

Correlating Spectral Variations of Malachite Green with Organic Co-Precursors in TEOS Silica Hybrid Glasses

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Abstract— Malachite Green (MG) doped inorganic-organic hybrid glasses are synthesized using monomers methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA) and inorganic precursor tetraethylorthosilicate (TEOS) by sol-gel technique. Various spectral properties of MG in these hybrid matrices are evaluated and compared to those in silica glass to determine their utility as optical material. Inclusion of HEMA in matrix reduced fluorescence quantum yield and lifetime; presence of collisional quenching as dominant non-radiative process considered responsible for it, whereas presence of MMA in matrix improved fluorescence quantum yield, lifetime and non-radiative transition probability, which is attributed to reduction in free space and immobilization of dye molecules within rigid pores of silica matrix. Luminescent properties in the hybrid matrix with MMA and TEOS are comparable to those in silica matrix.

Index Terms— Malachite Green, hybrid matrices, quantum yield, lifetime, Sol-gel glass, Luminescence Properties, TEM

1 INTRODUCTION

CHARACTERISTICS of dye molecules embedded in solid matrices are governed by the nature of matrices. Changes in nature of matrix can shift peak absorption and luminescence wavelengths, induce variations in fluorescence lifetime and modify photostability of the embedded dye.[1]. Therefore, comparison of photo-physical processes of a dye embedded in matrices of varied constituent and concentration can provide valuable information on the influence of host matrix on dye properties including host's feasibility with respect to application as luminescence conversion system[2], solid state dye laser material[3,4], nonlinear optics etc.. To obtain optimal optical, thermal and mechanodynamical properties of matrices for aforementioned applications the photo physical and photochemical property of the trapped dye requires proper adjustment of matrix structure and composition [5].

In context to the above discussion this paper reports a quantitative study of spectroscopic properties of Malachite Green (MG) (oxalate) doped in inorganic – organic hybrid glasses in an effort to develop a dye-host combination suitable for optical application. The spectroscopic properties in hybrid glasses are further compared to those in in-organic silica glass (reported in this work). Based on absorption recovery time study of the $S_0 \rightarrow S_1$ transition in MG doped xerogel around 620 nm, Canva et.al[6] predicted potential optical applications for MG doped xerogel. However, reported investigations on absorbance and luminescence of MG doped in different inorganic matrices [7-9] do not present detailed quantitative analysis of spectroscopic properties required to characterize optically MG doped materials. Such characterization of MG doped in inorganic-organic hybrid matrices are not known to be reported.

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In synthesis of organic compound based optical materials usually (polymethyl methacrylate) (PMMA) is preferred because of its high transparency in visible region of the spectrum, high resistance to radiation, and compatibility to many organic compounds. But in preparation of inorganic -organic glasses for the present study organic monomers methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) are taken because copolymerization of methyl methacrylate (MMA) with other monomers like 2-hydroxyethyl methacrylate (HEMA) can lead to synthesis of materials with different properties. Besides, in hybrid matrices organic polymers/monomers combine with inorganic glasses and have contribution from both components in their properties viz. flexibility, high optical uniformity, and low shrinkage of an organic component and rigidity, hardness, and thermal stability of the inorganic glasses [10].

2 MATERIALS AND METHODS:

2.1 Synthesis of glass:

Synthesis of inorganic and inorganic-organic hybrid glasses doped with 1×10^{-5} M of Malachite Green (oxalate) were carried out via 'wet' sol-gel process using acid (dilute HNO₃) catalysts. Concentration of MG was considered with respect to a total mixture of solvents consisting of Methanol, dilute nitric acid (HNO₃), distilled water and 'precursor'. Tetraethylorthosilicate (TEOS) was taken as the precursor in the inorganic M1 glass, whereas in the inorganic-organic hybrid glasses, TEOS mixed with adequate quantity of organic monomers viz. Methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) were used. The organic monomers and their quanti-

