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Structural implications of dopants in *Naga Parpam* – Match 3 analysis with Mg-doped ZnO Nano-Particles and SiO$_2$ doped ZnO – Delivery of drugs

V. Saraswathi[1], R. Ramasamy[2], R. Ramanathan[3]

[1]Department of Physics, Saranathan College of Engineering, Trichy-620012, India; [2]Department of Physics, National College (Affiliated to Bharathidasan University), Trichy-620001, India; [3]Department of Physics, Kulithalai Government arts College (Affiliated to Bharathidasan University), Kulithalai-639120, India.

ABSTRACT

Introduction: *Naga Parpam* is being used as a medicine in Siddha, which is a Zinc Oxide based nanoparticle. Detailed analysis of *Naga Pa*rpam was done which shows Mg, Si and K as dopants. Photoluminescence study was also conducted which shows a peak at 649 nm.

Aim and Objective: It is important to analyze due to which dopant this has occurred and hence two separate studies, Mg-doped ZnO and SiO$_2$ doped ZnO were conducted. PL studies done on SiO$_2$ doped ZnO shows significant peaks at 380nm and 649nm. Further, PL studies on Mg-doped ZnO shows a small peak at 381nm and two significant peaks at 640nm and 648nm.

Result: Though the peak at 380nm is the characteristic peak for ZnO, when it is doped with Mg, the PL shows only a small peak. This shows the structural implications of the dopant and Match 3. XRD analysis showed secondary peaks for Naga Parpam and Mg-doped ZnO but not for SiO$_2$. Match 3 analysis showed SiO$_2$ doped ZnO and ZnO has a hexagonal structure and Si has a cubic structure. In *Naga Parpam*, ZnO and Mg have a hexagonal while K and Si has a cubic structure. In the case of Mg-doped ZnO, both ZnO and Mg has a hexagonal structure. Hence in Si-doped ZnO, though there are two crystal systems hexagonal one and the other cubic, there are no secondary peaks observed in XRD, which has been established only from Match 3 analysis. But, in Mg-doped ZnO, it is observed that both ZnO and Mg has a hexagonal structure, from Match 3 analysis. PL analysis shows two sharp peaks at 640 nm and 648 nm and the characteristic peak of ZnO, which is the main constituent of the material is suppressed.

Conclusion: It is concluded that when the dopant changes its characteristic structure to that of the bulk material, in PL analysis, the bulk material characteristics are suppressed. This may be the mechanism for mimicking the molecule and hence, this analysis may be a potential contender for drug delivery.

Key Words: XRD, Match 3 Software, Nagaparpam, PL Spectra

INTRODUCTION

Metal metabolisms in the human system play an important role and are involved in essential bio functions. Some of the shifts in metal metabolism are specific in which positive and negative balances are observed for different pathologies. Zn plays an important role in mental balance in the body. For example, in cancerogenesis, there is depletion of Cu, Fe and Mg, and there is the accumulation of Zn and Mn and in diabetes, there is depletion of Cu, Mn and Cr; and there is the accumulation of Zn, etc. The correction in the concentration of these metals results in a therapeutic effect.[1] The complex compounds of biometals with different types of drugs are the considered most promising tool for introducing the required metal into the body. The important reason for choosing ZnO nanoparticles for use in cancer is the deep-rooted favourable cytotoxicity against cancer cells in the living organism. ZnO nanoparticles show a symptom of a high degree of cancer cell selectivity with the ability to excel the therapeutic indices of some commonly used chemotherapeutic agents in living cells.[2,3]

ZnO materials show different properties when it is doped. Hence they show well known structural and optical properties. Literature survey shows that depend upon the dopant nature ZnO shows a unique PL emission peak. These PL

emissions paved the path for optical amplification by tuning the bandgap of the material.[4] But it is not an easy task to distinguish whether PL emission arises due to the chemical or structural characteristics of the doped material. In general PL spectra show two emission region: one at UV region(Near Band Emission-NBE), and second at visible region(Deep Level Emission-DLE).[5] In some material DLE peak dominates and in few samples it is weak. The UV region is ascribed to be arises from radiative recombination of impurity- bound electron-hole pair and it is dominant in most of the sample. Normally the deep level emission arises due to the various defects in the ZnO. The visible region emits different colours and the intensity of the emission differs based on the morphology of the sample. Generally, blue, green luminescence emission is common in the visible region.[6] But yellow and red luminescences are rare to appear. These may be due to the increased in the oxygen and surface defects.

