



Morphological and Thermal and optical characterizations of the cerium and praseodymium co-doped calcium aluminates obtained by the gel using ethylenediaminetetraacetic acid and by the combustion with glycine and sucrose methods

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ABSTRACT

Calcium aluminate was synthesized doped with trivalent cerium ions (Ce^{3+}) by gel process with ethylene diamine tetraacetic acid (EDTA) as a chelating agent and was doped with trivalent praseodymium ions (Pr^{3+}). Calcium aluminates with praseodymium 1.0% and 0.5% were synthesized. The synthesized material was characterized by means of thermogravimetry and differential thermal analysis and fluorescence spectroscopy and by scanning electron microscopy. Calcium aluminates doped with praseodymium ion that showed less porosity in its grain structure and luminescent transitions that are dependent on the wavelengths of excitation and showing both types of transitions both 5d-4f and 4f-4f. Also, calcium aluminate was obtained by combustion mixing of

aluminum, calcium and cerium nitrates, with the respective organic compound used as fuel, glycine or sucrose, in quantity of moles calculated according to the stoichiometry of the redox reaction, with the values of the proportions total nitrate/fuel 1:1.5 for used in the synthesis of glycine and 1:0.2 for used fuel sucrose. The amounts of Ce^{3+} ions in molar concentrations were 0.25%, 0.5% and 1%. By fluorescence spectroscopy was observed emission bands at 390nm and 415nm related transitions of Ce^{3+} ion and 650nm related to electronic transitions in the matrix defects.

Keywords: calcium aluminate; cerium phosphor; praseodymium phosphors; thermogravimetry

1.INTRODUCTION

The identification and synthesis of materials that produce luminescence have been intensifying as technological growth is current, with the development of modern and economical materials used in electronic devices such as image screens, fluorescent lamps, safety materials and fiber optics^[1]. After identifying the uses and applications of luminescent properties, several researchers have been intensified in recent years with the purpose of discovering new and efficient materials. Among the most studied are matrices aluminate, in their work Clabau et al. ^[2] describe the silicates and aluminates serve as good host matrix because it reduces the effect of "quenching" (sharp decline in phosphorescence) due to activation recombination of the electron-vacancy on the emission of radiation from the ion activator and the presence of structural defects caused by the dopant ions in the aluminate, due the ionization of the oxygen element and imbalance loads, forming vacancies which act as traps for electrons, resulting in the prolongation of phosphorescence. The optical property of aluminates is investigated since 1996 with the first material $SrAl_2O_4: Eu^{2+}, Dy^{3+}$ characterized by an afterglow that lasts over 30 hours, far at present with $CaAl_2O_4: Eu^{2+}, Nd^{3+}$ and $SrAl_2O_4: Eu^{2+}, Dy^{3+}$ materials, which have luminescence in the blue and green respectively, which are commercially available. Recent studies have investigated the behavior of emission from ions Ce^{3+} , where the transition 4f-5d have a broad region of the visible electromagnetic emission, with the intensity dependence of the crystal field of the matrix. Phosphors afterglow doped with Ce^{3+} Chen et. al. in matrix $Ca_2Al_3O_6$ ^[3]. Luminescent afterglow

has applications in radiation detectors, optical sensors, signs, interior decoration, lighting and LED televisions. Phosphorescent systems doped with rare earth cerium has been investigated in several types of matrix because it has superior advantages such as abundance, cost and emission range, comparable replacement to current compounds that use Europium as activated ions. The choice of synthesis method is crucial to determine the physicochemical properties and intensify the reduction of costs at all stages reaction, with the control of lower energy, reagents used and higher yield of the final product. Ceramic materials can be obtained by various methods such as Pechinni, sol-gel, hydrothermal, electrofusion, and combustion in solution, and the latter with a saving of time, energy and reagents^[4-6]. The combustion method in solution consists of adding nitrate in the material composition corresponding metal as aluminum, calcium, cerium and praseodymium nitrates in the stoichiometric mole ratio of organic components to be used as fuel such glycine and sucrose. CaAl_2O_4 powders can be synthesized by gel process^[7-9]. This process synthesizes fine and homogeneous powders in low temperature, high homogeneity of the matrix and activating agents, among other methods^[10-12].

1.EXPERIMENTAL

1.1Gel synthesis of CaAl_2O_4 : Pr^{3+}

Synthesis of CaAl_2O_4 : Pr^{3+} (1.0%) was made by dissolving ammonium hydroxide solution in EDTA solution. Then, it was added solutions of aluminum nitrate and calcium nitrate. This mixture was heated at about 80 °C with continuous slow stirring for 2 hours to evaporate water. After this time, it was added solution of $\text{Pr}(\text{NO}_3)_3$, heating at around 140 °C with continuous stirring to form a viscous solution and gelled. The precursor was precalcined at 200 °C in a muffle furnace, pulverized and calcined with temperature ramp of 20 °C/min to 800 °C for 2 hours. Synthesis of CaAl_2O_4 : Pr^{3+} (0.5%) was performed in the same manner. For the characterization of powders of doped CaAl_2O_4 we used the techniques of scanning electron microscopy (SEM) and spectrofluorimetry.