ties used in the synthesis of three hybrid glasses are presented in Table-1. In synthesis of the glasses 2ml of 'precursor' with requisite proportion of the monomers was mixed with a previously prepared solution of Malachite Green in 10.5 ml mixture of methanol(8.75 ml), distilled water (1.25 ml) and dilute nitric acid (0.5 ml), taken in proportion of 70(Methanol): 10 (H₂O): 4 (HNO₃) parts and stirred in a magnetic stirrer with Teflon coated stirrer bar for 1h. The 2ml precursor constituted 16 parts in a total solvent mixture of 12.5 ml used in each of these preparations. Hydrolysis and polymerization of the 'precursor' solution in methanol under the catalyst action of doubly distilled water and dilute nitric acid results in formation of gel after about 1h of stirring. The gel was then poured into plastic moulds and left to dry and solidify at room temperature (25-27⁰C). With further progress of hydrolysis the gel solidified to form a deep orange coloured stiff hard mass (Xerogel / sol-gel glass) in 48-72 hrs.

Table-1

Constituents quantities in the three inorganic-organic hybrid and one inorganic MG doped glasses

Glass	MG (g)	MG (x10 ⁻³ M)	Methanol (ml)	H ₂ O (ml)	HNO ₃ (ml)	TEOS (ml)	HEMA (ml)	MMA (ml)
TMM1	0.00011	1	8.75	1.25	0.5	1	-	1
THM1	0.00011	1	8.75	1.25	0.5	1	1	-
THMM1	0.00011	1	8.75	1.25	0.5	1	0.5	0.5
M1	0.00011	1	8.75	1.25	0.5	2	-	-

2.2 Instruments and Methods:

A commercial UV-VIS-NIR spectrophotometer (CARY-5E) was used to record the VIS absorption spectra of Malachite Green doped in the inorganic and hybrid matrices in the range 400-700 nm and their corresponding fluorescence spectra were taken in a JY Fluorolog-3-11 spectrofluorometer, excited by 445 nm wavelength of a 450W Xenon lamp, keeping slit widths at 5nm, integration time of 0.1s and step size of 1nm. Fluorescence life time measurements of the same samples at their peak emission wavelength were performed in FLUOROCUBE - a life time measurement system from JOBIN-YVON. The Instrument Response Function (IRF) of the instrument was 1.263ns obtained using LUDOX SM-30 colloidal suspension in water. The excitation source for decay time measurement is a 460nm LED. Transmission Electron Micrographs (TEM) and diffraction pattern were recorded in a JEOL JEM-2100 ultra high resolution Transmission Electron Microscope. The microscope was operated at an accelerating voltage of 200 kV. All measurements and recordings were done in room temperature (25-27⁰C).

3 THEORETICAL CONSIDERATIONS:

Several spectroscopic properties of MG are evaluated from recorded spectra of different glasses synthesized for a comparative analysis described in this paper. Oscillator strength of bands at absorbance maxima are derived from integrated absorption coefficients using the formula

$$f = 4.32 \times 10^{-9} \int \epsilon(\nu) d\nu, \text{ where } \int \epsilon(\nu) d\nu \approx \epsilon(\nu) \times \Delta\nu \dots (1)$$

In Eqn. (1), $\epsilon(\nu)$ is the molar absorption co-efficient at frequency ν (cm⁻¹) and $\Delta\nu$ is the band width at $\frac{1}{2}\epsilon(\nu)$ (FWHM) measured directly from absorption spectra. Molar absorption co-efficient of MG is calculated directly from the absorption profile presented in Fig. 1 using the relation for Absorbance, $A = \epsilon(\nu)lc$ (where l =path length, c =Molar concentration). The absorbance values in Fig. 1 are for identical sample path length (l) of 0.1 cm and MG concentration (c) of 1×10^{-5} M. Beer-Lambert law is obeyed for the given concentration.

