Thermoluminescence Response of Phosphate Glasses doped with Dy^{3+} and containing silver nanoparticles

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Abstract– ***We report the fabrication, luminescence characterization and effect of Ag concentration on the thermoluminescent (TL) response in the phosphate glasses doped with Dy^{3+} and containing silver nanoparticles. The Scanning electron microscopy (SEM) show the formation of silver nanoparticles (SNP), Absorption spectra of the samples show the presence of bands in 420nm and 450nm associated with the SNP (plasmón effect), and 750nm, 800nm, 875nm, 1098nm and 1278nm belonging to the Dy^{3+} . Emission spectra show two prominent bands in 480nm, 574nm and one faint band in 665nm, all bands under 364nm pumping, and the fluorescence in the 550nm and 590nm spectral range enhanced 2 times. The TL response to UV irradiation was studied, the glow curve show significant dependence of the Tl intensity with the increment the SNP in the samples.***

Keywords— Phosphate glasses, thermoluminescence, silver nanoparticles, rare earths.

I. Introduction

The study of luminescence materials it has been a great interest throughout the last decade, principally doped materials with rare earths [1-3]. Several investigations focused on finding new lasers, particularly with glass matrices [4, 5]. On the other hand, Dy^{3+} ion doped glass matrices is a excellent candidate to be used in lasers especially in the visible region, because it has many technological applications in commercial displays and optics devices. Dy^{3+} ion has two dominant bands in the visible emission spectrum, yellow band (574 nm) that corresponds to the transition $^4F_{9/2} \rightarrow {}^6H_{13/2}$ and blue band (480 nm) that correspond to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition [1-3].

Phosphate glass has been identified as promising optical material [2-3, 6]. As for the characteristics of the material, we should mention that it is soft and transparent from the ultraviolet (UV) to near infrared (IR), and relatively strong from the mechanical point of view. Has an another important properties as high density (3 g/cm3), high refractive index and thermal conductivity, besides its high phonon energy [2] useful to be used as a optical device and possibly as a dosimetric device [7].

On the other hand, some authors have realized several studies on the effect that provides the metallic's nanoparticles in different glass matrices co-doped with rare earths [3, 8-9], resulting in an enhancement in the optical properties of the materials, due to the plasmon effect.

In this work we present the luminescence characterization of phosphate glasses doped with Dy^{3+} and containing silver nanoparticles, we show that the visible emission in 574 nm and 480 nm, and the nucleation of silver nanoparticles in the process of the synthesis, that are analyzed morphological through Scanning Electron Microscopy (SEM), and checking by absorption, finally, we study the thermoluminescence results for analyze the possibility of being used the phosphate glasses doped with Dy^{3+} and containing silver nanoparticles as dosimetric device.

II. EXPERIMENTAL

The experiments were performed using samples (A, B, C, D and E), whose compositions are $NaH_2PO_4H_2O$, $Dy_2(SO_4)_3$ and $AgNO_3$ respectively (see Table 1). In the process of synthesis we used the melt-quenching technique at ambient atmosphere conditions. The chemical products were obtained (99.5-99.0% purity; to Aldrich). The reagents were melted in a porcelain crucible in air at 1050°C for 4h. Afterward, the samples were annealed at 450°C for 2 h to produce metallic SNP. The glasses were cut to 5 mm for 5mm in long and 3 mm in thickness.

TABLE I
GLASS COMPOSITION IN WEIGHT PERCENTAGE (WT%)

Samples	Composition of samples		
	NaH2PO4H2O [%]	Dy2(SO4)3 [%]	AgNO3[%]
A	99.98	0.0	0.02
B	99.46	0.5	0.04
C	99.44	0.5	0.06
D	99.42	0.5	0.08
E	99.4	0.5	0.1

Absorption and emission spectra, as well as the scanning electron microscopy (SEM) measurements, revealed the presence and nucleation of metallic SNP in the glass samples. SEM analyses were performed using a scanning electron microscope Zeiss, EVOHD15LS (Germany). The SEM result for the sample E, show the nucleation of silver nanoparticles (see Figure 1).

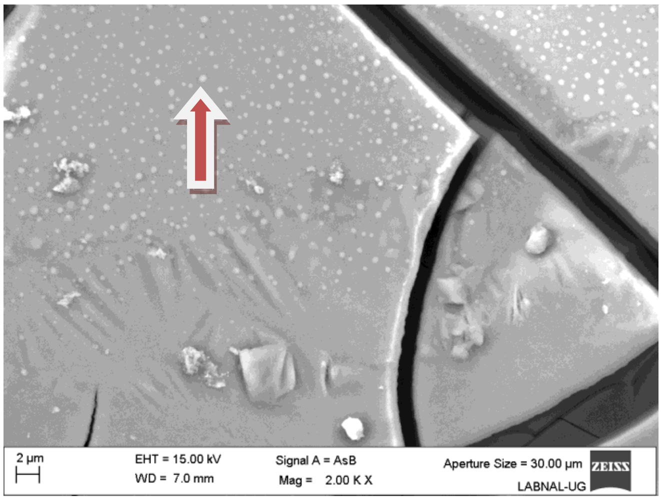

Fig. 1 SEM micrograph of sample E showing nanoparticles.

Figure 2 shows the UV-Vis absorbance spectra of the samples were obtained using a Cary 5000 UV-Vis-NIR (Agilent Technology, Santa Clara, CA, USA) spectrophotometer, at room temperature. Spectra were recorded between 400nm at 1400nm.

