Journal of Advanced Scientific Research

Available online through http://www.sciensage.info

ISSN
0976-9595
Research Article

EFFECT OF IMPURITIES ON PHOTO- AND TRIBO-LUMINESCENCE PROPERTIES OF $Mn(Ph_3PO)_2Br_2$ COMPLEX

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ABSTRACT

This current study describes the simple synthesis and characterization of $[Mn(Ph_3PO)_2Br_2]$ complex and find the effect of impurities (HBr and $HgCl_2$) on their optical, structural, photo and triboluminescence properties. Optical properties (absorption and emission) of the complex were recorded using UV-vis and fluorescence spectrophotometer. The functional group and structure of the complex were confirmed through FT-IR and XRD technique. It is observed that the absorption of the synthesized complex exist around 330 nm while when impurities doped into complex, the absorptions were blue-shifted to 350 nm. It is also found that the emission intensity of the synthesized complex is strongly influenced by doping. The photoluminescence emission efficiency of the $HgCl_2$ doped complexes emit much lower than its corresponding undoped and HBr doped complex, which is may be due to the presence of chlorine ions providing more non-radiative decay pathways. Triboluminescence properties of the complex were conducteted by the specially designed drop tower method. This work will be useful in developing organometalic phosphors for various applications like smart sensors.

Keywords: $Mn(Ph_3PO)_2Br_2$ complex, Dopant, Photoluminescence, Triboluminescence

1. INTRODUCTION

Over a century earlier, the researchers found that many organic and inorganic materials emit triboluminescent light. Since that time, scientists have been trying to fully understand and explore this fascinating phenomenon. It has been estimated that 30% of organic complexs and 50% of inorganic complexs are triboluminescent. [1] One of the most distinctive complex properties is the ability to emit light when fraction occurs over the complex [2-6]. Despite this knowledge, all the processes involved in producing triboluminescent emission are still not well understood.

Recently, TL materials have been proposed as smart sensors of structural damage [7, 8]. The majority of the known TL materials do not emit light with sufficient intensity to allow detection with compact and inexpensive detectors. Over the past 40 years some materials have been reported that TL with sufficient intensity for the light emission to be easily observed with the naked eye [9]. Among these materials, divelant manganese complexes $[(Mn(Ph_3PO)_2X_2)$ X= Cl, Br, I] is one of the brightest green TL materials and shows a potential candidate for application to this type of damage sensor [9].

Divalent manganese ions have attracted considerable interest as green or red phosphors because of their emissions from the $^4T_1(G)\rightarrow{}^6A_1$ transition which is strongly dependent on the complex field [10]. However, photoluminescence of them are less intense than the ionic ones, and $MnCl_2\,(Ph_3PO)_2$ is actually non-luminescence. In order to increasing TL emissions, additional materials can be combined with or ''doped'' into the divalent manganese complex. Dopants are trace impurities that are purposely added to alter the electrical or optical properties of a material.

The present work concentrates on enhancing the luminescence efficiency of the $[Mn(Ph_3PO)_2Br_2]$ complex by adding trace amount of dopant materials. The FT-IR spectrum of the synthesized triboluminescence materials was recorded using KBr pellets in the range of 4000-400 cm^{-1}. Optical absorption spectrum of the complex was recorded using UV-vis spectrometer. The PL emission spectra were obtained on Cary Eclipse fluorescence spectro-photometer. The complex structure of the synthesized complex was studied by X-ray powder diffraction (XRD) technique.

2. MATERIAL AND METHODS

2.1. Material

All required chemicals were commercially available, of analytical grade, and used without further purification.

2.2. Preparation of [$Mn(Ph_3PO)_2Br_2$] complex

For preparation of the complex, 0.13 mol of triphenylphosphine oxide and 0.04 mol of $MnBr_2.4H_2O$ were dissolved in 5ml of hot absolute ethanol separately and mixed. The mixture was stirred well and refluxed at 60°C for 1h. The mixture was naturally cooled to room temperature. Afterwards, the reaction mixture was filtered and stored in room temperature for several days. Finally, Light green $Mn(Ph_3PO)_2Br_2$ complexs were obtained which are filtered-off, washed with cold absolute ethanol, and dried in vacuum.