The radiative (K_r) and non-radiative (K_{nr}) transition probabilities are calculated using the following relations [11]:

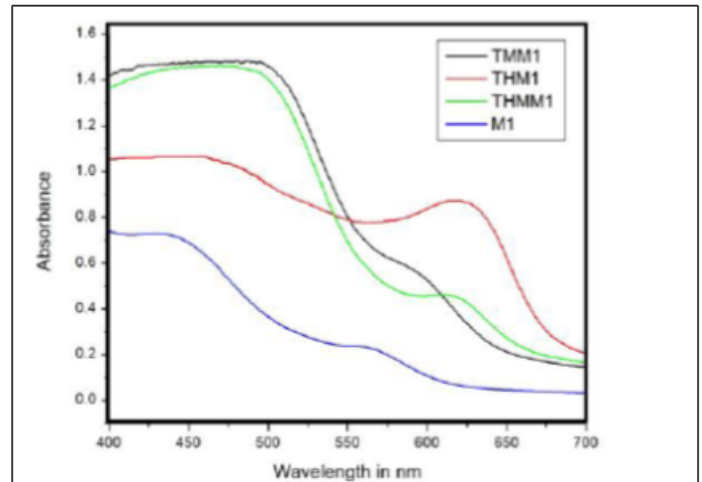


Fig.1 VIS absorption spectra of Malachite Green doped inorganic-organic hybrid (TMM1, THM1 and THMM1) and inorganic (M1) glasses.

$$K_r = \frac{\phi}{\tau} \quad (2)$$

and

$$K_{nr} = \frac{(1-\phi)}{\tau} \quad (3)$$

Where ϕ and τ are measured fluorescence quantum yield (QY) and life time (non-intrinsic), respectively, of MG in the matrices.

Fluorescence Quantum Yield (ϕ) is measured by comparison to a reference fluorophore of known QY using the single point method from the equation [12].

$$\phi = \phi_r \times \frac{I}{I_r} \times \frac{OD_r}{OD} \quad (4)$$

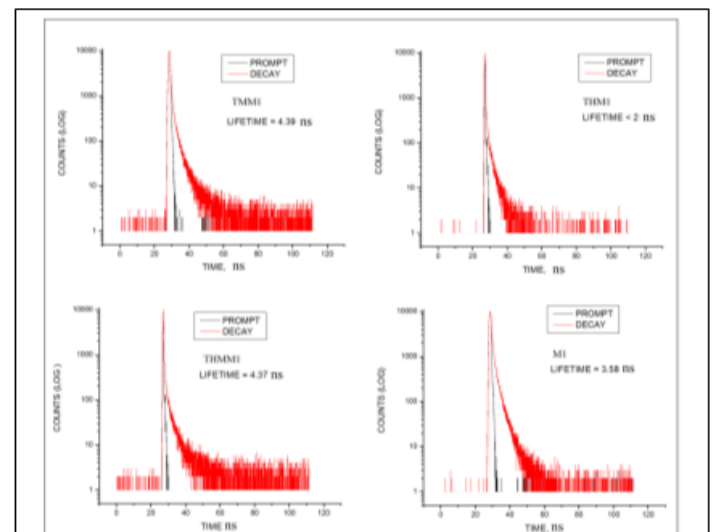


Fig.2 Fluorescence decay curves of Malachite Green doped inorganic-organic hybrid (TMM1, THM1, THMM1) and inorganic (M1) glasses

In Eqn.(4), ϕ_r is the quantum yield of the reference fluorophore.

Riboflavin with $\phi_r = 0.3$ is taken dissolved in ethanol as the reference fluorophore. I is the integrated fluorescence intensity, OD is the optical density. Subscript r refers to the reference fluorophore. Fluorescence life time (τ) of MG in these glasses is estimated by double exponent iteration of the recorded curves given in Fig. 2 above.