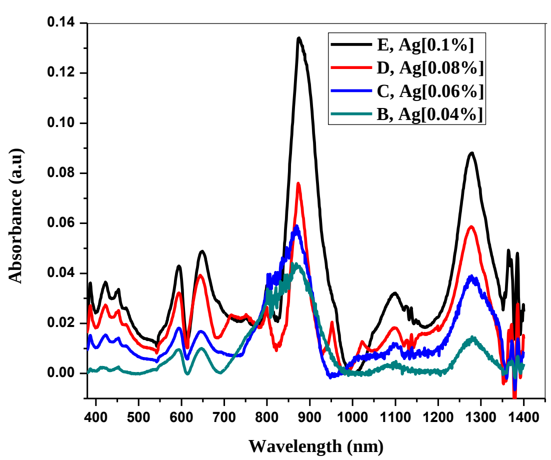

Fig. 2 Room temperature absorption spectra of samples B, C, D and E.

In figure 3 we can see the emission measurements were carried out by using a 75 W Xe lamp and an Acton Pro 1500i monochromator under excitation in 364nm. The fluorescence emission was analyzed with a second Acton Pro 2300i monochromator. The system was controlled with a PC where excitation and emission spectra were recorded.

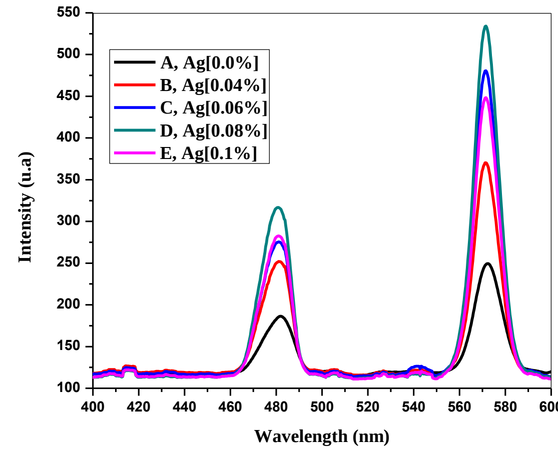

Fig. 3 Emission spectra of phosphate glasses doped with Dy^{3+} and contained silver nanoparticles.

Thermoluminescent response (see figure 4) of samples was measured using a TL Reader Harshaw 3500, Thermo Scientific (UK). First the dosimeters were annealed at 400°C during 1h in a ceramic plate, using a muffle MA12D, Terlab (Mexico). For irradiation, an UV 75 W Xe lamp was used (Newport, USA).

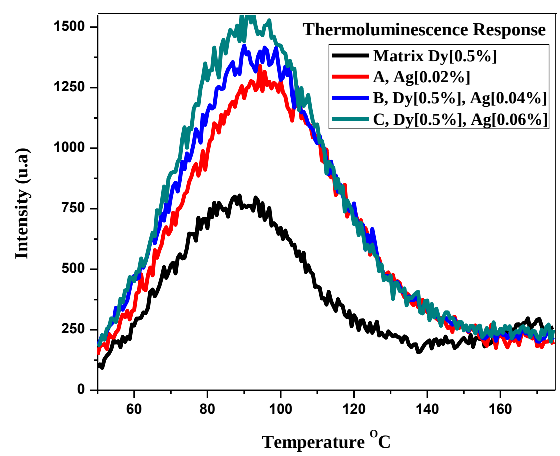

Fig. 4 TL intensity curves of samples of phosphate glass doped with Dy^{3+} and containing silver nanoparticles.

III. RESULTS AND DISCUSSION

Figure 1 shows high resolution images of sample E and clearly demonstrates the presence of SNP, this nucleation occurs for thermal decomposition of $AgNO_3$.

From figure 2 we can see the absorption bands corresponding to Dy^{3+} in: 750 nm, 800 nm, 875 nm, 1098 nm and 1278 nm, which is produced by the $^6H_{15/2}\rightarrow {}^6F_{3/2}$, $^6H_{15/2}\rightarrow {}^6F_{5/2}$, $^6H_{15/2}\rightarrow {}^6F_{7/2}$, $^6H_{15/2}\rightarrow {}^6F_{9/2}$ and $^6H_{15/2}\rightarrow {}^6F_{11/2}$ transitions. It's clear that the absorption coefficient grows as the silver concentration in the samples increase. The peaks in the range to 380 nm at 600 nm, is a combination to Dy^{3+} ($^4I_{13/4}$ + $^4G_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$) and the plasmon effect associated with the SNP.

The emission spectra off the samples pumping at 364 nm are show in figure 3. In the spectra's we can see two peaks centered in 480 nm and 574 nm, corresponding to Dy^{3+} ($^4F_{9/2}\rightarrow {}^6H_{15/2}$ and $^4F_{9/2}\rightarrow {}^6H_{13/2}$) transitions. The enhancement of the fluorescence suggests that the SNP concentration in the sample influences the Dy^{3+} levels.

The TL show in figure 4 presents one increment in the intensity in the glow curves centered in 90 °C, which represents an enhancement in the sensitivity of glasses samples in the UV radiation, possibly derivative for the addition of silver nanoparticles, which would cause an increase imperfections in the matrix.

IV. CONCLUSIONS

We conclude that the luminescence properties of the material are improved when the silver concentration in the sample is increased, the absorption and emission enhancement (4 times) when the samples containing SNP unlike samples without SNP. The enhancement in the glow curves present the possibility being used as dosimetric device specialty for UV radiation.

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