2.3. Preparation of [$Mn(Ph_3PO)_2Br_2$]: HBr complex

One mL of HBr was added into the hot absolute ethanol solution containing $MnBr_2.4H_2O$ (0.04 mol) and Ph_3PO (0.13 mol). The solution was stirred well and refluxed at 60°C for 1 h, and then naturally cooled to room temperature. The reaction mixture was filtered and stored at room temperature for several days to growth of light green complexs.

2.4. Preparation of [$Mn(Ph_3PO)_2Br_2$]: HBr complex

A mixture of triphenylphosphine oxide (0.13 mol) and $MnBr_2$ (0.04 mol) was dissolved in ethanol (5 mL) separately and mixed well, and 1mL $HgCl_2$ was added. The mixture was stirred for 1h at room temperature and heated at 60°C for 1 h, and then naturally cooled to room temperature. The reaction mixture was filtered and stored in room temperature for several days. Light green complexs were obtained, washed with ethanol and dried in air.

2.5. Characterizations

The FT-IR spectrum of the synthesized triboluminescence materials was recorded using KBr pellets in the range of 4000-400 cm^{-1}. Optical absorption spectrum of complexs was recorded using a Perkins-Elmer Lambda 35 UV-vis spectrophotometer over the range of 300-1100 nm. The luminescence emission spectra of the prepared samples were obtained on Cary Eclipse fluorescence spectrophotometer excited using wavelength of 480 nm. The X-ray diffraction analyses revealed by Panalytical X-PERT-PRO powder diffractometer using Cu Kα radiation (λ= 1.5418 Å).

2.6. Experimental method to measure TL

Fig.1 shows a schematic diagram of a specially designed drop tower. The tower was constructed from 0.75 in. (19 mm) thick medium density fiberboard, a 0.25 in. (6 mm) thick plexiglass plate, and a common 1.25 in. (32 mm) diameter piece of PVC pipe. The pipe has holes drilled in uniform increments denoting the net distance of the drop. A simple pin is used as the release mechanism and to set the drop height to the desired distance.

A measurement begins by placing a pile of sample powder under the plexiglass plate as shown in Fig. 1a. The powder is spread out so that it has a minimum thickness and positioned around the center of the tube. A 63.71g steel ball is positioned on a pull pin a distance of 112 in. (1.1m) above the material. The pin is pulled and the ball falls and impacts with the sample material producing TL. After each test, the drop tube is removed, the ball is cleaned, and the sample powder is redistributed near the center of the target area. A 20.76g of ceramic ball also has been used in this experiment [11].

The obtained complex were pressed using a pressure device and triboluminescence emission was recorded using video camera. Pictures reproduced from the video camera were captured on a personal computer. Triboluminescence spectrum was measured by using a grating monochromator and a CCD detector.

3. RESULTS AND DISCUSSION

3.1. FT- IR Spectra analysis

The FTIR spectra of the Dibromo-(bis-triphenyl phosphineoxide) manganese are shown in Fig. 2(a-c). As can be seen in Fig. 2, the peak appear at 1155 cm^{-1} indicates the presence of P=O stretching frequency of triphenylphosphine oxide. The two bands at 3051 and 1595 cm^{-1} confirms the presence of aromatic ring stretching frequency. The doublet peak appears at 726 cm^{-1} and 686 cm^{-1} corresponds to Mn-O stretching and bending. All these assignments clearly revealed that the formation of [$Mn(Ph_3PO)_2Br_2$]complex.

3.2. UV-Vis Spectra analysis

Electronic Spectra of [$Mn(Ph_3PO)_2Br_2$] complexes were shown in Fig. 3(a-c) The prepared TL materials exhibits onset absorption peaks at 320, 292 and 280 nm, respectively. All of the three compounds absorb only in the UV range due to their singlet-singlet ($\pi-\pi^*$) electronic transitions. The absorption bands centered at 292 nm and at around 288 nm in complexes are due to $\pi-\pi^*$ absorption of ligand. [12] This is may be due to the charge transfer transition shifts to longer wave length as ligand become more easily oxidized. The extensive π-bonding on bromine ligand are excited to the π^* orbital of the metal and it is responsible for the colour of the compound. Therefore the charge transfer transition occur ligand to metal (L→M). Compared to that of the core complex (λ_{max}=320 nm), the absorption maxima are slightly blue-shifted to 280 nm in all the doped complexes.