4 RESULTS

4.1 Absorption Spectra and Properties:

Absorption spectra of the four glasses are presented in Fig.1. Each spectra has two peaks - one in the blue spectral region and the other in the yellow-red region. The peaks in hybrid matrices are red shifted with respect to peaks recorded in inorganic M1 glass. As absorption maxima in the four matrices lie in the blue spectral region, quantitative analysis of the bands in the blue region is only carried out. The peak absorption wavelength (λ_{abs}), oscillator strength (f), FWHM ($\Delta\nu$) of these bands and the molar absorption co-efficient of MG ($\epsilon(\nu)$) at absorption maxima derived for the four glasses as discussed in Sec.2 are compiled in Table- 2 for comparison. The oscillator strength and molar absorption co-efficient of MG in the hybrid matrices are enhanced with respect to values in inorganic M1 glass, but the corresponding FWHM is increased only in THM1 glass, i.e. the hybrid matrix with 1:1 ml of HEMA: TOES. In presence MMA i.e. in THMM1 and TMM1 glasses the oscillator strength, molar absorption co-efficient and FWHM of the bands are almost equal.

Table-2
Absorption wavelength (λ_{abs}), oscillator strength(f), FWHM ($\Delta\nu$) of band with Abs. Max. and Molar Absorption coefficient($\epsilon(\nu)$) of MG in hybrid and inorganic sol-gel glasses

Glass	MG Conc. ($\times 10^{-5}$) M	Matrix type*	Peak Abs. WL (λ_{abs}) nm	Oscillator Strength(f)	FWHM ($\Delta\nu$) cm^{-1}	Abs. Co-eff ($\epsilon(\nu) \times 10^4$) $\text{M}^{-1}\text{cm}^{-1}$
TMM1	1	T+M	463	5.25	8163	14.9
THM1	1	T+H	448	9.54	21225	10.4
THMM1	1	T+H+M	454	5.05	7956	14.7
M1	1	T	441	3.93	11377	8

*Matrix type:[T=TEOS, M=MMA, H=HEMA]

4.2 Luminescence Spectra and properties:

Luminescence properties calculated using Eqn. 2-4 together with peak emission wavelength (λ_p), effective band width ($\Delta\lambda_{eff}$) of transitions measured from the luminescence spectra presented in Fig. 3 and measured fluorescence lifetime of MG in the inorganic and inorganic-organic hybrid glasses are compiled in Table -3. Large red shifts up to ~ 100 nm in peak emission wavelength and narrower band width of MG transitions compared to those in the inorganic SiO_2 glass are observed in hybrid glasses. Further, its observed that inclusion of monomer HEMA in the SiO_2 in matrix (inTHM1 glass) drastically reduces fluorescence quantum yield, fluorescence life time and increases the non-radiative transition probability compared to SiO_2 matrix. The situation improves with addition of MMA (in THMM1 glass) and in the matrix with MMA + TEOS (in TMM1 glass) fluorescence intensity and quantum yield, lifetime are enhanced and non-radiative transition probability is reduced (compared to SiO_2 matrix).

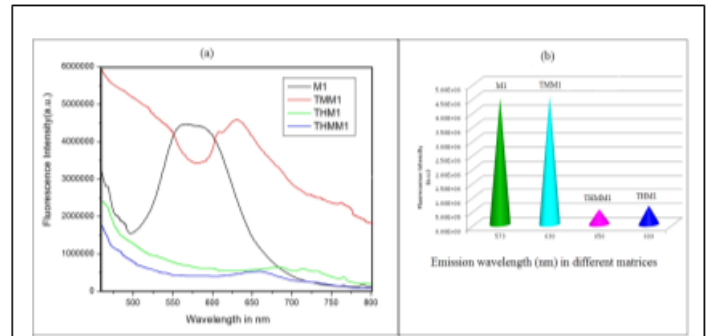


Fig. 3 (a) Fluorescence spectra and (b) relative intensity distribution at peak emission wavelength of Malachite Green doped inorganic – organic hybrid (TMM1, THM1 and THMM1) and inorganic (M1) glasses under 445 nm excitation.

