

Luminescent Properties of the Mn²⁺ Ion in Zinc Phosphate Glass

Frida Lissete Flores Rivera¹, Dulce Yolotzin Medina Velazquez^{1*},
Gabriela Verenice Arredondo Martínez¹, Jorge Roberto Oliva Uc²,
Carlos Eduardo Rodriguez Garcia³, Miguel Angel Barron-Meza¹, Joan Reyes Miranda¹

¹Autonomus Metropolitan University, Material Area, Mexico City, Mexico

²Potosino Institute for Scientific and Technological Research, Advanced Materials Division, San Luis, Mexico

³Faculty of Physics-Mathematics, Autonomous University of Coahuila, Saltillo, Mexico

Email: *dyolotzin@azc.uam.mx

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Abstract

In the development of new optoelectronic devices, mainly those related to solid state technology (SSL), the generation of luminescent materials with high intensity in visible region and low cost is of vital importance. For this reason, this work presents the luminescent properties of zinc phosphate glasses doped with the manganese ion 2⁺. The manganese ion offers a series of advantages with respect to rare earths, such as a more accessible cost and an intense emission in the red color that make it a great candidate for the generation of new optoelectronic devices. The methodology for the synthesis is presented in this work, as well as its luminescent properties, for concentrations of 2%, 10%, 13% and 15% atomic.

Keywords

Luminescence, Manganese, Advanced Glasses

1. Introduction

The process for the generation of light, and of greater importance in this project, is the luminescence, which is the phenomenon that some materials experience when absorbing part of the energy with which they are irradiated (ultraviolet light, infrared, X-rays, among others), causing valence electrons to be excited to a higher energy level; then these electrons return to their base state, by means of processes of phononic relaxation, emitting a photon and thus obtaining light in the visible spectrum. The emitted light is of a wavelength greater than the incident [1].

There are two processes by which a material can emit electromagnetic radia-

tion after absorbing a certain amount of energy. In the first of these processes, the absorbed energy is converted into heat energy, which is diffused through the material, and then emitted as thermal radiation. In the second case, an appreciable amount of absorbed energy excites the atoms of the material, leading to certain processes (radiative transitions and inelastic collisions), which compete with each other, to produce de-excitation, thus generating luminescent radiation [2].

Phosphate glasses are used as optical material with non-linear properties. The melting temperature is up to 1100°C and has a significantly high chemical durability. Recently, Zinc Phosphate is considered an active substrate for use in waveguide lasers and amplifiers. It is well known that the structure of phosphate glasses is best described as a network of phosphate tetrahedra (**Figure 1**) that are linked through the covalent bond of the oxygen atoms shared at the corners, known as the oxygen atom bridge [3].

Some of the properties that the glass presents and that are useful for optical applications, are the following:

- Lack crystalline structure
- Have short-range structural arrangement
- Has no definite melting point
- Softening temperature exceeds 600°C
- Transparent
- Hard
- Chemically stable

In 1852, Stokes laid down the first law of luminescence, which established that the wavelength of the incident radiation was much less than that of the light emitted. This phenomenon was first called luminescence until 1888 by Wiedemann, who also gave a first definition, which turned out not to be very accurate. Currently, luminescence is defined as the process by which a material emits light, as a result of absorbing energy [4].

Moreover, studies carried out by Hua Wan M. *et al.*, in 1972 [5], have shown that Mn²⁺ ions, when incorporated into a vitreous matrix, cause a red emission of light. This ion has been of great interest due to the high chemical durability it provides to the matrix and the high light emission [6].

For this reason, in this work, the synthesis of zinc phosphate glasses doped with the manganese ion 2⁺ will be carried out at different concentrations, and their excitation and emission spectra of each of the synthesized glasses will be obtained to later obtain their respective coordinates of chromaticity. It will finally be shown that they are optimal candidates for the generation of new low-cost optoelectronic devices.

