

## Comparison of the luminescence properties of phosphate-tungsten bronze and cerium doped phosphate-tungsten bronze

Tijana V. Maksimović<sup>1\*</sup>, Ljubinka G. Joksović<sup>1</sup>, Dimitrije Mara<sup>2,3</sup>, Rik Van Deun<sup>4</sup>,  
Zoran P. Nedić<sup>5</sup>, Marina Simović-Pavlović<sup>6</sup>, Maja C. Pagnacco<sup>7</sup>

<sup>1</sup> University of Kragujevac, Faculty of Science, Department of Chemistry, 34000 Kragujevac (Radoja Domanovića 12), Serbia

<sup>2</sup> University of Belgrade, Institute of General and Physical Chemistry, 11 158 Belgrade (Studentski trg 12/V P.O. Box 45), Serbia

<sup>3</sup> KU Leuven, Molecular Imaging and Photonics, Department of Chemistry, Leuven (Celestijnenlaan 200 D, box 2425, B-3001), Belgium

<sup>4</sup> Ghent University, L<sup>3</sup>-Luminescent Lanthanide Lab, Department of Chemistry, Ghent ( Krijgslaan 281-S3, B-9000), Belgium

<sup>5</sup> University of Belgrade, Faculty of Mining and Geology, 11 120 Belgrade (Đušina 7), Serbia

<sup>6</sup> University of Belgrade, Faculty of Mechanical Engineering, Belgrade (Kraljice Marije 16), Serbia

\* Corresponding author

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**Abstract:** Phosphate-tungsten bronzes (PWBs) constantly attract a lot of attention owing to their interesting chemical, mechanical, and optical properties. Furthermore, tungsten bronzes as inert inorganic solids, exhibit interesting and useful electronic properties when rare-earth ions are incorporated into their structure. Cerium doped phosphate-tungsten bronze (Ce-PWB) is obtained in the process of phase transformations of  $\text{CePW}_{12}\text{O}_{40}\times 6\text{H}_2\text{O}$  (Ce-PWA) salt. The brown crystals of Ce-PWB are formed after heating of Ce-PWA in a furnace, in a temperature range from room temperature to 650 °C. In the present paper the luminescence properties of undoped PWB and Ce-PWB are analyzed and compared. Regarding the characterized luminescence properties of PWB and Ce-PWB, only PWB matrix showed luminescence, while dopant  $\text{Ce}^{3+}$  had no significant influence on the change of the emission spectra with characteristic spectra for this ion. The obtained CIE chromaticity diagrams showed that both samples emit in the deep blue region, suggesting their possible use as a blue emitting source for white light-emitting diodes (LEDs).

**Keywords:** phosphate-tungsten bronze, cerium doped phosphate-tungsten bronze, luminescence properties

### 1. Introduction

Heteropoly acids (HPAs) are acids made of hydrogen, oxygen, and specific metals and non-metals. They have attracted interest in scientific research for over a century due to their high protonic conductivity at room temperature [1-3]. Keggin's type HPAs have a general formula of  $\text{H}_{(8-x)}\text{XM}_{12}\text{O}_{40}\times n\text{H}_2\text{O}$ , where X represents heteroatoms like  $\text{P}^{5+}$ ,  $\text{Si}^{4+}$ ,  $\text{As}^{5+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Th}^{4+}$ , and M represents metal addenda atoms like W, Mo, V, Nb. One particular

HPA, 29-PWA ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\times 29\text{H}_2\text{O}$ ), has been found to be a suitable precursor for synthesizing phosphate-tungsten bronze (PWB) and cerium-doped phosphate tungsten bronze (Ce-PWB) [4-7]. PWBs have distinct structural features with different types of canals, leading to monophosphate tungsten bronzes and diphosphate tungsten bronzes [8]. These compounds possess unique properties in mechanics, electronics, and optics, making them valuable for photonics and optoelectronics applications such as LEDs, lasers, and photodetectors. PWBs also exhibit intriguing electronic and magnetic characteristics when alkali, alkaline earth, or rare earth ions are incorporated into their structure [9]. This study focuses on Ce-PWB, which is a monophosphate tungsten bronze doped with cerium ions from the rare earth group. The luminescence properties of undoped PWB and doped Ce-PWB, are analyzed and compared to gain insights into their behavior and potential practical applications.

## 2. Experimental

### 2.1 Synthesis of heteropoly acid hydrate $\text{H}_3\text{PW}_{12}\text{O}_{40}\times 6\text{H}_2\text{O}$ (6-PWA)

Synthesis of the heteropoly acid hydrate  $\text{H}_3\text{PW}_{12}\text{O}_{40}\times 6\text{H}_2\text{O}$  (6-PWA) was done the same way as described in references [4,10]. Afterward, 6-PWA was used as the initial compound for the synthesis of doped PWB.