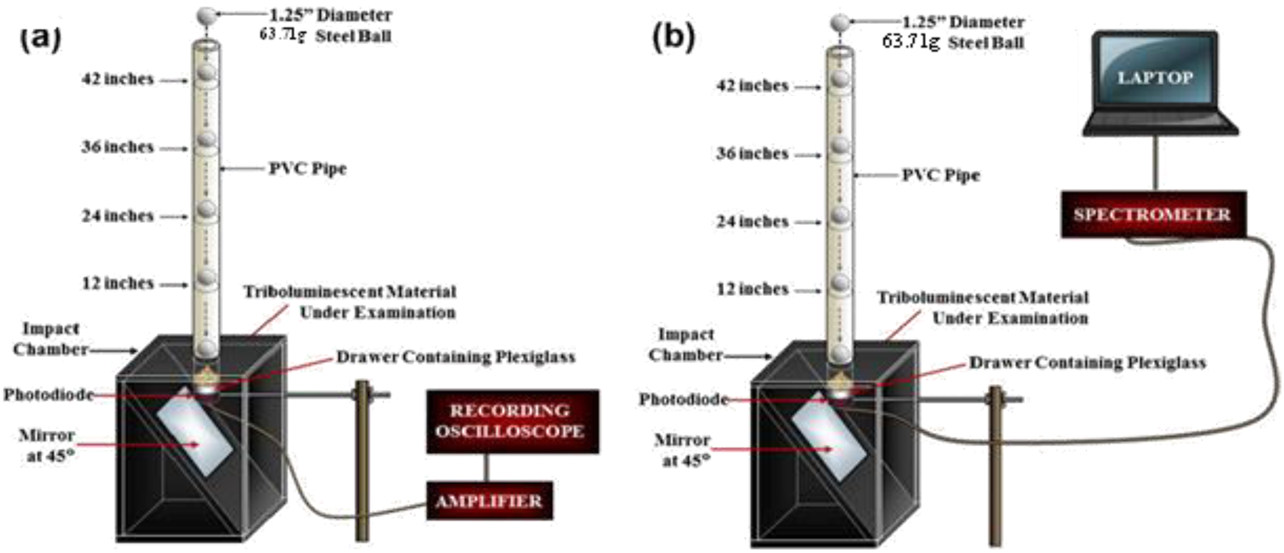

Fig. 1: Schematic diagram of the specially designed drop tower used to measure the triboluminescent: (a) integrated light yield, and (b) visible spectrum

