching
4	1718	1717	1718	1718.12	carbonyl (C=O) stretching
5	1589	1592	1591	1588.90	The skeletal vibrations of aromatic rings
6	1291	1292	1293.13	1291.55	Plane bending of aromatic C-H bonding
7	740	741	740.74	740.65	Out of Plane aromatic C-H bonding

3.3 Hardness Measurement

Mechanical behaviors were depended on the structure and its nature of bonding in the crystalline solids. Microhardness measurements were carried out using Shimadzu microhardness tester fitted with a diamond indentor. PN and M1N crystals were placed on the platform of the microhardness tester and the different loads were applied over a fixed indentation time 10-15 s. The Vicker's hardness number had been manipulated for using the formula $H_v = 1.8544P/d^2$ kg/mm^2, where P is the applied load in kg and d is the diagonal length of the indentation mark in micrometer[18-20]. In Fig. 4, the hardness numbers for both crystals had been increased with high in load and it was also revealed that reverse indentation effect of size. 28% of variation observed in the M1N crystals. Microhardness increases for the liability of magnesium into the lattice site of the M1N crystals.

In this test, the hardness parameters (*i.e.*) work hardneing coefficient(n) was noted in different loads (P). The work hardening coefficient (n) was measured from the *log p* versus *log d* plots. Onitsch stated that a value of n lies between 1 and 1.6 for hard materials and for soft materials it is above 1.6. The coefficient values of PN and M1N was noted as 6.45 and 3.21 as well. So, the developed PN and M1N crystals considered as soft category materials. From the results the magnesium doped ninhydrin mechanical stability slightly enhances compared with undoped ninhydrin. Therefore, it can be used in the device fabrication processing and many optical applications[14]. In the previous literature, Microhardness measurements were calculated using Leitz Weitzler hardness tester and the fixed indentation time 8 s. The work hardening coefficient values for pure ninhydrin, copper and cadmium doped ninhydrin was greater than 2, 1.0 and 1.06 respectively. From the report it was noticed that pure ninhydrin is soft category material, copper and cadmium doped ninhydrin was hard materials[13, 16].

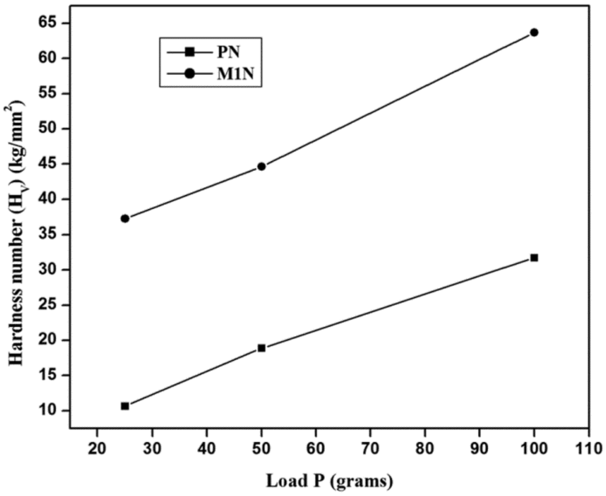

Fig. 4 — Variations of hardness with load for PN and M1N crystal

The value of work hardening coefficient (n) for PN sample is greater (n=6.45) than the literature value (n=2). Generally, the value of "n" depends on some parameters like indentation size, deformation of indenter and generation of dislocation near the indentation site. So, indentation process plays vital role in the value of hardness and work hardening coefficient (n). Variation in the size of the crystal, hardness tester type and its respective indentation process like geometry of the tip, fixed indentation time rate, elastic and plastic deformation characteristics might have been differ and hence the difference may be observed n" values. Nucleation in growth process and multiplication of dislocations will also impact the size of the crystals and hence the value "n". From the results M1N work hardneing coefficient (n=3.21) is slightly different from PN (n=6.45), because of the bonding forces between the molecules in M1N samples are quite strong. From the studies, PN and M1N were soft category materials then, it can be used in opto-electronics and communication applications.

3.4 EDAX Analysis

Figure 5(a-b) describes the EDAX spectrum of PN and M1N crystal. The elemental weight percentage of carbon and oxygen in the developed PN crystals is 59.73, and 40.27 respectively. While, the weight percentage of carbon, oxygen as well as magnesium in the developed M1N crystals was 53.94, 45.78 and 0.28 respectively.