2. Methodology

First, the following molar ratio was used to obtain 5 g of Zn₃(PO₄)₂:

3.0 ZnO: 2.0 NH₄H₂PO₄: 1.0 Zn₃(PO₄)₂

The molecular masses of the precursors are shown in **Table 1**.

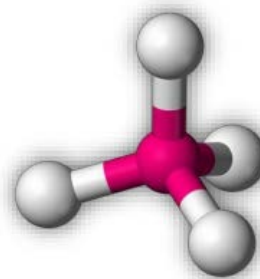


Figure 1. Ideal structure of a tetrahedral molecule with a central atom.

Table 1. Molecular masses of the precursors.

Type compound	Molar mass (g/mol)
ZnO	81.37
NH ₄ H ₂ PO ₄	114.97
Zn ₃ (PO ₄) ₂	386.05
NH ₃	17.03
H ₂ O	18.01
TbCl ₃	265.27

Once the Zinc Phosphate was obtained, we worked with the following concentrations of the Mn ions shown in **Table 2**.

By increasing the concentration of the manganese ion, it is expected to reach a greater intensity, and also have a greater purity of color.

Taking as a starting point the melting point of the zinc phosphate, as well as its best heat treatment at the time of the formation of the glass, the following methodology will be carried out to obtain of zinc phosphate glass doped with ions, Mn (**Figure 2**).

3. Results and Discussion

The glasses obtained presented an amorphous structure and high transparency that makes them excellent candidates for incorporation in optoelectronic devices.

On the other hand, they presented adequate luminescent properties as shown in **Figure 3**, in black the excitation spectrum at 480 nm emission, and in red the emission spectrum at 210 nm excitation of the sample corresponding to 13% atm of Mn. The characteristic emission transitions of the manganese ion at 420, 480 and 550 nm are observed, the most intense being the one corresponding to 480 nm.

The evaluation of the luminescence emission for different manganese concentrations led to the conclusion that the best luminescence properties are found for a concentration of 13% atm of Mn as shown in **Figure 4**, because when the concentration increases there is the phenomenon of “quenching” or passivation of luminescence due to the high proximity of Mn ions with others.

Finally, obtaining the chromatic coordinate for all the concentrations evaluated made it possible to find that all the glasses emit in a chromatic coordinate very similar between the orange and red color, as shown in **Figure 5**, with the emission closest to red corresponding to 13% Mn.

The chromatic coordinate values are shown in **Table 3**.

Table 2. Concentration of Mn ions in zinc phosphate glass.

Glass	Mn concentration (%)
1	2
2	10
3	13
4	15

Table 3. Zinc phosphate glass CIE coordinate.

Mn concentration (%)	CIE	Color Purity (%)
2	0.52, 0.46	91.24
10	0.55, 0.43	96.75
13	0.54, 0.45	88.06
15	0.53, 0.46	88.93

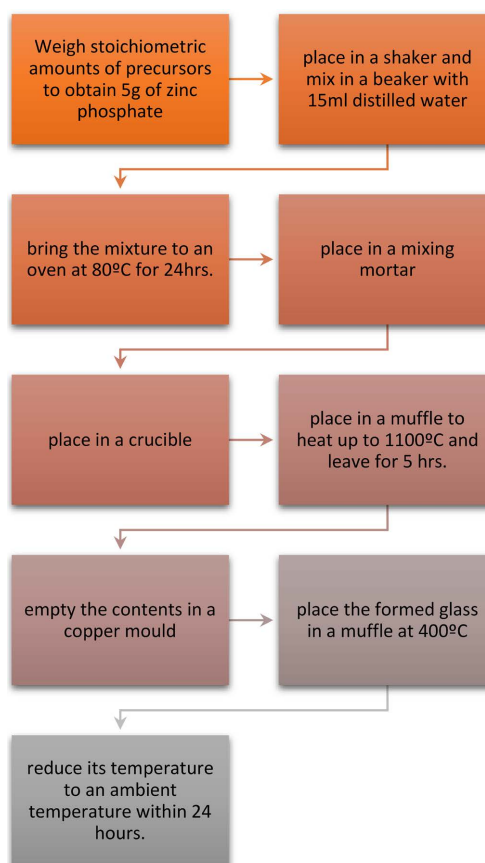


Figure 2. Diagram of the methodology for the manufacture of zinc phosphate glass doped with ions, Mn.