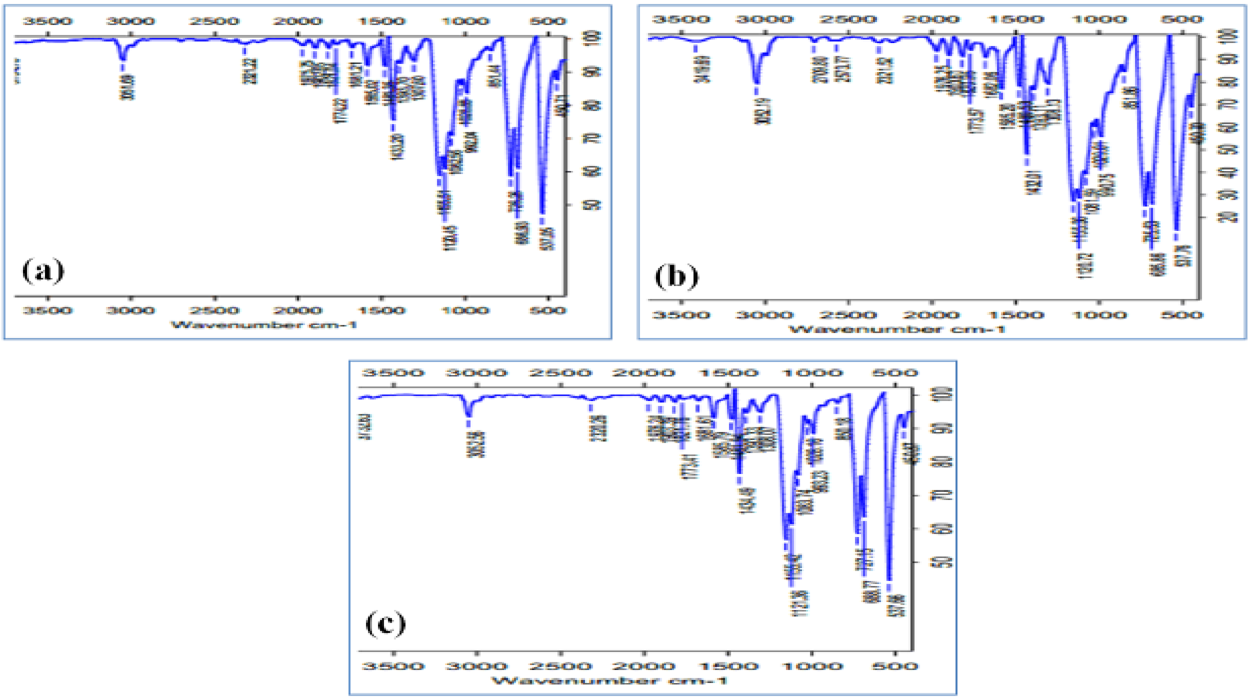

Fig. 2: IR Spectra of (a) pure [$Mn(Ph_3PO)_2Br_2$], (b) HBr and (c) $HgCl_2$ added [$Mn(Ph_3PO)_2Br_2$] complex