Naga Parpam is a Siddha formulation which contains ZnO as the main component. Standardization for *Naga Parpam* was carried out and in the XRD secondary peaks were observed and the EDAX shows the presence of Zn 34.74%, O 60.78%, Mg 0.93%, Si 3.18% and K 0.36% by weight. Further PL studies were also conducted which shows a broad peak at 525 nm and a small peak at 649 nm. The peak at 649 nm was attributed to the presence of Si.[7] ZnO was doped with SiO_2 and its physicochemical properties were analyzed.[8] Its PL characteristics shows a peak at 649 nm which was attributed to the presence of Si.[9] But, *Naga Parpam* has Mg also and the effect of doping Mg with ZnO was also analyzed and its PL spectra show two sharp peaks at 640 nm and 648 nm.[10]

Doping with Mg ions inside the ZnO matrix enhances the photocatalytic and antibacterial efficacy.[11] Further, specific species of bacteria were analyzed for antibacterial property which also shows that the sample has a single phase.[12] Calcinations of the polymer precursor, which is Mg-doped ZnO at 650 °C gives particles causes shrinkage of lattice parameter c. Further, Mg doping shifts the absorption onset to blue (360–338 nm).[13] Hence, it is very important to analyze the effect of dopant material in ZnO, since, the doping of either Si or Mg, or both Si and Mg as in the case of *Naga Parpam* shows redshift around 650 nm. It is important to analyze the importance of secondary phases which arise due to the presence of dopants like Si and Mg in the medicine *Naga Parpam*. Already characterization has been done in the case of *Naga Parpam*, SiO_2 doped ZnO and Mg-doped ZnO has also been analyzed. Hence, in the present work, Mg is doped with ZnO and characterized. Further, structural analysis is made using Match 3 software for *Naga Parpam*, SiO_2 doped ZnO and Mg-doped ZnO. Comparison of EDAX of the samples is shown the Table 1.

MATERIALS AND METHODS

Synthesis and characterization of *Naga Parpam* can be seen in our previous paper.[7] Synthesis and characterization of SiO_2 doped ZnO can be seen in our previous papers.[8,9] Synthesis and characterization of Mg-doped ZnO can be seen in our previous paper.[10]

Software used for analysis: Match 3 software used to analyze the result of XRD.

RESULTS

XRD (Structural Analysis)

The XRD graph is shown in **Figure 1** for all the combinations. The presence of the secondary peaks in *Naga Parpam* and Mg-doped ZnO is already reported. The Silicon is present without secondary peaks also reported. The XRD Match 3 software is used to study the phase change. In SiO_2 doped ZnO, the ZnO forms the wurtzite hexagonal phase and Silicon present in the Cubic phase and the result are tabulated in **Table 2**. Hence due to Si doping, the disruption of the hexagonal structure has taken place which has changed the optical property of the material. In *Naga Parpam* the elements present are Zn, Mg, Si, K. Mg, which is present as MgO, which has a cubic structure, has changed its structure to hexagonal structure, which is a major element in *Naga Parpam* and it is tabulated in **Table 3**. But Si and K disrupt the structure due to that secondary peaks are present and they present in the cubic phase itself. In Mg-doped ZnO secondary peaks are and the crystal structure changed to hexagonal[7] and shown in **Table 4.**