1.2Gel synthesis of CaAl_2O_4 : Ce^{3+}

Two syntheses were performed, the first one with 1.0% mol Ce^{3+} ions in the matrix of CaAl_2O_4 and other with 0.5% mol Ce^{3+} ions. Synthesis of CaAl_2O_4 : Ce^{3+} (1.0%) was made by mixing NH_4OH solution in EDTA solution. Then, it was added solutions of

$\text{Al}(\text{NO}_3)_3$ and $\text{Ca}(\text{NO}_3)_2$. This mixture was placed on a heating plate at about $80\text{ }^\circ\text{C}$ with continuous and slow stirring for 2 hours to evaporate water. After this time, it was added a solution of $\text{Ce}(\text{NO}_3)_3$ with 1.0% mol, increasing to $140\text{ }^\circ\text{C}$ the temperature of the heating plate, keeping the mixture with continuous stirring to form a viscous solution which gelled. The solid formed in this phase is called precursor. The precursor was pre-calcined at $200\text{ }^\circ\text{C}$ in a muffle furnace, pulverized and calcined with temperature ramp of $20\text{ }^\circ\text{C}/\text{min}$ until $800\text{ }^\circ\text{C}$ for 2 hours. This calcination at $800\text{ }^\circ\text{C}$ synthesized a fine product. Synthesis of the $\text{CaAl}_2\text{O}_4:\text{Ce}$ (0.5%) was made the same way, just replacing the cerium nitrate 1.0 % for 0.5 %. Powders of $\text{CaAl}_2\text{O}_4:\text{Ce}^{3+}$ were characterized using thermogravimetry (TG) and differential thermal analysis (DTA) and spectrofluorimetry.

1.3 Combustion synthesis of $\text{CaAl}_2\text{O}_4:\text{Ce}^{3+}$

Samples doped of calcium aluminate were obtained using the procedure of adding solid aluminum nitrate nonahydrate (Dinamica, P.A- 98%) into a Becker 250 ml and added distilled water only in dissolving minimal amount, the same procedure with the solid calcium nitrate tetrahydrate (CETUS, PA - 98%) and glycine (Vetec 98.5%) or sucrose. The ratio of reactants used of the stoichiometric coefficients second redox reaction is calculated using the ratios of 1:0.2 and 1:2 in samples which employs the fuel sucrose and glycine, respectively. After all the solutions were mixed in a single Becker, was added to the quantity for molar concentrations of 0.25%, 0.5% and 1%, calculated according to weight of the calcium ion used, the solution of cerium nitrate homogenized and heated plate model corning stirred / hot place until the ignition at approximately $200\text{ }^\circ\text{C}$. The precursors are calcined in a muffle furnace (Quimis Q318S24) with a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ to $800\text{ }^\circ\text{C}$ for 2h. The characterization of powders of Ce^{3+} doped CaAl_2O_4 used the fluorescence spectrofluorimetry.

2. RESULTS AND DISCUSSION

The morphological characterization was made by scanning electron microscopy (SEM) images were obtained to $\text{CaAl}_2\text{O}_4:\text{Pr}^{3+}$ (1.0%) showing the morphology of doped calcium aluminate. Fig.1 (A) shows the shape of the particles is less varied in size and more irregular, presenting a more compact structure with less porosity and having a continuous distribution and defined nanoparticulate material, as seen in Fig.1 (B). Energy Dispersive X-ray (EDS) Spectrometry was used to perform an elemental

analysis of $\text{CaAl}_2\text{O}_4:\text{Pr}^{3+}$ (1.0%). Fig. 2 shows EDX spectra which were observed the presence of calcium (Ca) in the positions indicated by the peaks of energy from 3.8keV to 4.0keV approximately. Other factors found are aluminum (Al) with a peak power of approximately 1.7keV and praseodymium (Pr) with energy peaks at 1.0keV and 1.1keV approximately. The characterization of luminescence was performed by spectrofluorimetry, as shown in Fig. 3 The excitation and emission spectra of the samples doped with Pr (1.0%) and (0.5%) are shown in Fig. 3(A) and Fig. 3(B), respectively. The spectra have been normalized for ease of comparison. The wavelengths of the spectra were compared with the energy level diagrams in the literature^[8,9]. Fig. 3(A) shows emission spectrum with $\lambda_{\text{exc}} = 280\text{nm}$ having a broadband, related to an allowed d-f transition. For emission spectrum with $\lambda_{\text{exc}} = 465\text{ nm}$ appeared a sharp band assigned to a f-f transition due to $^1\text{D}_2 \rightarrow ^3\text{H}_5$. Fig. 2(B) shows the emission spectrum with $\lambda_{\text{exc}} = 300\text{nm}$ having a peak at 20533 cm^{-1} (487nm), which was attributed to $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transition and a less intense band at 16181 cm^{-1} (618nm) due to $^1\text{D}_2 \rightarrow ^3\text{H}_5$ transition. In the emission spectrum with $\lambda_{\text{exc}} = 565\text{nm}$ there is an intense peak at 16207cm^{-1} (617nm), which the transition is assigned to $^3\text{P}_0 \rightarrow ^3\text{H}_6$. Those transitions were found for $\text{CaAl}_2\text{O}_4:\text{Pr}^{3+}$ (1.0%) and $\text{CaAl}_2\text{O}_4:\text{Pr}^{3+}$ (0.5%) and corroborated at Ronda et al.^[9]

The first characterization technique was thermogravimetry (TG) and differential thermal analysis (DTA), which were done simultaneously. This technique was employed in the analysis of precursors $\text{CaAl}_2\text{O}_4:\text{Ce}^{3+}$ (1.0%) and (0.5%). The results for these precursors are shown in Figure 4. The TGA curves shown in Figs. 4(A) and 4(B) show that there was a marked weight loss. This indicated that the precursors of doped aluminates do not absorb humidity, this may be due to pre-calcination at a temperature lower than the final calcination. Another observation in Figs. 4(A) and 4(B) were the similarity of the endothermic and exothermic peaks in the DTA curve, indicating that the phases were similar^[11]. The second characterization technique used was fluorescence spectrofluorimetry, used in doped aluminate calcined at $800\text{ }^\circ\text{C}$. The emission and excitation spectra obtained on spectrofluorimetry were normalized to facilitate comparison between them. After normalization of the spectra, it were performed comparison of the wavelengths of the spectra obtained with the energy level diagrams shown in the literature^[7,8]. The results are shown in Figs. 5 and 6 for the emission and excitation spectra, respectively. Figs. 5(A) and 5(B) show the emission

spectra of CaAl₂O₄: Ce³⁺ (1.0%) and (0.5%), respectively. The wide emission bands at both emission spectra indicate that the optical transition is d-f^[9].