3.5 TG/DTA Analysis

The phase transition and the decomposition points of the developed crystals were noted using thermal analysis. This TGA and DTA curves of PN and M1N crystals were described in Fig. 6. In TGA curve, the basic weight loss of the PN and M1N samples were marked/ noted at the temperature level of 110-163^o C. In the beginning, the endothermic peaks were marked/ noted at 149.66 ^{o}C for PN and 154.86 ^{o}C for M1N crystal samples. The decomposition point for PN and M1N crystals had been observed at 256.91 ^{o}C and 261.51 ^{o}C respectively. The M1N crystal sample decomposition temperature is slightly higher than the

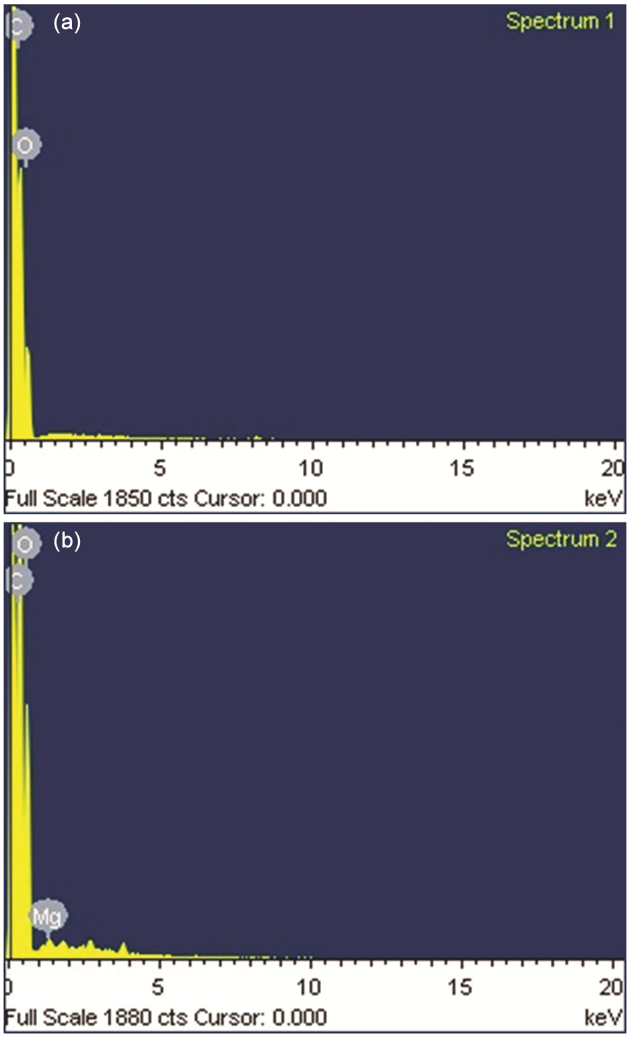

Fig. 5 — (a). EDAX spectra of PN crystal (b). EDAX spectra of M1N crystal

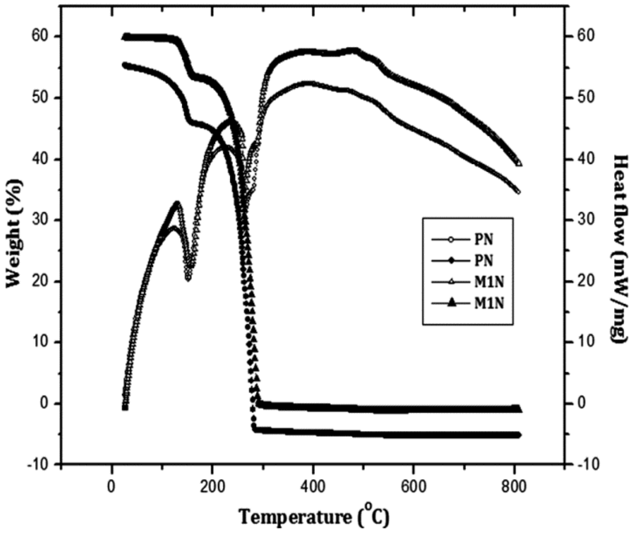

Fig. 6 — TG-DTA curve of PN and M1N crystal

PN samples, because the dopant magnesium ions increase the bond energy. Similarly the decomposition temperature of copper nitrate (249.81 °C), cadmium nitrate (254.31 °C) doped ninhydrin (262.51 °C) crystals are also increases and it was observed in the literature[13, 16].

3.6 Photoluminescence studies

Photoluminescence studies were performed for PN and M1N crystals. From the studies the excitation and emission peaks were observed. For the spectra of PN and M1N drawn in Fig. 7, that would correspond the sample was excited at 360 nm and emitted 411, 438, 490 nm. The results noted that PN and M1N crystal has a blue fluorescence emission. The presence of magnesium may be the reason for the M4N excitation and emission peak range increment. The variation in the excitation peak depends on the size dependent properties, solvent selection, and type of lamp/laser used.

From the literature reports T. Uma devi *et al.*, reported the pure ninhydrin (growth process using constant temperature bath) sample was excited at 290 nm and emission peaks range 450 and 470 nm, so the crystal has blue fluorescence emission[13]. N. Vijayan *et al.*, noted that the pure ninhydrin (growth process using constant temperature bath) excitation range is 400 nm and strong emission peak observed at 423 nm and negligible signature of defect related PL emission observed in the range of 500-700 nm[15]. Hence they are promising materials for the use of sensitizers to other visible luminescent organic/inorganic entities, scintillators, light emitting