PL Studies: In SiO_2 doped ZnO the PL spectra **(Figure 2)** shows the basic (i) strong near band edge (NBE) emission located in UV region at 380 nm and (ii) weak deep emission(DLE) at 432 nm, 466 nm and a green peak at 536 nm. In *Naga Parpam* the PL (**Figure 3**) shows the green peak (DLE) at 525 nm. In Mg-doped ZnO the PL spectra (**Figure 4**) shows a weak peak at 381 nm (NBE). The emission peaks observed in all the samples in the UV region and up to the green range in the visible range are the characteristic peaks of ZnO. In all the samples the last peak is observed in the red emission region. (i) SiO_2 doped ZnO shows peak at 649 nm, (ii) *Naga Parpam* at 649 nm and, (iii) Mg-doped ZnO at 640 nm and 648 nm which arises due to oxygen vacancies. The intensity of the red peak of SiO_2 doped ZnO and *Naga Parpam* is small and for Mg-doped ZnO it is maximum. Si disrupted the structure but there is no phase change and in Mg-doped ZnO the Mg disrupted the structure and there is a phase change for Mg hence, the intensity is maximum.

PL analysis and the formation of peaks are discussed in our previous papers.[4,6,7] In this paper, from Match 3 analysis,

some important things are noted. Firstly, due to doping of either Si or Mg, peaks at around 640 nm are observed. This is the case of *Naga Parpam* also. Further, the natural orientation of the crystal structure for ZnO is hexagonal and in all the three samples, *Naga parpam*, SiO_2 doped ZnO and Mg-doped ZnO the hexagonal structure is preserved. But, from XRD analysis, secondary peaks are seen in the case of *Naga Parpam* and Mg-doped ZnO. No secondary peaks are observed in the case of SiO_2 doped ZnO. Hence, from XRD analysis alone, it will be seen that SiO_2 which has a cubic structure has gone into the structure of ZnO, which is the major constituent without disrupting the structure. But, in that case, redshift, the peak near 640 nm cannot be explained. But, from Match 3 analysis, it is clear that Si has a cubic structure and ZnO has a hexagonal structure. Further, the calculated density is high for ZnO, which is the major component for all the three samples. In the case of Mg, which will be in the form of MgO, it also has a natural cubic structure and due to the synthesis method, it changes itself into the hexagonal structure from match 3 analysis. Further, secondary peaks are also observed for both *Naga Parpam* and also Mg-doped ZnO, both have Mg as its component. Further, from the PL analysis, in the case of Mg-doped ZnO, it is clear that the characteristic peak of ZnO has been suppressed and the two peaks which have very high intensity near 640 nm is attributed to the doping of Mg. Further, it is clear that due to the doping of Mg, ZnO loses its identity in the PL spectra and only the dopant or it's oxygen vacancy which is the reason for those peaks gets predominance. Since these peaks correspond to electronic transitions, and when these materials are potential contenders which can be used as drugs. In the case of cancer, there is an accumulation of Zn in the system, but cells lack Zn. This is because; Zn is not recognized by the system. In these cases, Zn cannot be supplemented since; penetration will not be there into the cells. When these drugs are made into nano sizes and introduced into the system, then there will be penetration into the cell but, in this case, also toxicity will be there due to the supplementation of Zn.

DISCUSSION

From the present work, it is observed that when drugs like *Naga Parpam*, which has ZnO and Mg, which are in the hexagonal structure and which has secondary peaks in its XRD, will mimic as some other material and will penetrate the cell since if it is recognized as Zn, then there will be rejected from the cell either due to autoimmunity or due to some defect. But, if the cell does not recognize it as Zn, then it will be accepting it and the problem will be solved. Since the primary Zn peak near 380 nm in PL, studies is itself not present in Mg-doped ZnO and also these are electronic transitions which are present in the sample. Cell penetration depends

on the electronic transitions and this has been a simple way for mimicking substances without harming the whole system or overloading the system with unwanted drugs. Hence, this may be the model for drug delivery also, which requires further studies.