Figure 6(A) and 6(B) show the excitation spectra for CaAl₂O₄: Ce³⁺ (1.0%) and (0.5%), respectively. The spectra have peaks of the maximum wavelength and similar energy, Fig. 5(A) with 22 nm corresponding to the energy of 45045 cm⁻¹ and Fig. 5(B) has 222nm with energy at 44642 cm⁻¹. This energy is attributed to optical 4f-5d transition, characteristic of the Ce³⁺ ion. This transition 4f-5d is due to electric dipole transitions of the Ce³⁺ ion allowed from the ground state ⁴F₁ (term 2F) deployed by spin-orbit (sub-levels ²F_{5/2} and ²F_{7/2}) to the excited state 5d^[7].

Fig. 7 shows the fluorescence spectra for the CaAl₂O₄: Ce³⁺ made by combustion synthesis. As can be noted in Fig. 7(A), emission broad bands were observed at 390nm, 427nm, 450nm and 650nm, which the two first transitions were related to Ce³⁺ ion and overlapped with the other centers, these emission broad bands were related to the electronic transitions of the intrinsic defects of the matrix. Observing overlapping bands centered at 450nm, the lower Ce³⁺ ions concentration the lower on the intensity and shifted of emission 390nm and 427nm, showing the activator ion emission as well as the minor amount of dopants causes less structural defects in matrix related to positive vacancies which decrease as the energy of combustion is higher. When it was used sucrose as fuel, because it was more energetic, the defects reduced and the emission intensity observed was smaller in these spectra as noted in Fig. 7(B).

3.CONCLUSION

Gel synthesized Calcium aluminates doped with praseodymium ion showed less porosity in its grain structure were prepared. The calcium aluminate doped with praseodymium is luminescent with transitions that are dependent on the wavelengths of excitation and showing both types of transitions both 5d-4f and 4f-4f. Also, It was concluded that the gel is very efficient route for the synthesis of calcium aluminate doped, and doping the matrix of calcium aluminate with cerium ion is very effective for the study of luminescence. When the calcium aluminate matrix was obtained by the method of combustion in solution had luminescent centers with emission at 450nm (blue) which are related to the activator Ce³⁺ ion and 650nm (red) caused by intrinsic defects in the matrix. The condition of higher relative intensity compounds are doped in

concentrations of 1%, but the matrix aluminate shows the emission of the Ce ion is observed at concentrations of 0.25% and 0.5%.

FIGURE CAPTIONS

Figure 1: SEM images for CaAl₂O₄: Pr 1,0%. Magnification of (A) 300X. (B) 7000X.

Figure 2: Energy Dispersive X-ray Spectrum for CaAl₂O₄: Pr(1.0%).

Figure 3: Fluorescence Spectrum for CaAl₂O₄: Pr³⁺: (A) CaAl₂O₄:Pr(1.0%). (B) CaAl₂O₄:Pr(0.5%)

Figure 4: TG and TGA curves for the calcium aluminate precursor. (A) CaAl₂O₄: Ce³⁺ (1.0 %); (B) CaAl₂O₄: Ce³⁺ (0.5 %)

Figure 5: Fluorescence spectrum for the calcium aluminate doped with cerium. (A) $\lambda_{exc} = 275\text{nm}$ for CaAl₂O₄: Ce³⁺ (1.0 %); (B) $\lambda_{exc} = 275\text{nm}$ for CaAl₂O₄: Ce³⁺ (0.5 %).

Figure 6: Excitation spectrum of the calcium aluminate doped with cerium. (A) CaAl₂O₄: Ce³⁺ (1.0 %); (B) CaAl₂O₄: Ce³⁺ (0.5 %).

Figure 7: Fluorescence emission spectra of the samples doped with Ce³⁺; (A) synthesis using glycine; (B) synthesis using sucrose; blue line at the concentration of 0.25%; red line at 0.5% and the black line by 1%.