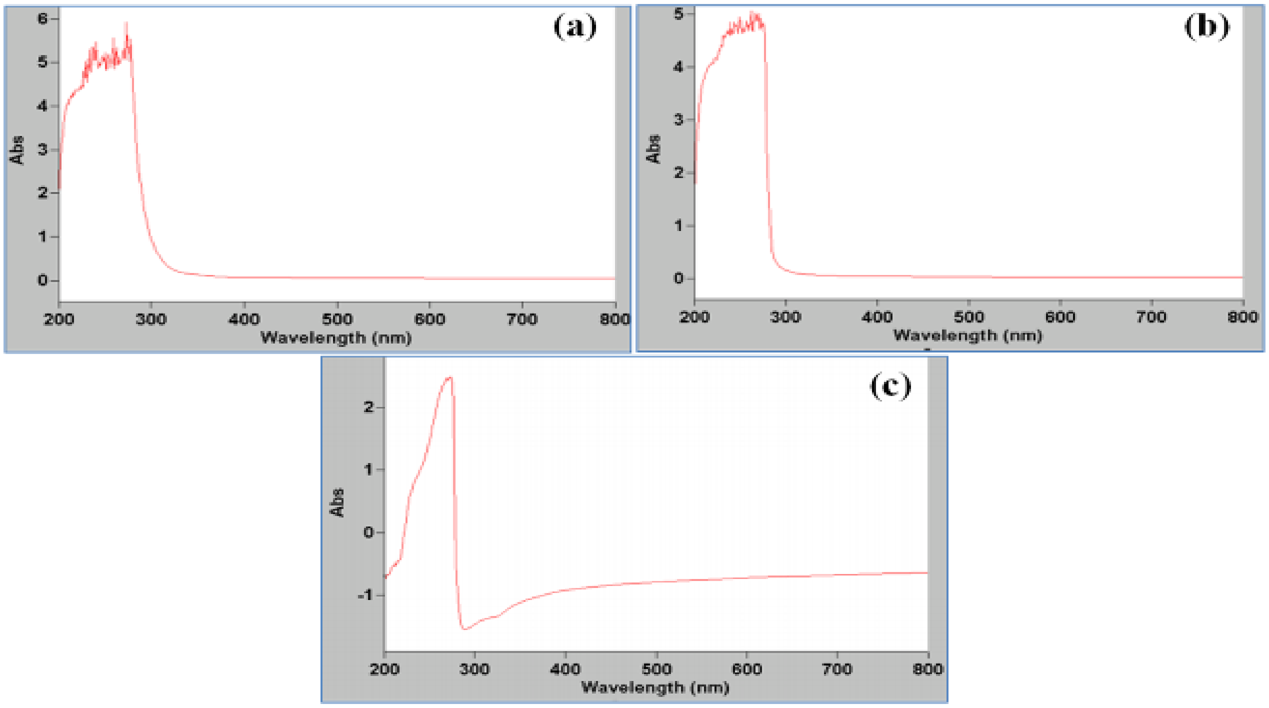

Fig. 3: UV-Vis Spectra of (a) pure [Mn(Ph_3PO)$_2$$Br_2$], (b) HBr and (c) $HgCl_2$ added [Mn(Ph_3PO)$_2$$Br_2$] complex

3.3. Photoluminescence Spectra

Photoluminescence (PL) spectra were used to check the optical quality of [Mn (Ph_3PO)$_2$$Br_2$] and the possible effects of presence of HBr and $HgCl_2$ is shown in Fig. 4(a-c).

The excitation spectrum (Fig. 3) of the complexes exhibits a broad band between 250 and 350 nm, which is attributable to the $\pi-\pi^*$ transition of the. On the other hand, the excitation maxima of doped complexes are blue-shifted to 280-290 nm (due to $\pi-\pi^*$ transition of the ligand).

The photoluminescent properties of core and doped complexes are presented in Fig. 4(a-c). The emission peaks complexes are broad and correspond to the characteristic $^4T_1(G) \rightarrow {}^6A_1$ radiative transition. Complexes display green emissions located at 528 nm. Solid state emission spectra of core complex has a moderate quantum efficiency, while HBr doped [Mn(Ph_3PO)$_2$$Br_2$] complexes glow brightly with higher emission efficiencies. However, the photoemission intensity of $HgCl_2$ doped [Mn(Ph_3PO)$_2$$Br_2$] complexes decreased largly.

We also measured the photoluminescence emission efficiency of the $HgCl_2$ doped [Mn(Ph_3PO)$_2$$Br_2$] complexes emit much lower efficiency than its corresponding [Mn(Ph_3PO)$_2$$Br_2$] and HBr doped complex, which is most likely due to the presence of chlorine ions providing more non-radiative decay pathways.

3.4. X-Ray Diffraction Spectra

The complex structure of core and doped [Mn(Ph_3PO)$_2$$Br_2$] complexes were characterized from the X-ray diffraction patterns and their corresponding spectra are shown in Fig.5(a-c). XRD data revealed that the synthesized material of [core and doped Mn(Ph_3PO)$_2$$Br_2$] complexes exist Monoclinic complex structure. The cell parameters of the synthesized materials are a = 12.580 Å, b = 11.364 Å and c= 9.595 Å. The obtained X-Ray diffractograms were matched well with standard JCPDS Data [Card No 100773].

3.5. Triboluminescence Spectra

Triboluminescence (TL) caused by mechanical energy applied to a material has generated extensive research interest over the years [13-16] because of its potential application for real-time sensors of mechanical stress, and structural damage. The researcher has elaborated comprehensively the origin of excitation process caused by rubbing the TL materials [17, 18]. However, the fundamental mechanism for the emission process is still unclear.

The triboluminescent emission spectra for impurities added [Mn(Ph_3PO)$_2$$Br_2$] are shown in Fig. 6(a) and (b).

The known complex structures of Mn^{2+} complexes showing TL are non-centrosymmetrical [2]. However, the intensely triboluminescent doped compounds presented here are centrosymmetric and non-ionic, and no disordered groups in them were found during structure refinement (from XRD). Thus the mechanism for TL in these compounds must be different from these two previously-proposed mechanisms. Since the greenish colour of TL (Fig. 7) for complex is similar with PL, the TL can be assigned to the same $^4T_1(G)\rightarrow{}^6A_1$ transition as PL [2]. Bourhill suggested that TL efficiency could be improved by increasing the PL quantum yield [19]. Hence, a high PL quantum yield is desirable to obtain intense TL, and that is what we have demonstrated with these compounds.

The stresses and TL emissions of the synthesized undoped and doped Dibromo-bis-(triphenylphosphineoxide) manganese complex were measured by different hights using two different balls (shown in table 1).