CONCLUSION

Mach 3 analysis shows the structural analysis from XRD for the three samples, *Naga Parpam*, SiO2 doped ZnO and Mg-doped ZnO, from which it is concluded that structural analysis plays an important role in the PL analysis also since PL spectra show the electronic transitions in the material. Further, from this analysis, it is concluded that the electronic transitions in the material are due to the structure of the material and also in the present study it is concluded that when doping Mg with ZnO, it is observed that both MgO and ZnO has a hexagonal structure and the characteristic peak of ZnO is insignificant while the redshift becomes more predominant in the PL spectra. Hence, this may be the mechanism of action of drugs as in the case of *Naga Parpam*, which mimics some other electronic transition for penetrating the cells. This model may explain the action of drugs and *Naga Parpam* may be a potential contender for supplementation in cancer.

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Table 1: Tabulation showing the presence of elements in SiO$_2$ doped ZnO NP and *Naga Parpam* and Mg-doped ZnO

Elements	SiO$_2$ doped ZnO NP		Naga Parpam		Mg-doped ZnO	
	Weight %	Atomic %	Weight %	Atomic %	Weight%	Atomic%
Zn	77.04	45.27	67.4	34.74	72.42	39.58
O	22.57	54.20	28.86	60.78	26.00	58.09
Si	0.39	0.53	2.65	3.18		
Mg			0.67	0.93	1.58	2.32
K			0.42	0.36		
TOTAL	100	100	100	99.99	100	100

Table 2: Match 3 for SiO$_2$ doped ZnO

| Formula sum	ZnO(95.4 %)	Si (4.6 %)
Entry number	96-900-4180	96-900-3103
Figure-of-Merit	0.881547	0.459944
Total number of peaks	32	24
Peaks in range	32	24
eaks matched	17	06
Intensity scale factor	0.64	0.02
Space group	P 63 mc	F d-3m
Crystal system	Hexagonal	Cubic
Unit cell	a= 3.2533 Å, c= 5.2073Å	a= 5.4304 Å
Calc.density	5.663 g/cm³	2.330 g/cm³

Table 3: Match 3 for Nagaparpam

Formula sum	Zn O (39.4 %)	Mg (5.1 %)	K (2.0 %)	Si (1.6 %)
Entry number	96-900-4180	96-901-3062	96-901-1973	96-152-6656
Figure-of-Merit	0.890621	0.804144	0.6638782	0.501574
Total number of peaks	32	32	24	22
Peaks in range	22	22	14	9
Peaks matched	22	18	4	4
Intensity scale factor	0.64	0.05	0.02	0.01

Table 3: *(Continued)*

Formula sum	Zn O (39.4 %)	Mg (5.1 %)	K (2.0 %)	Si (1.6 %)
Space group	P 63 mc	P 63/m mc	I m -3 m	F d -3 m
Crystal system	Hexagonal	Hexagonal	Cubic	Cubic
Unit cell	a= 3.2533 Å c= 5.2073 Å	a= 3.2485 Å c=5.2772 Å	a= 4.9360 Å	5.3810 Å
I/Ic	6.47	4.14	9.55	4.86
Calc. density	5.663 g/cm³	1.674g/cm³	1.080 g/cm³	2.394 g/cm³