FIGURE 1

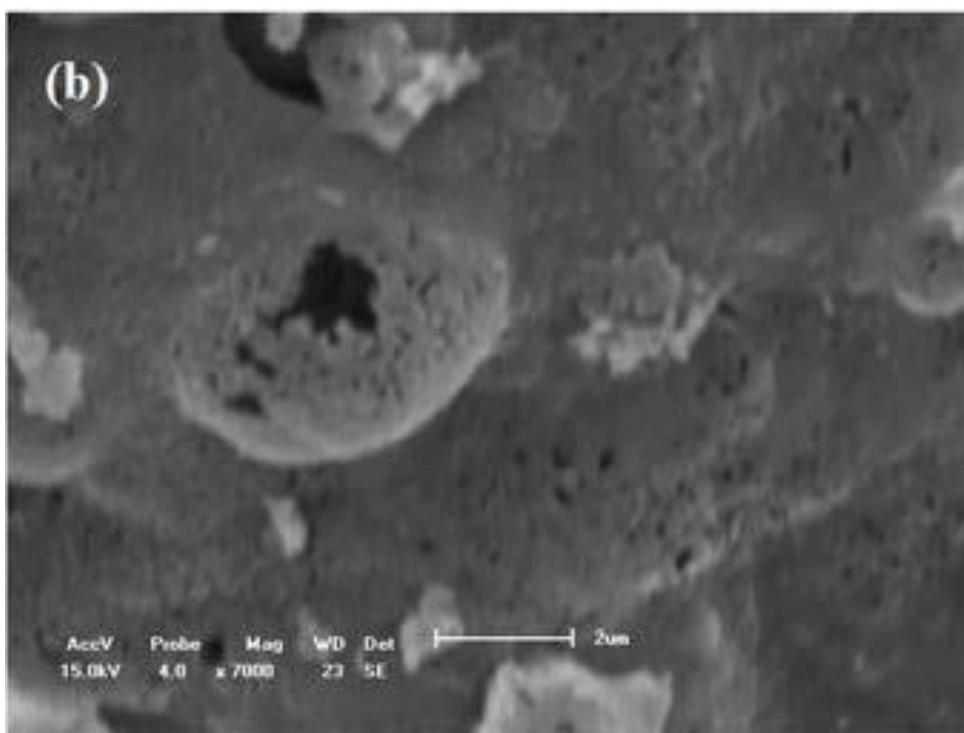
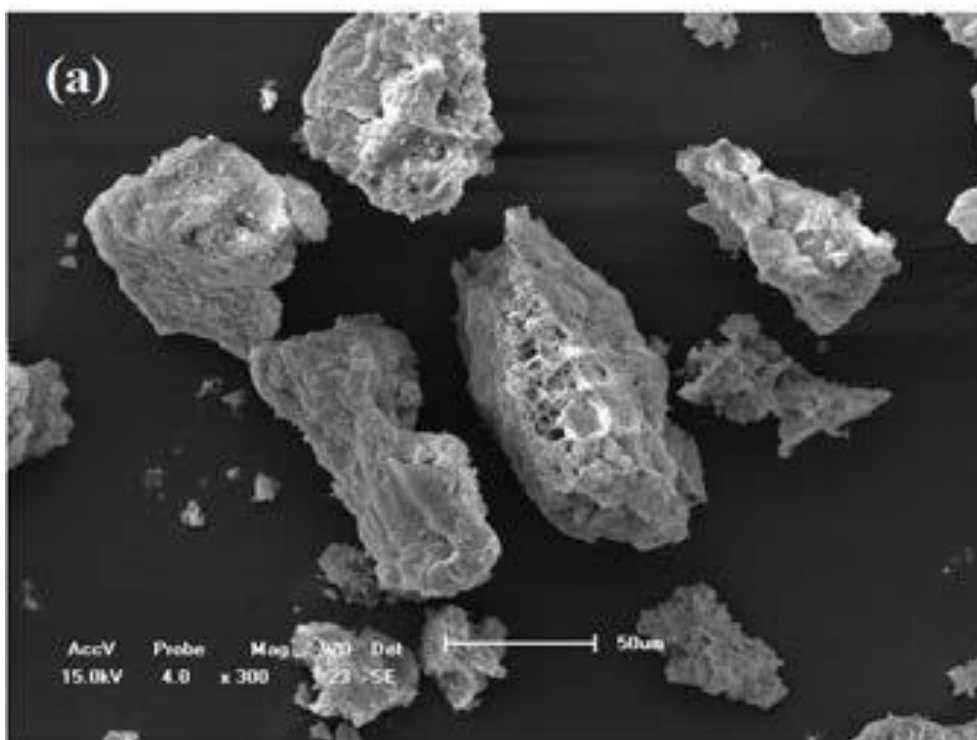


