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## SYNTHESIS OF CALCIUM DOPED PHOSPHATE TUNGSTEN BRONZE

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### ABSTRACT

A study is presented of phase transitions of acid  $\text{CaHPW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$  salt of 12-tungstophosphoric acid and characterized in the temperature range from room temperature to 1093 K. The structure and its phase transformations were characterized by thermal analysis (TGA and DSC), X-ray powder diffraction (XRPD) and Fourier-transform infrared spectra (FTIR). Dehydration processes are finished at about 770 K. Keggin's anions are transformed by solid-solid recrystallization at about 873 K in calcium doped phosphate tungsten bronze.

### INTRODUCTION

Heteropoly acids Keggin's type with general formula  $\text{H}_{3-x}\text{XM}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$  ( $x=0-1$ ;  $\text{X}=\text{P}^{5+}$ ,  $\text{Si}^{4+}$ ,  $\text{As}^{5+}$ ,  $\text{Ge}^{4+}$ ,  $\text{Ce}^{4+}$ ,  $\text{Th}^{4+}$ ;  $\text{M}=\text{Mo}$ ,  $\text{W}$ ,  $\text{V}$ ,  $\text{Nb}$ ;  $n=31-6$ ) belong to new materials, primarily interesting because of their high protonic conductivity at room temperature [1-3]. Our investigations at high temperature of 12-tungstophosphoric acid calcium salt 6-hydrate show that this heteropoly compound could be used as a precursor for the synthesis of calcium doped phosphate tungsten bronze [4,5]. The potential application of tungsten bronzes is in their installation in batteries and fuel cells and as catalysts for electroreduction of oxygen [6]. Numerous structural studies concerning adaptability of the  $\text{PO}_4$  tetrahedra to an  $\text{ReO}_3$  type framework of corner-sharing  $\text{WO}_6$  octahedra showed the existence three families of such intercalated compounds: monophosphate tungsten bronzes with pentagonal tunnels ( $\text{MPTB}_p$ ) or with hexagonal tunnels ( $\text{MPTB}_h$ ), and diphosphate tungsten bronzes with hexagonal tunnels ( $\text{DPTB}_h$ ) [7]. The physical properties of monophosphate tungsten bronzes yielded interesting

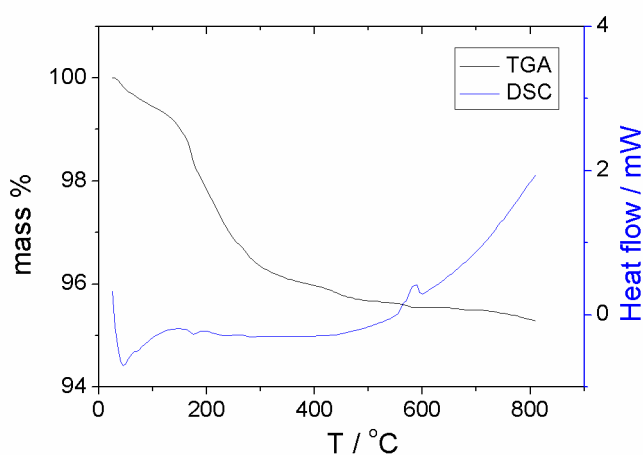
correlations between their electromagnetic properties and crystal structure [8]. The present paper deals with the synthesis and characterizations of calcium doped phosphate tungsten bronze, obtained in the process of high-temperature transformation of 12-tungstenphosphoric acid calcium salt.

## EXPERIMENTAL

The 12-tungstenphosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 29\text{H}_2\text{O}$ ) was synthesized by the procedure described in detail in [9]. The salt acid  $\text{CaHPW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$  prepared ionic exchange  $\text{H}^+$  in heteropoly acid with calcium ion. Thermal investigation were performed using TA Instruments STD 2960 Simultaneous DSC-TGA scanning rate 10 K/min. X-ray powder diffraction (XRPD) patterns were obtained using a Rigaku Ultima4 automated diffractometer with a Cu tube operated at 40 kV and 40 mA. The instrument was equipped with a curved graphite monochromatic diffraction beam, and Xe-filled proportional counter. The diffraction data were collected in the  $2\theta$  Bragg angle ranges from  $10^\circ$  to  $90^\circ$ , counting for 2 deg/min at every  $0.05^\circ$  steps. The divergence and receiving slits were fixed at  $0.5^\circ$  and 0.15 mm, respectively. The XRPD measurements were performed *ex situ* at room temperature in a stationary sample holder. Diffractometer alignment was checked by means of a standard Si powder material. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700, using KBr technique with 64 scan and  $2\text{ cm}^{-1}$  resolution.