Table 4: Match 3 for Mg doped ZnO

Formula sum	Mg(64.0 %)	ZnO(36.0%)
Entry number	96-901-3062	96-210-7060
Figure-of-Merit	0.810618	0.808555
Total number of peaks	32	36
Peaks in range	32	36
Peaks matched	18	14
Intensity scale factor	0.38	0.35
Space group	P 63/m mc	P 63/m mc
Crystal system	Hexagonal	Hexagonal
Unitcell	a= 3.2485 Å, c= 5.2772Å	a= 3.2417 Å c= 5.1876Å
Calc.density	1.674 g/cm³	5.725 g/cm³
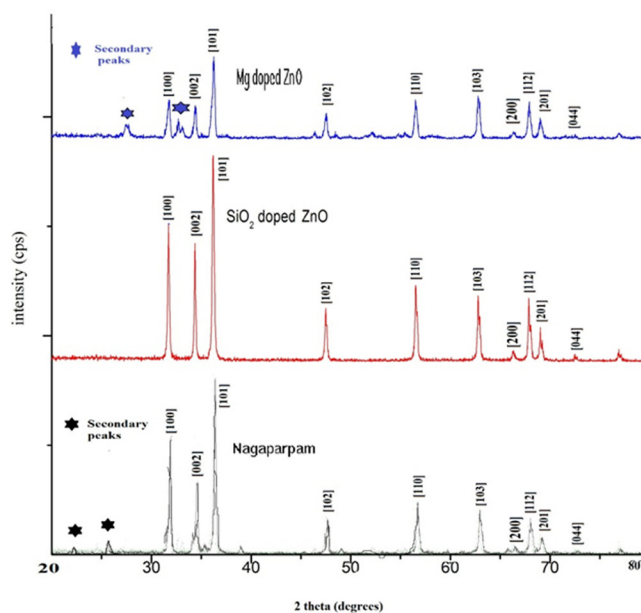
Figure 1: XRD graph for *Naga Parpam*, SiO$_2$ doped ZnO, Mg doped ZnO
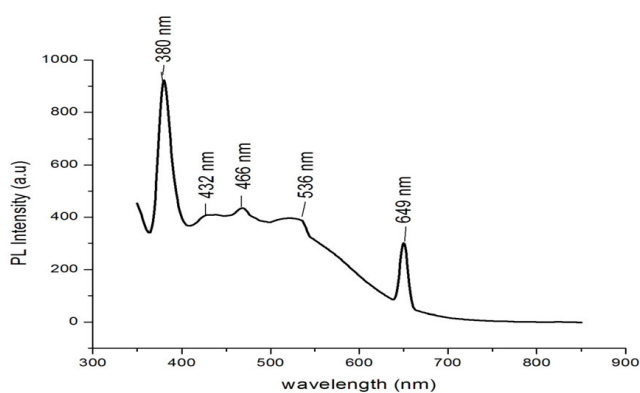
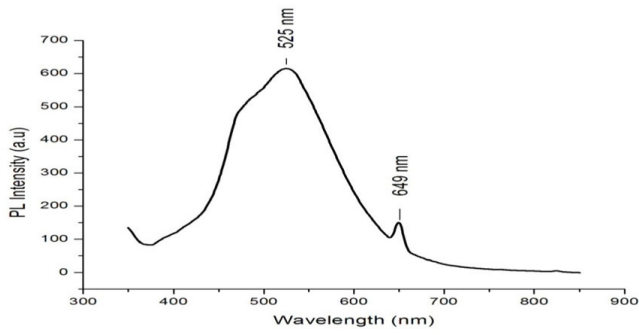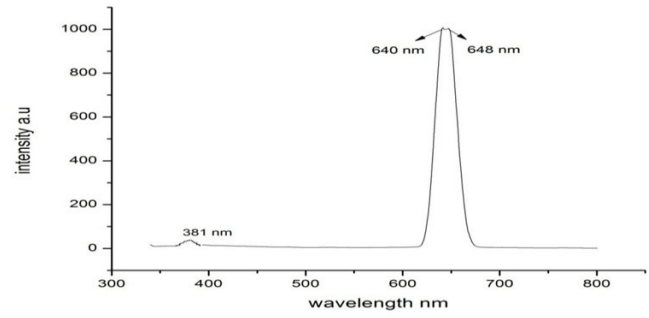**Figure 2:** PL spectra of SiO2 doped ZnO

Figure 3: PL spectra of Naga Parpam

Figure 4: PhotoLuminescence for temp 400 °C