FIGURE 2

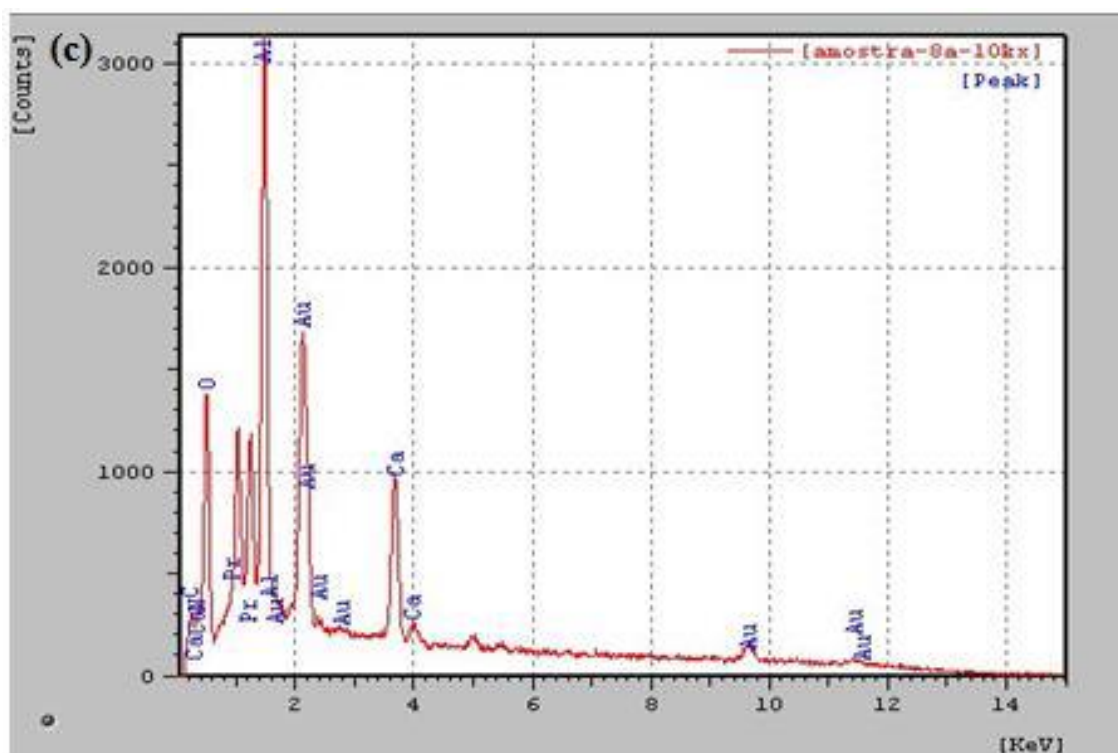


FIGURE 3

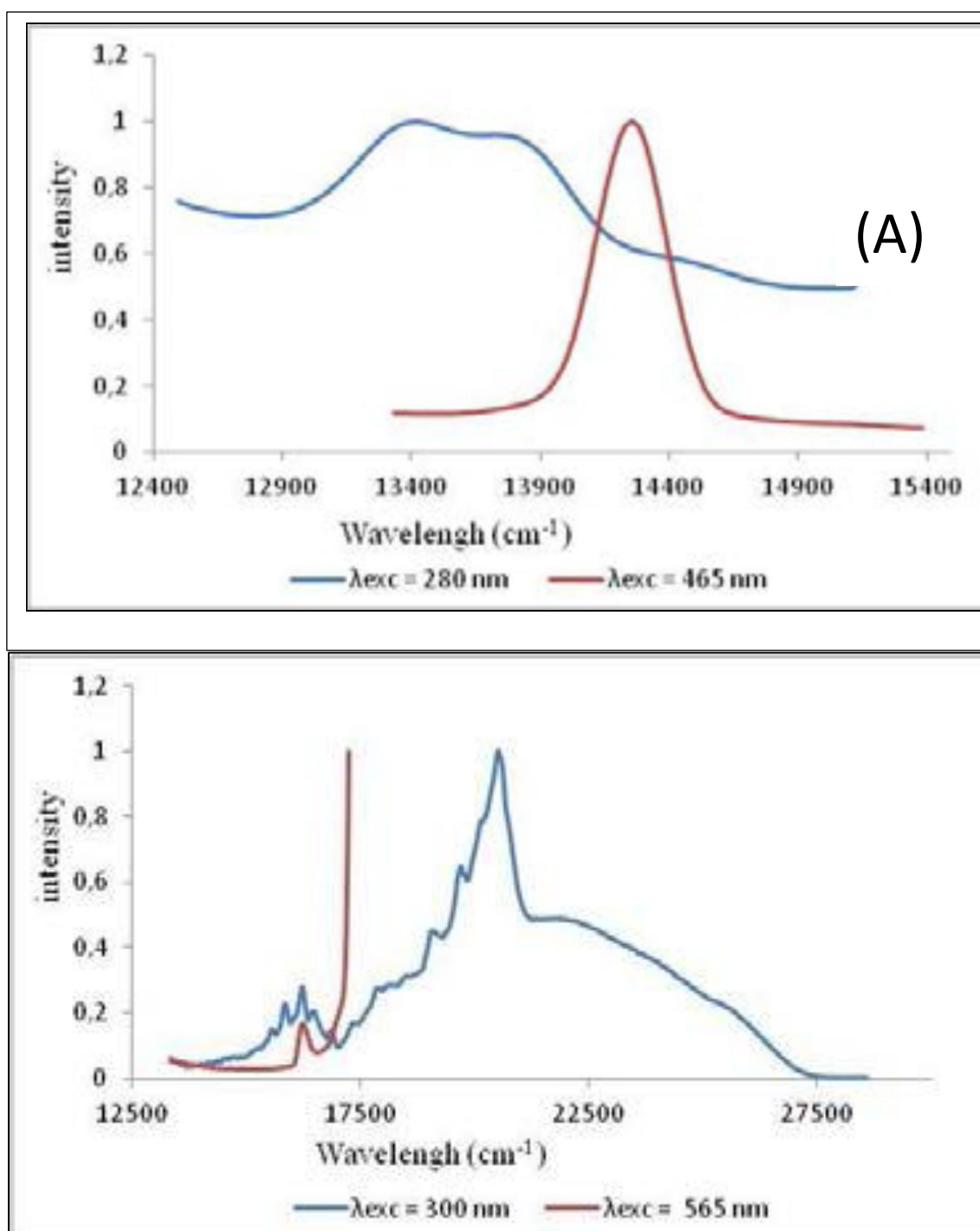