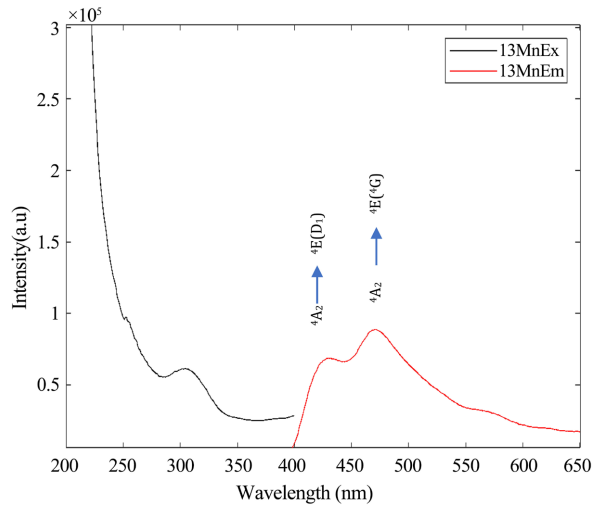


Figure 3. Excitation and emission spectrum of zinc phosphate glass with 13% Mn.

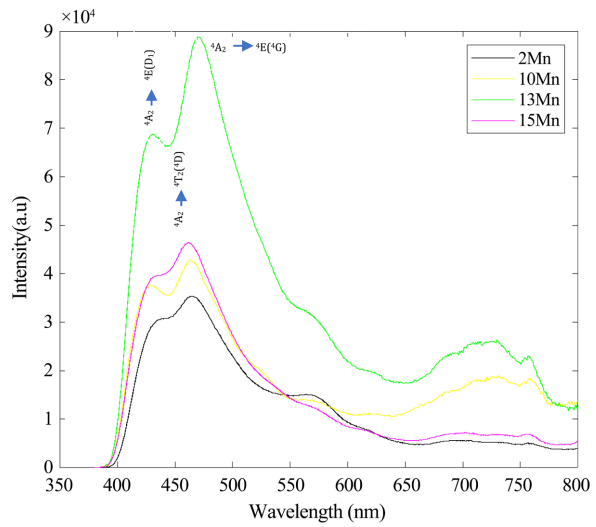


Figure 4. Emission spectra of zinc phosphate glass with 2%, 10%, 13% and 15% Mn.

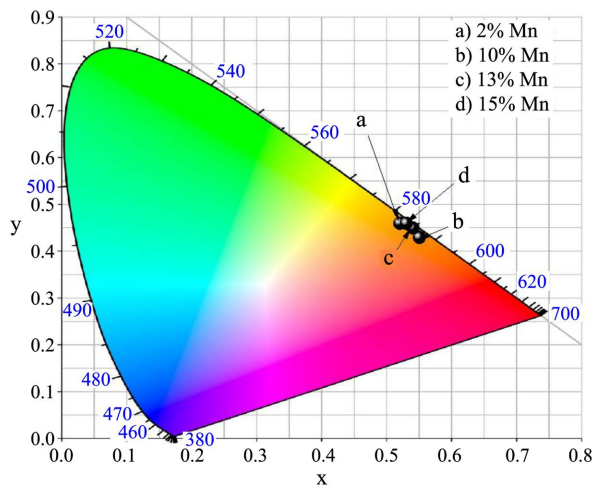


Figure 5. Chromatic coordinate of the zinc phosphate glasses with 2%, 10%, 13% and 15% Mn.

4. Conclusion

The zinc phosphate glasses doped with manganese have an adequate luminescence in the red color. With an CIE of 0.55, 0.43 for the most intensive 10% atm manganese sample, these results are precursors to a global study to find substitutes for rare earths that are with similar efficiently but more sustainable.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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