### 2.2 Synthesis of Ce-PWA and Ce-PWB

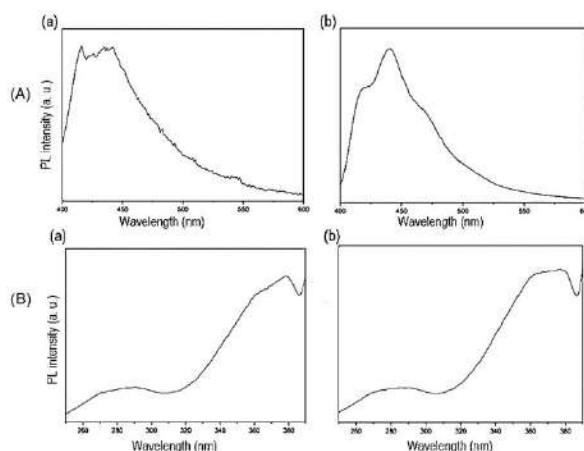
Ce-PWA was prepared by mixing the aqueous solution of 6-PWA, prepared by dissolving in distilled water, with an aqueous solution  $\text{CeCl}_3\times 7\text{H}_2\text{O}$  solution, prepared by dissolving 0.9975 g of  $\text{CeCl}_3\times 7\text{H}_2\text{O}$  (Acros Organics, Belgium) in distilled water. The obtained solution was slightly heated and left over night at room temperature to complete the crystallization process. Subsequently, the synthesized Ce-PWA salt was heated in a furnace in a temperature range from room temperature to 650 °C (at 10 °C  $\text{min}^{-1}$ ), and brown crystals of Ce-PWB were formed.

### 2.3 Characterization

Luminescence measurements were conducted using an Edinburgh Instruments FLSP920 UV-Vis-NIR spectrometer. To induce excitation, a stationary 450W Xe lamp was used. Time-resolved measurements were captured using a 60 W Xe lamp, operating at a frequency of 100 Hz. The emitted signals within the visible region were recorded using a Hamamatsu R928P photomultiplier tube. All luminescence measurements were performed under ambient room temperature conditions. For powder samples, the powders were carefully positioned between quartz plates, specifically Starna cells of type 20/C/Q/0.2. The time-resolved measurements were then fitted with a monoexponential function for analysis.

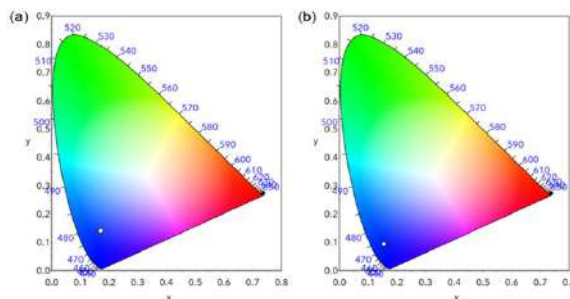
## 3. Results and discussion

The photoluminescence (PL) properties of PWB and Ce-PWB have shown only the luminescence of the matrix PWB, while the dopant  $\text{Ce}^{3+}$  has no significant effect on the change of the emission spectra with characteristic emission for this ion. The emission and excitation spectra of PWB and Ce-PWB are shown in Figure 1. The  $\text{Ce}^{3+}$  emission was not observed when excited in one of the  $\text{W}=\text{O}$  charge transfer bands, possibly due to a low doping fraction of this lanthanide ion or its inability to integrate into the PWB matrix, preventing successful excitation. The matrix displays fluorescence properties with broadband emission spanning from 400 to 500 nm. The addition of  $\text{Ce}^{3+}$  to the matrix does not exhibit the typical emission peaks found in the  $\text{Ce}^{3+}$  ion emission spectrum.



**Figure 1.** (A) Emission spectra of: (a) PWB and (b) Ce-PWB excited at 376 nm at room temperature; (B) Excitation spectra of: (a) PWB and (b) Ce-PWB monitored at the emission peak maximum  $\sim 430$  nm at room temperature.

According to the CIE chromaticity diagrams, presented in Figure 2, both samples, PWB and Ce-PWB, emit light in the deep blue region, suggesting their potential application as a blue-emitting source for white light LEDs.



**Figure 2.** The CIE chromaticity diagrams of: (a) PWB and (b) Ce-PWB excited at 376 nm.

#### 4. Conclusions

In this research, Ce-PWB is synthesized through the thermal conversion of Ce-PWA, derived from 12-tungstophosphoric heteropolyacid as the precursor. Notably, cerium, a rare earth metal lanthanide ion, is introduced as a novel dopant for PWB. The

resulting brown crystals of Ce-PWB are formed by heating Ce-PWA in a furnace, with temperatures ranging from room temperature to 650 °C. The obtained results indicate that

doping PWB with Ce<sup>3+</sup> ions, resulting in Ce-PWB, shifts the emission towards the red region. Additionally, both samples, PWB matrix, and Ce-PWB, emit light in the deep blue range, which indicates their potential application as a blue-emitting source for white light LEDs.

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