FIGURE 4

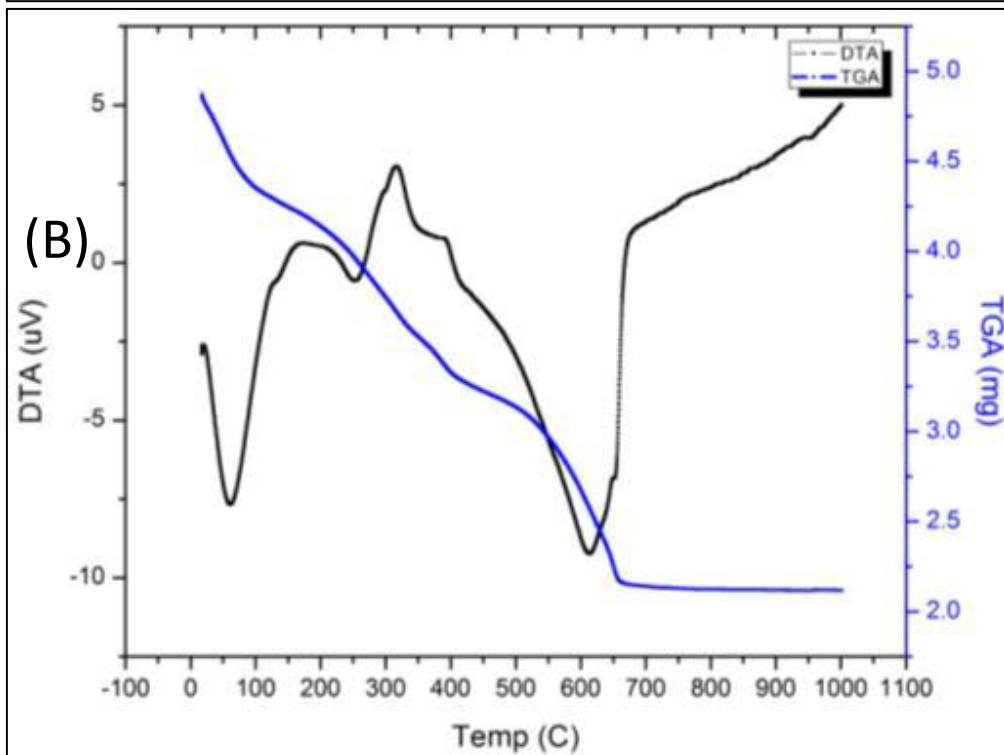
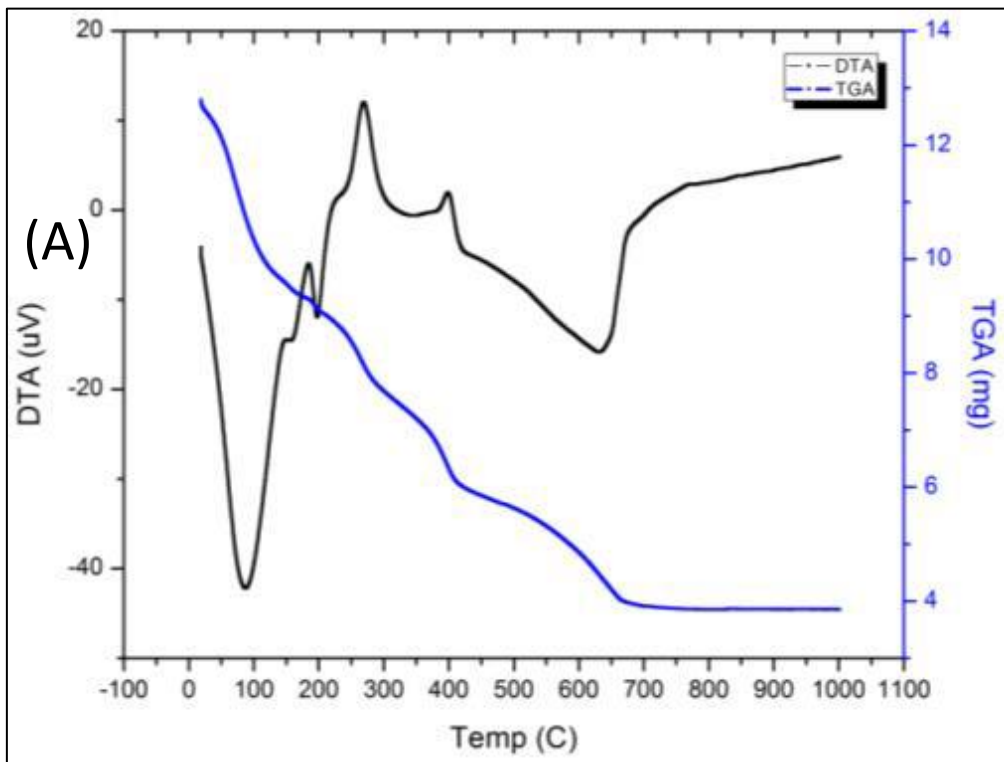