Table-3
Peak emission wavelength (λ_p), Effective band width ($\Delta\lambda_{eff}$), Fluorescence Quantum Yield(ϕ), Fluorescence life time (τ), Radiative transition probability (K_r) and Non-radiative transition probability (K_{nr}) of MG in hybrid and inorganic silica

Glass	MG Conc. ($\times 10^{-5}$) M	Matrix type*	Peak Em. Wavelength (λ_p) nm	Effective Bandwidth ($\Delta\lambda_{eff}$) nm	QY (ϕ)	Life Time (τ) ns	Radiative Trans. prob. (K_r) ($\times 10^3$) s^{-1}	Non-radiative Trans. prob. (K_{nr}) ($\times 10^3$) s^{-1}
TMM1	1	T+M	630	101	0.06119	4.39	0.13938	2.13852
THM1	1	T+H	689	17	6.7E-05	1.78	0.00038	5.6176
THMM1	1	T+H+M	656	49	0.0005	4.37	0.00115	2.28/18
M1	1	T	573	133	0.06045	3.58	0.16884	2.62445

*Matrix type:[T=TEOS, M=MMA, H=HEMA]

4.3 TEM micrographs and diffraction pattern of matrices:

Transmission Electron Micrographs (TEM) and their diffraction patterns of the matrices presented in Fig. 4(a) and 4(b) clearly shows variation in structure with matrix composition. From the radiative properties compiled in Table-3 its evident that the matrix with coarse texture and diffraction pattern of spotless rings (TMM1 glass) is the most rigid among the hybrid matrices. Appearance of TEM diffraction pattern reflects on the phase nature of the specimens. Patterns of micro –crystalline or amorphous matrices like polymers and metallic glasses that lack long – range order in atomic lattice consists of concentric rings [13]. Diffraction ring patterns marked by reflection spots, as in THM1 and THMM1 glasses, often refers to matrices formed by large collection of crystallites with different orientations. The individual reflections from such crystals appear as spots on the rings. Luminescence parameters derived for these two hybrid glasses are not encouraging.

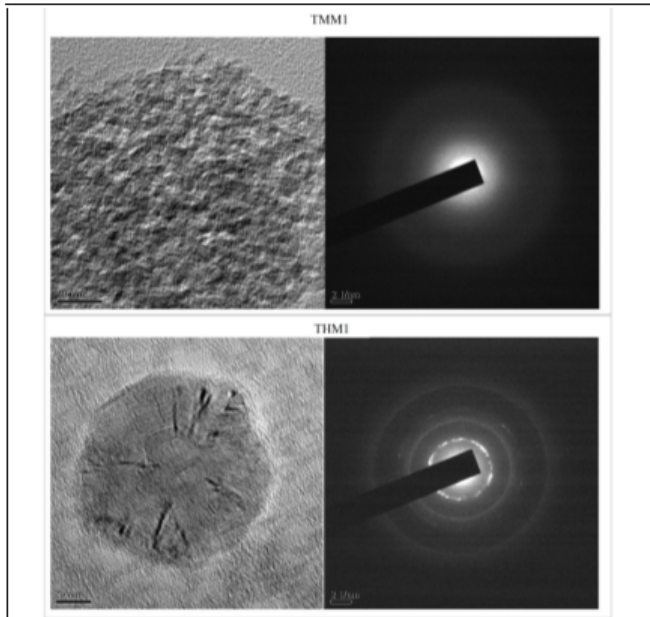


Fig. 4(a) TEM micrographs along with their diffraction pattern of Malachite Green doped TMM1, THM1 inorganic –organic hybrid glasses