TL spectra sometimes less than PL spectra at the short wavelength side of the emission peak wavelength. The solid-state PL is to a first approximation a surface effect, whereas TL can be generated within the bulk of solid sample.

Table 1: The stress of the Dibromo-bis-(triphenylphosphineoxide) manganese complex

Name of the compound	Type of ball	Height (cm)	Nature of the sample	TL signal	Stress (N/mm^2)
Dibromo-bis(triphenyl phosphineoxide) manganese (II)	Steel ball	35	Powder	Yes	11.0152
		65	Powder	Yes	20.4569
		95	Powder	Yes	29.8986
		110	Powder	Yes	34.6194
		112	Powder	Yes	35.2489
	Ceramic ball	35	Powder	Yes	1.8514
		65	Powder	Yes	3.4383
		95	Powder	Yes	5.0253
		110	Powder	Yes	5.8188
		112	Powder	Yes	5.9246

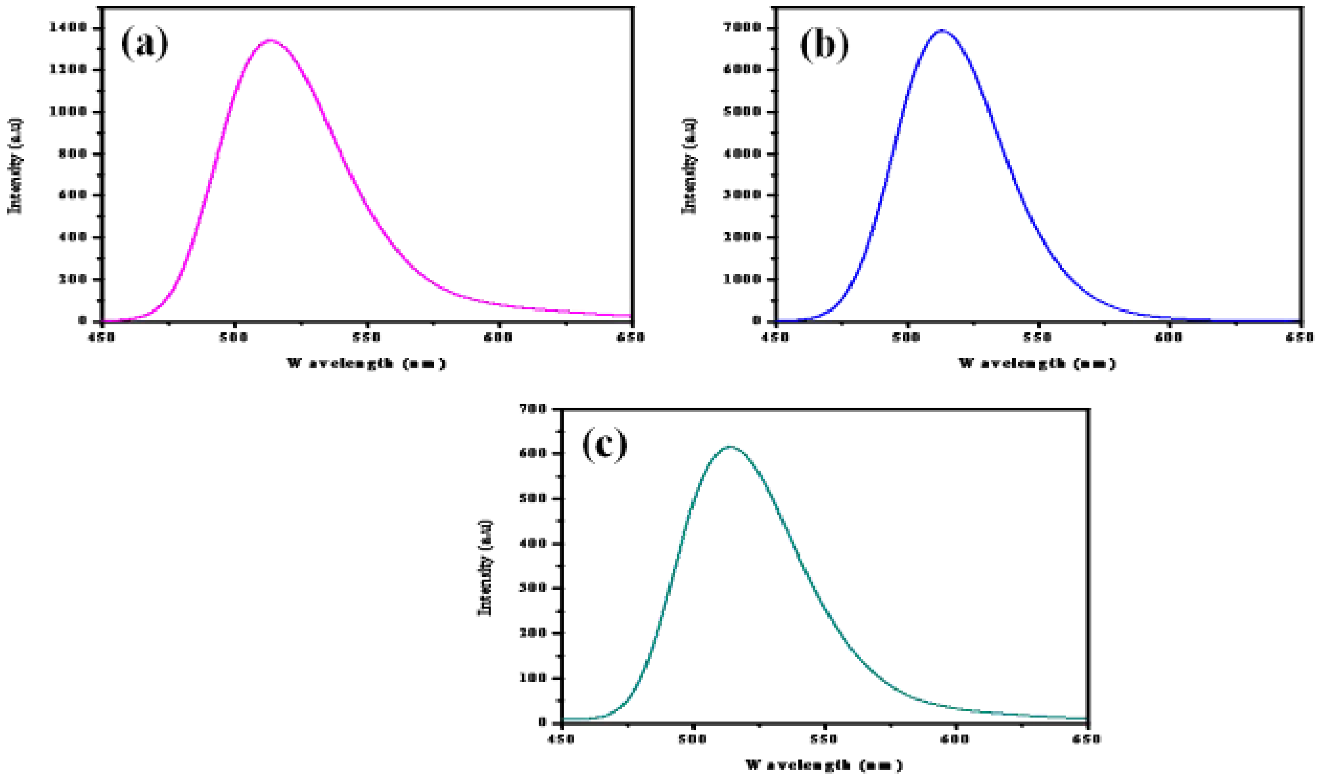

Fig. 4: PL Study of (a) pure [Mn(Ph$_3$PO)$_2$Br$_2$], (b) HBr and (c) HgCl$_2$ added [Mn(Ph$_3$PO)$_2$Br$_2$] complex