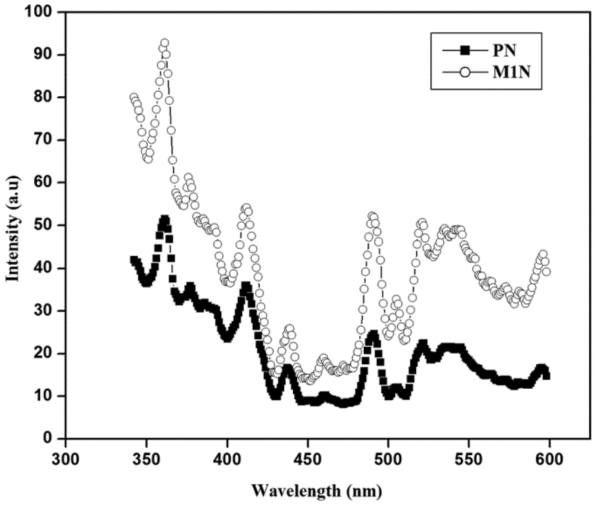

Fig. 7 — Photoluminescence spectra of PN and M1N crystal sample

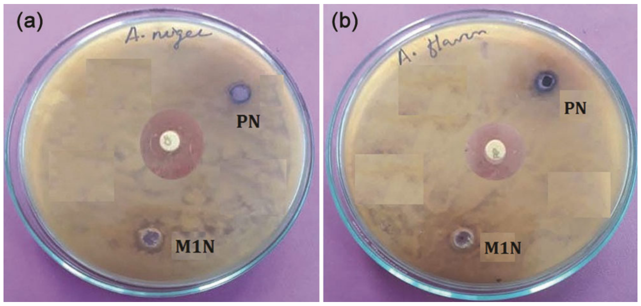

Fig. 8 — (a). Antifungal activity of PN and M1N against *Aspergillus niger*. (b). Antifungal activity of PN and M1N against *Aspergillus flavus*.

diodes, biochemical and medical research fields to analyze the organic compounds[13-16].

3.7 Nonlinear Optical studies

Kurtz-Perry powder technique was concentrated to perform the Second harmonic generation test process[21]. Input energy 0.70 joule was used and the KDP output energy is 8.91 mJ. PN and M1N output energy was 11.49 and 18.1 mJ. From the studies, it was found that the SHG efficiency of respectively PN and M1N was 1.28 and 2.03 times greater than potassium Dihydrogen phosphate (KDP) respectively. The SHG efficiency of magnesium doped ninhydrin was enhanced because of the inclusion in the metal ions of the crystal lattice site. The SHG efficiency of the M1N crystal were depended on the electron-phonon interactions between the magnesium metals and the phonon subsystems[16].

3.8 Antifungal activity

The antifungal study was performed against two fungus like species (*i.e*) *Aspergillus niger, Aspergillus flavus.* Antifungal activity images of pure ninhydrin (PN) and magnesium doped ninhydrin (M1N) presented in Figs. 8(a-b). Standard Fluconazole/Nystatin, PN and M1N zone of inhibition is 13, 7 and 8 mm for *Aspergillus niger.* Standard Fluconazole/Nystatin, PN, M1N zone of inhibition is 12, 6 and 9 mm for *Aspergillus flavus*. The toxic effect of magnesium released in M1N samples and in contact with the cell membranes of the microbes. The inclusion of magnesium ions was the main source for the increasing of antifungal activity. Similarly, the dopant magnesium ion penetrates into the cell membrane and enhances the inhibition rate of M1N samples because of its cytotoxic activities. Similar results for copper and cadmium doped ninhydrin crystals were the zone of inhibition 11 mm, 12 mm for *Aspergillus flavus* and zone of inhibition 12 mm, 15 mm for *Aspergillus niger* were observed in the literature[16]. This research concludes that, the co-existence of antibacterial activity in PN and M1N single crystals could be used in many agriculture, medication and forensic applications[14-16].

4 Conclusion

The optical quality of undoped ninhydrin (PN) and magnesium doped ninhydrin (M1N) single crystals were successfully developed in the slow evaporation method. The powder XRD studies suggested that both crystals had the monoclinic crystal structure with non-centro symmetric space group ($P2_1$). FTIR spectrum confirms the elemental functional groups present in the crystals. The EDX analysis provides the percentage of elements present in the undoped and metal doped crystals. Micro hardness measurements implied that the pure and magnesium doped ninhydrin comes under the soft materials category. It was noticed that the magnesium improved the hardness. The thermal studies of TGA and DTA curve, described that while comparing with the undoped ninhydrin, the magnesium doped ninhydrin crystals were increased in the decomposition temperature. Photoluminescence studies shows that the emission peak observed near 411, 490 nm so the pure and doped samples were blue fluorescence emission. So it can be used in scintillators, light emitting diodes, biochemical and medical research fields. The SHG efficiency of undoped and magnesium doped ninhydrin was noted as greater than KDP and marked as 1.28 and 2.03. The antifungal activity of magnesium doped ninhydrin was slightly higher than the undoped ninhydrin. To sum up, it could be used in many applications like sciences, medicine and agriculture. From this result, it confirmed that the magnesium doped ninhydrin single crystals give better NLO efficiency and it was recommended to many industrial and optical communication applications.

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