## RESULTS AND DISCUSSION

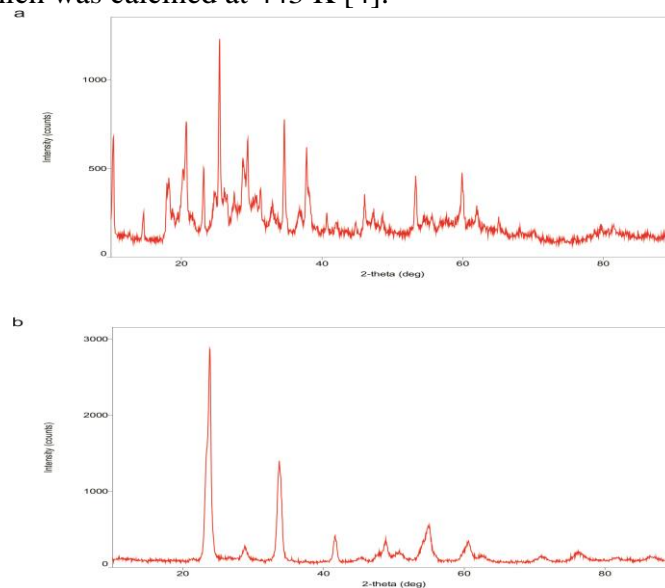
The results of thermal analysis of  $\text{CaHPW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$  from room temperature to 1100 K are presented in Fig.1. The DSC curve for the sample



**Figure 1.**  
DSC and TGA  
curves of  
 $\text{CaHPW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ .

in Fig.1. show two endothermic peaks (at 323 K and 443 K) and one exothermic (at about 863 K). The sample loss molecules water and anhydrous phase of  $\text{CaHPW}_{12}\text{O}_{40}$  is formed. The exothermal process correspond to solid-solid transformations of Keggin's anions and to bronze formation.

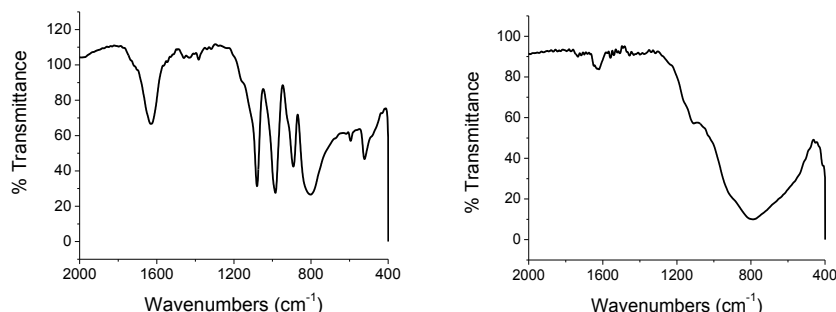
XRPD patterns of Ca-WPA and Ca-WPB are shown in Fig.2. and Table 1. The obtained data indicate that these two studied samples are obviously very different. The main reason is in their structure differences, and that there was phase temperature transition occurred. Namely, the data for Ca-WPA are very similar to those obtained for cubic stable phase determined as 6-WPA which was calcined at 443 K [4].



**Figure 2.** XRPD patterns of: (a) Ca-WPA; and (b) Ca-WPB.

On the other hand, the data for Ca-WPB are very similar to those obtained for WPB crystallized as monoclinic at temperature conditions of 1023 K [4]. It should be also mentioned that this calcium derivative also significantly differs from its Li analog synthesized at the same temperature of 923 K, which is most probably orthorhombic or triclinic [10]. The investigations about their structures are in progress, and it will be published later.

FTIR spectra of polycrystalline Ca-WPA and Ca-WPB at room temperature are shown Fig.3. In the spectrum Ca-WPA there are band characteristic of  $\text{PO}_4$  tetrahedral and  $\text{WO}_6$  octahedral. In the process of calcination, definite changes are evident, the destruction of Keggin's ions bronze is formed (Ca-WPB).



**Figure 3.** FTIR spectra of: (a) Ca-WPA; and (b) Ca-WPB.

### CONCLUSION

In this work thermally phase transformation of acid calcium salts of 12-tungstenphosphoric acid in the temperature range from room temperature to 1100 K is presented and characterized. The dehydration processes are finished at 843 K. Increasing the temperature above 860 K new material synthesized from Keggin's anion framework as precursor was formed by solid-solid recrystallization.

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