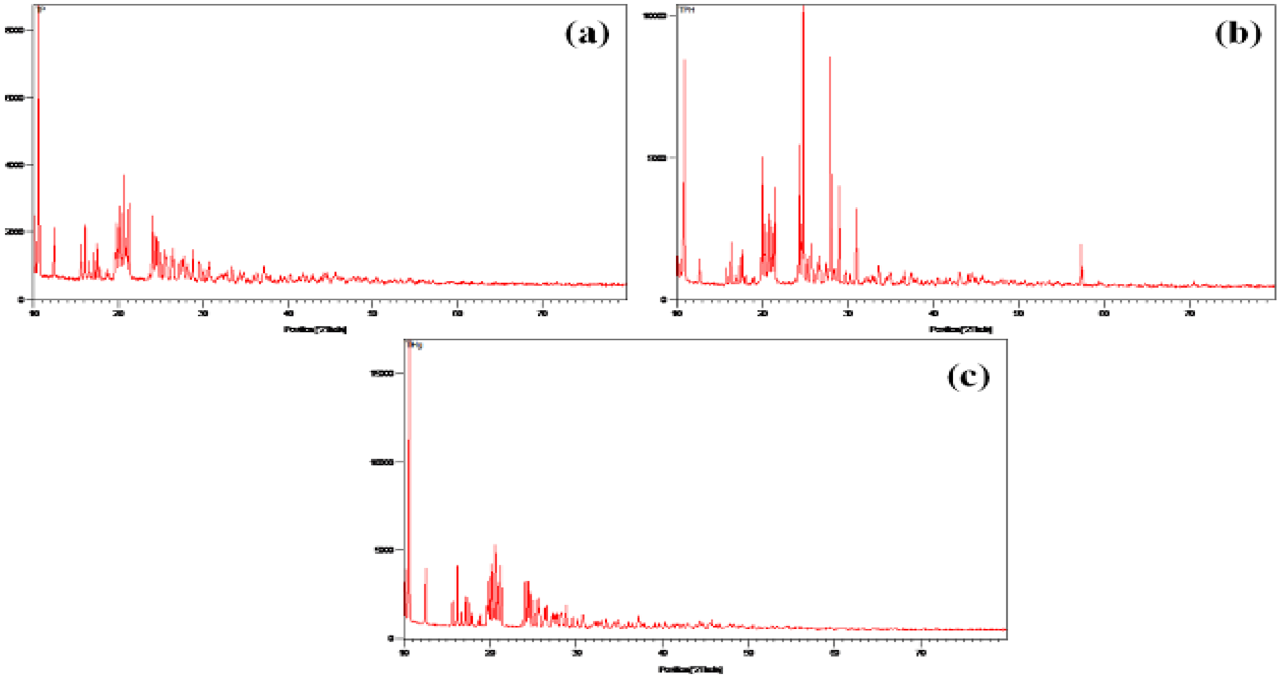

Fig. 5: XRD spectra of (a) pure [Mn(Ph_3PO)$_2$$Br_2$], (b) HBr and (c) $HgCl_2$ added [Mn(Ph_3PO)$_2$$Br_2$] complex