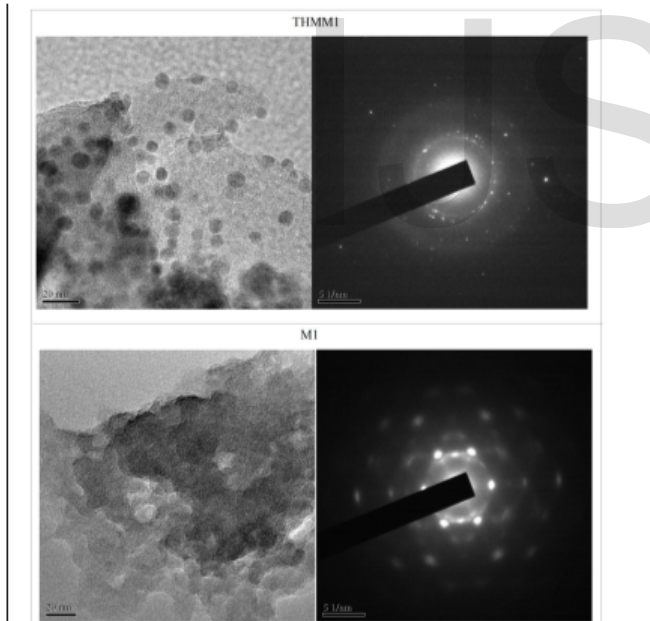


Fig. 4(b) TEM micrographs along with their diffraction pattern of Malachite Green doped inorganic –organic hybrid THMM1 and inorganic M1 glasses

5 DISCUSSIONS:

Malachite Green (oxalate) dye -a member of the Triarylmethane group-is considered a non-fluorescent dye which in non-viscous solvents has a low quantum yield of as low as $\sim 10^{-4}$ [14]. But when it is confined within rigid pores of SiO₂ solid matrix the quantum yield is enhanced $\sim 10^3$ times (Ref. Table-2). This is caused by confinement of the dye molecules within the rigid pores of matrix, which restricts non-radiative routes for deactivation of excited confined molecules and enhances photoluminescence intensity and quantum yield. Rigidity of the pores reduces space for rotational motion of the molecules

and thereby limits non-radiative relaxation channels of excited trapped molecules. Impregnation of PMMA in such SiO₂ matrix further fills up the pores and increases rigidity of matrices by reducing free space within the pores, and eventually the quantum yield [15].

The simultaneous decrease observed in fluorescence lifetime and intensity (quantum yield) of MG in THM1 glass is indicative of the presence of collisional quenching as a dominant non-radiative process [12], where fluorophore de-excites non-radiatively to its surrounding environment via collision with fluorescence quenchers like O₂ (in presence of HEMA in matrix). The collisional quenching rate is defined as $K_c = k_o [C]$, where k_o is related to the diffusivity and the hydrodynamics radii of the reactants and $[C]$ is the quencher concentration [12]. As such, reduction in the quantity of HEMA i.e. $[C]$ (adding equal quantity of MMA) in SiO₂ matrix (as in THMM1 glass) decreases non-radiative transition probability rate and causes improvement in fluorescence quantum yield and lifetime, but the values still remain much smaller than that in SiO₂ matrix.

The slight enhancement in fluorescence intensity and quantum yield in TMM1 glass with respect to SiO₂ matrix is a result of reasons cited in case of 'impregnation of PMMA' in SiO₂ matrix. Observation of a simultaneous decrease in non-radiative transition probability in the glass is indicative of restrictions imposed on non-radiative channels of de-excitation of excited trapped molecules. But, a fluorescence lifetime greater than in M1 glass slightly reduces radiative transition probability in TMM1 glass.

The red shift observed in the peak wavelengths of transition bands in the hybrid matrices (compared to the SiO₂ matrix) may be attributed to the ligand field of the matrices acting on the vibrational levels of the trapped molecules [16]. The different TEM diffraction pattern of the hybrid matrices also infers a variation of field in the matrices that resulted in red shifts of different magnitude.

6 CONCLUSIONS:

Several absorption and luminescence properties of MG were evaluated in inorganic-organic hybrid glasses synthesized with organic monomers MMA, HEMA and inorganic precursor TEOS by the sol-gel technique and studied in comparison to SiO₂ matrix derived from TEOS. The investigation revealed how presence of different monomers in SiO₂ matrices controlled the luminescence properties and hence the efficiency of the matrices either by increasing rigidity of matrix and /or promoting collisional quenching. The quantum yield, fluorescence lifetime of MG evaluated for the MMA-TEOS hybrid matrix (TMM1 glass) were slightly improved compared to TEOS inorganic matrix (M1 glass) and when considered together with their radiative and non-radiative transition probabilities, TMM1 glass emerged as the most efficient amongst the three hybrid matrices considered in the present study. However, conclusive evidence on its utility as optical material can be had only after study of its photostability.

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