Synthesis and characterization of cerium salt of 12-tungstophosphoric heteropoly acid – Ce-PWA

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Abstract: Cerium salt of 12-tungstophosphoric heteropoly acid – Ce-PWA has been successfully synthesized. For the preparation of cerium salt (Ce-PWA), the 12-tungstophosphoric heteropoly acid $H_3PW_{12}O_{40}\times 29H_2O$ (PWA) is used as the starting material. PWA is obtained by combining the aqueous solution of the $Na_2WO_4\times 2H_2O$ with the mixture containing H_3PO_4 and HCl. Afterward, PWA was transformed into $H_3PW_{12}O_{40}\times 6H_2O$ (6-PWA) by heating it to 80 °C in a kiln. The aqueous $CeCl_3\times 7H_2O$ solution was prepared by dissolving 0.9975 g $CeCl_3\times 7H_2O$ in distilled water. This solution is then mixed with an aqueous solution of 6-PWA, slightly heated in order to start the crystallization process, and left during the night to finish the crystallization. The synthesized Ce-PWA salt is then characterized by the following techniques: thermal analysis (TGA and DTA), X-ray powder diffraction (XRPD) and Fourier-transform infrared spectra (FTIR). Synthesized salt Ce-PWA can be successfully used as a precursor in the synthesis process of cerium-doped phosphate tungsten bronze (Ce-PWB).
Keywords: heteropoly acids, cerium salt of 12-tungstophosphoric heteropoly acid (Ce-PWA), synthesis of Ce-PWA, characterization of Ce-PWA

1. Introduction

Heteropoly acids (HPAs) are a distinctive class of metal–oxygen cluster compounds composed of transition metal oxides and a central heteroatom (e.g., P, Si, As). They combine structural diversity, versatile physicochemical properties, and high proton

conductivity at ambient temperature [1], making them attractive for applications in catalysis, ion exchange, electrochemistry, and materials science. Among the various structural types, Keggin-type HPAs are particularly notable for their high stability and well-defined composition, expressed as $H_{(8-x)}XM_{12}O_{40}\times nH_2O$, where X denotes the heteroatom, M is W^{6+} or Mo^{6+}, and n (6–31) determines hydration level and influences reactivity [1, 2]. Cerium salts of 12-tungstophosphoric acid, especially in their hexahydrate form, have been reported as effective precursors for the synthesis of cerium-doped phosphate tungsten bronze (Ce-PWB). In the present study, the cerium salt of 12-tungstophosphoric heteropoly acid (Ce-PWA) was synthesized, providing a foundation for the development of novel functional materials derived from HPAs.

2. Methodology

2.1 Synthesis of heteropoly acid hydrate $H_3PW_{12}O_{40}\times 6H_2O$ (6-PWA)

Synthesis of the heteropoly acid hydrate 6-PWA was done in the same way as described in references [4,10]. Afterward, 6-PWA was used as the initial compound for the synthesis of Ce-PWA**.**

2.2 Synthesis of cerium salt of 12-tungstophosphoric heteropoly acid (Ce-PWA)

The aqueous 6-PWA solution was prepared by dissolving 8 g of 6-PWA in distilled water. The aqueous solution of $CeCl_3\times 7H_2O$ was prepared by dissolving 0.9975 g $CeCl_3\times 7H_2O$ in 10 mL of distilled water. The Ce-PWA solution was obtained by mixing these two previously mentioned solutions. The obtained Ce-PWA solution was slightly heated and left overnight at room temperature to complete the crystallization process.

2.3 Characterization

The Ce-PWA salt was characterized by DTA/TGA (TA SDT 2960, 10 °C min^{-1}, ambient–800 °C, N_2 flow), FTIR (Thermo Nicolet iS20, KBr pellet, 32 scans, 4 cm^{-1}), XRPD (Rigaku Ultima 4, Cu Kα, 40 kV, 40 mA, 2θ = 10°–90°, 0.05° step, 1.5 s/step, 23 °C, Si standard), and PL (Edinburgh FLSP920, 450 W Xe steady-state, 60 W Xe 100 Hz time-resolved, Hamamatsu R928P, quartz cuvettes, monoexponential decay).