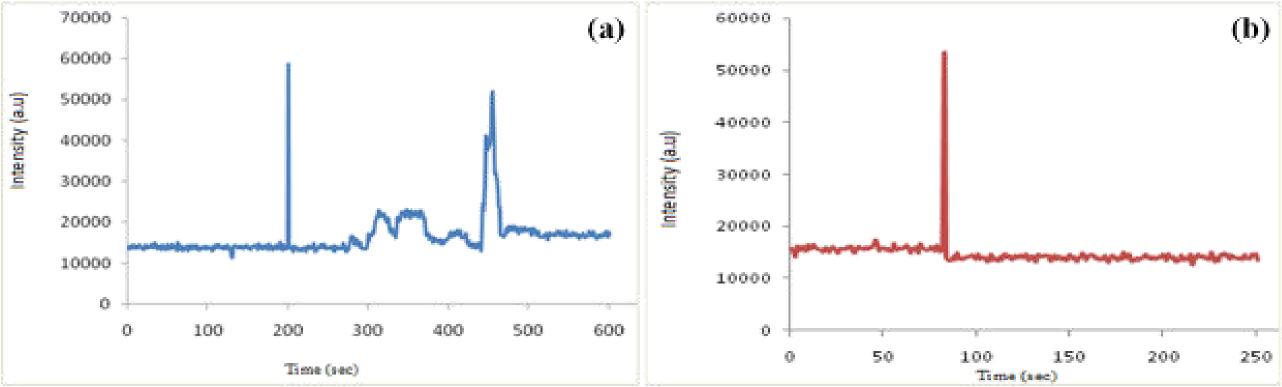

Fig. 6: TL spectrum of (a) HBr and (b) HgCl2 added [Mn(Ph3PO)2Br2] by using steel ball

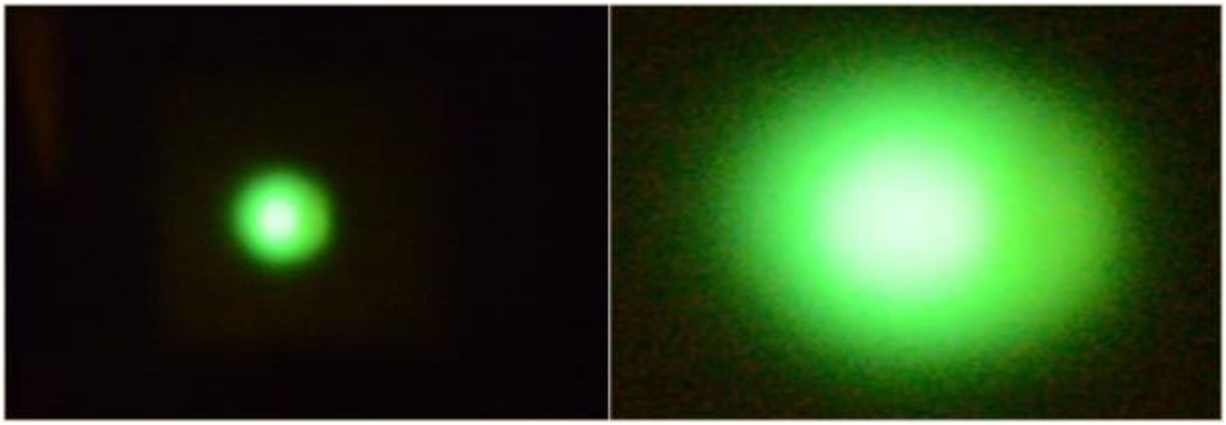

Fig. 7: Colour of the TL emission from [Mn(Ph_3PO)$_2$$Br_2$]recorded using a NAC GX-1 high-speed camera at a frame rate of 1000 Hz using Steel ball

4. CONCLUSION

In this work, we report the effect of impurities on manganese bromide complexes with a bidentate phosphine oxide ligand; the introduction of the dopant not only increases the stability of the Mn (II) compounds, but also acts as a sensitizer for luminescence. Here, the HBr doped complex showing high photoluminescence emission intensity as compared to $HgCl_2$ doped complex. The presence of absorption bands may be due to their singlet-singlet ($\pi-\pi^*$) electronic transitions. Additionally, the photo-luminescence emission efficiency of the $HgCl_2$ doped complexes emit much lower efficiency than its corresponding undoped and HBr doped complex, which is may be due to the presence of chlorine ions providing more non-radiative decay pathways. XRD data revealed that the synthesized material of undoped and doped $Mn(Ph_3PO)_2Br_2$ complexes exist Monoclinic complex structure. The synthesized complex showed a excellent green PL and TL emission as potential applications in smart sensors.

Conflicts of interests

The Authors declares that there is no conflict of interest.

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