FIGURE 5

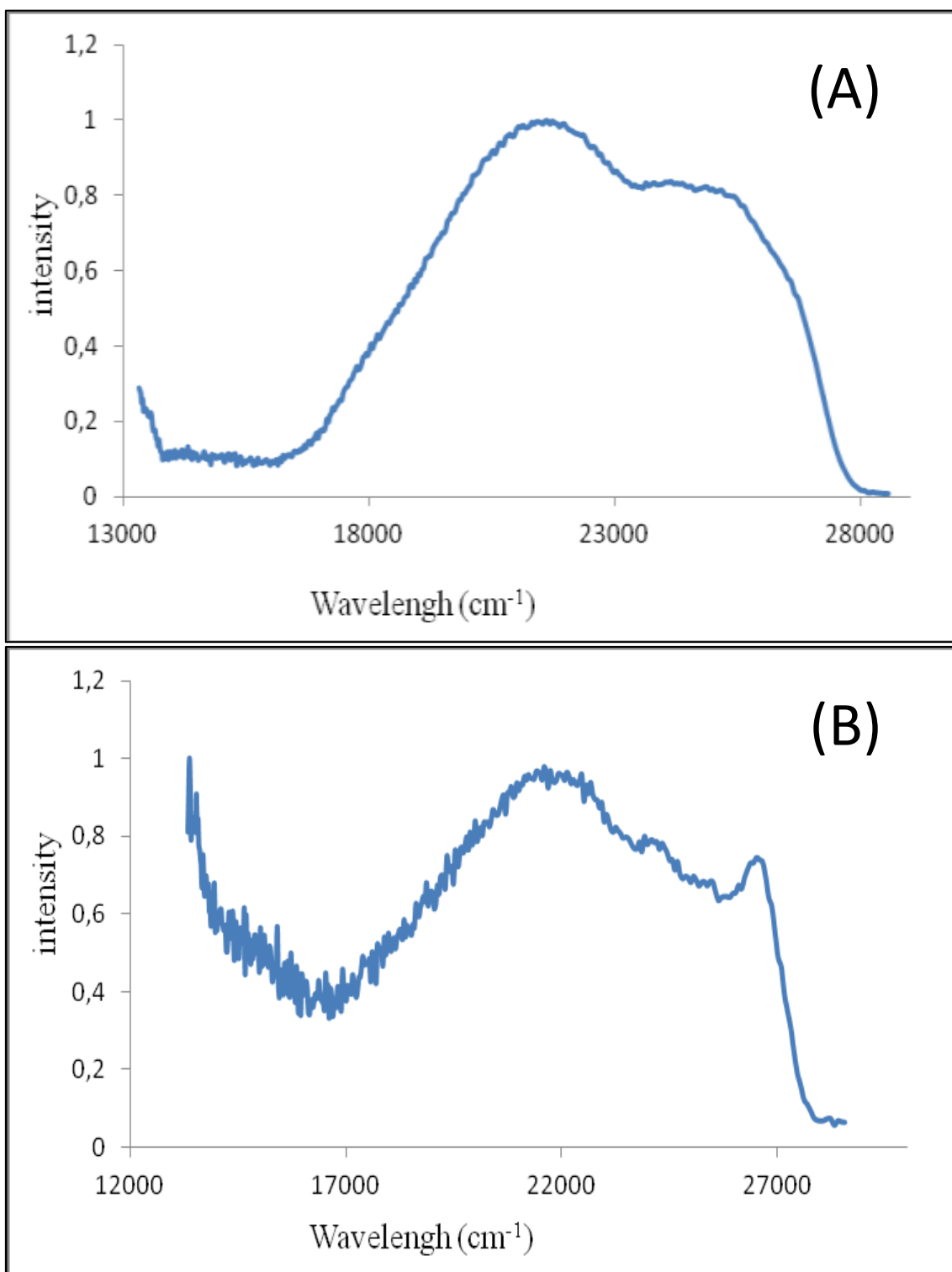


FIGURE 6

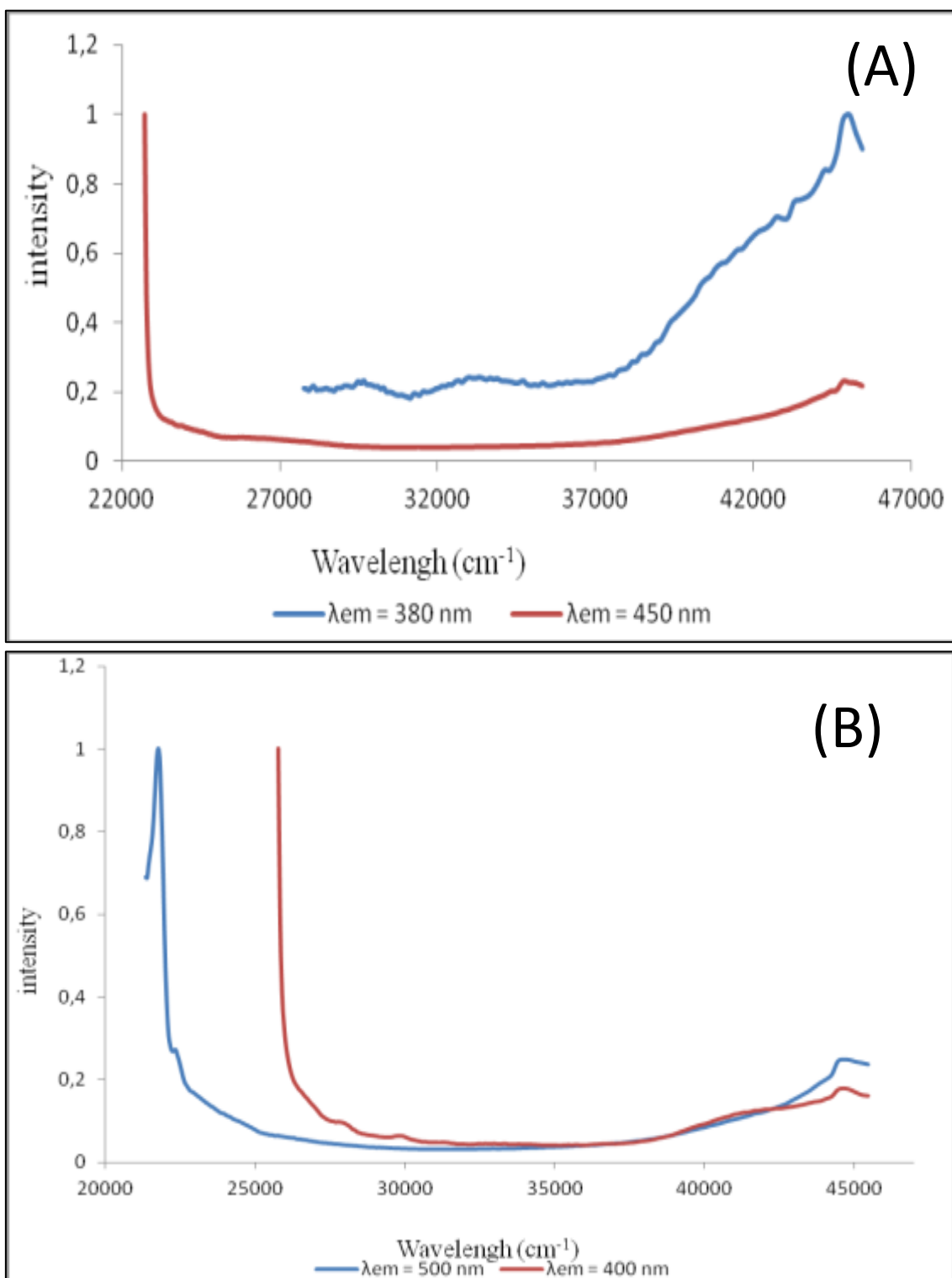
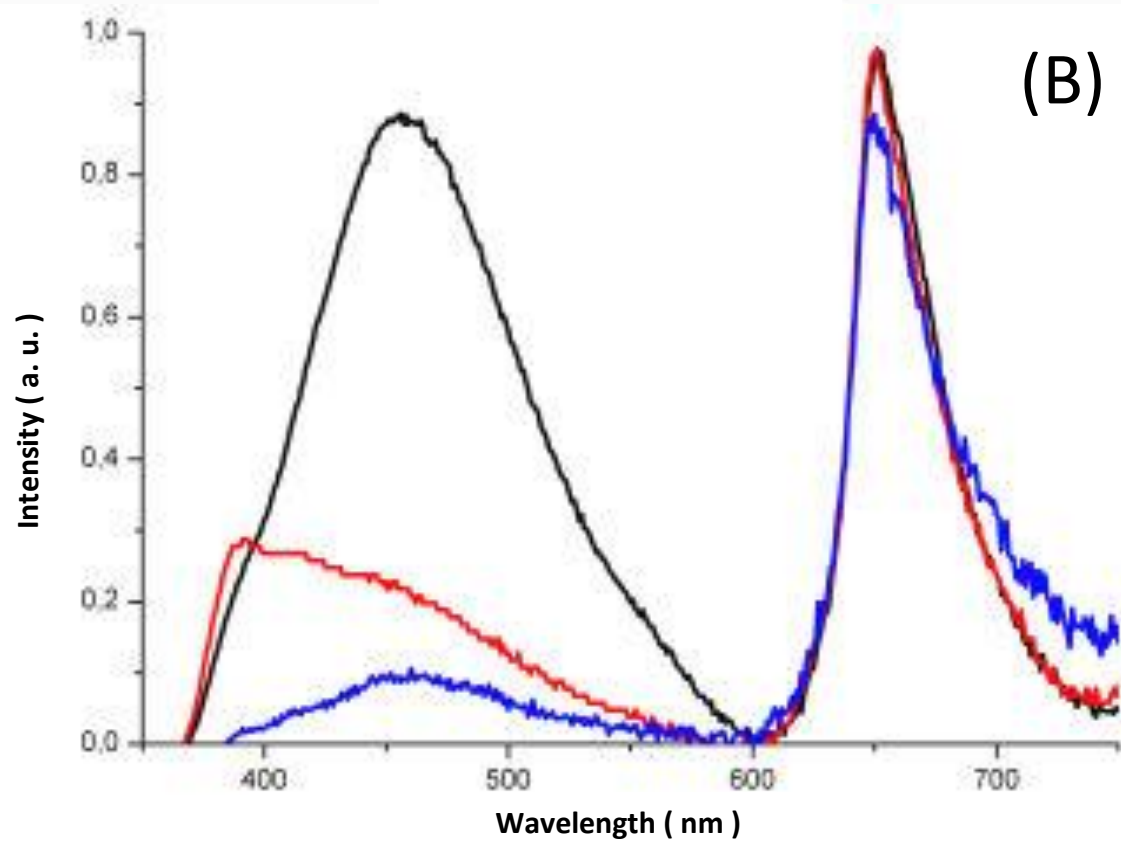