3. Results and Discussion

3.1 Thermal analysis (DTA and TGA)

The results of thermal analysis of CePWA, in a temperature range from room temperature to 900 °C, are shown in Figure 1. The DTA curves are represented in blue color, while the TGA curves are represented in green color. The DTA curve of Ce-PWA shows three endothermic peaks at 60 °C, 180 °C (doublet), and 340 °C, and one exothermic at about 600 °C. Anhydrous phase of CePWA is formed when the samples lose molecules of water.

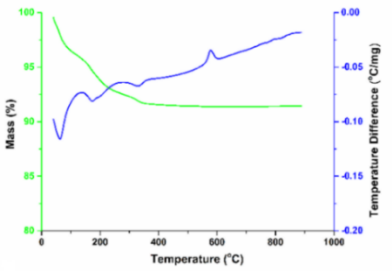

Figure 1. DTA and TGA curve of Ce-PWA

3.2 Fourier transformed infrared spectra (FTIR)

In Figure 2 are shown FTIR spectra of: (a) PWA and (b) Ce-PWA, recorded at room temperature. In both FTIR spectra, bands characteristic of the H_2O molecule, the PO_4 tetrahedron, and the WO_6 octahedron are observed. The broad band in the spectral range from 4000 cm^{-1} to 3500 cm^{-1} corresponds to the stretching vibrations ν(OH) of water molecules, while the bands around 1600 cm^{-1} confirm the in-plane bending vibrations δ(OH) of water molecules.

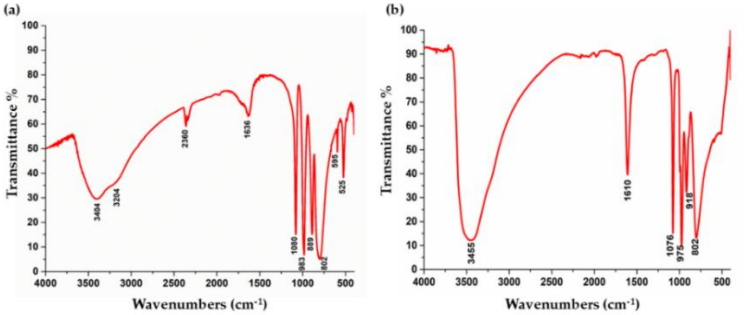

Figure 2. FTIR spectra of: (a) 6-PWA and (b) Ce-PWA

3.3 X ray powder diffraction (XRPD)

The observed XRPD pattern of Ce-PWA is shown in Figure 3. At first glance, the presented graph shows slight to moderate deviations from that obtained for cubic 6-PWA (calcined at around 60–170 °C [3]). This likely indicates that this compound was not sufficiently dehydrated and, as a result, contains more than 6 water molecules, meaning the 6-PWA structure was not fully formed at 80 °C.

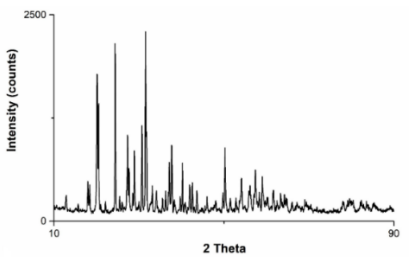

Figure 3. XRPD patterns of Ce-PWA

3.4 Luminescence measurements

The CIE chromaticity diagrams of PWA and Ce-PWA are shown in Figure 4. The CIE chromaticity diagrams show that both examined samples emit in the deep blue region which gives these materials potential use as blue emitting sources for white-light LEDs.

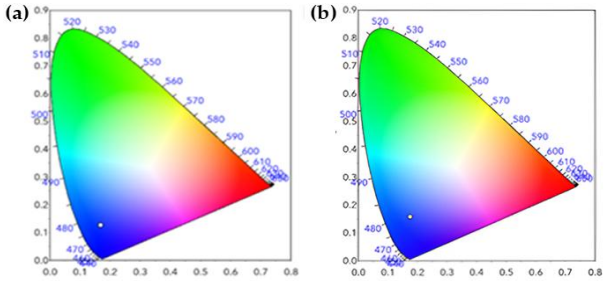

Figure 4. The CIE chromaticity diagrams of: (a) PWA and (b) Ce-PWA excited at 320 nm

4. Conclusions

In this study, we successfully synthesized the cerium salt of 12-tungstophosphoric heteropoly acid (Ce-PWA). The obtained salt is characterized by DTA/TGA, XRPD, FTIR, and PL. Synthesized salt Ce-PWA can be successfully used as a precursor in the synthesis process of cerium-doped phosphate tungsten bronze.

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