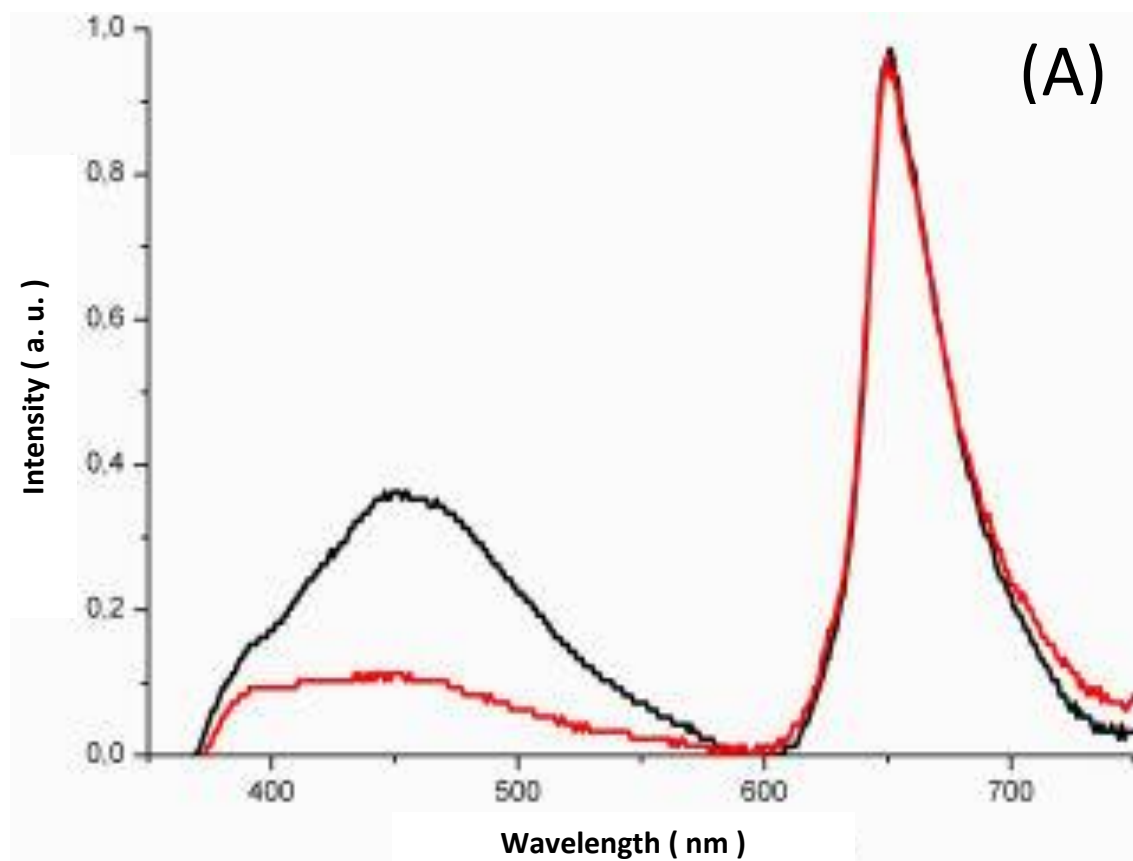


FIGURE 7



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