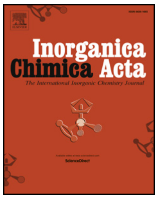
Inorganica Chimica Acta 480 (2018) 177–182

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Research paper

Structural, physical and photoelectrochemical characterization of a new semiconductor single crystal: $[(Htrz)_3][PW_{12}O_{40}].6H_2O$

D. Meziani[a], Y. Roumila[a], R. Bagtache[a], K. Abdmeziem[a], M. Trari[b,*]

[a] Laboratory of Electrochemistry-Corrosion, Metallurgy and Inorganic Chemistry, Faculty of Chemistry, USTHB, BP 32, 16111 Algiers, Algeria
[b] Laboratory of Storage and Valorization of Renewable Energies, Faculty of Chemistry, USTHB, BP 32, 16111 Algiers, Algeria

ARTICLE INFO

Keywords:
Hydrothermal synthesis
Crystal structure
Hybrid material
Semiconductor

ABSTRACT

The crystal structure, physical properties and photoelectrochemical characterization of a new single crystal hybrid semiconductor, based on α-Keggin-type polyoxometalate and 1H-1,2,4-triazole [trz] assembling $[(Htrz)_3][PW_{12}O_{40}].6H_2O$ is studied for the first time. The single-crystal X-ray diffraction of the compound, synthesized by hydrothermal method, reveals an organic-inorganic hybrid framework constructed from Keggin anions $[PW_{12}O_{40}]^{3+}$ with three monocationic triazoles, and six water molecules and crystallizing in $R\bar{3}$ space group. Further characterizations by FT-IR and Raman spectroscopy, thermal analysis and UV–Vis absorption spectra support the molecular formula. The optical study shows two transitions, directly (3.30 eV) and indirectly allowed (3.12 eV) attributed to Keggin anions. The semiconductor behavior is revealed by the electrical conductivity measurement, which follows an Arrhenius-type law with activation energy of 33 meV and electron mobility of $9.4\ 10^{-6}\ cm^2\ V^{-1}\ s^{-1}$. The photo-electrochemical study, performed in Na_2SO_4 medium, indicates *n*-type conduction with a flat band potential of -0.33 V_{SCE} and electrons density of $2.14\ 10^{17}\ cm^{-3}$.

1. Introduction

Polyoxometalates (POMs)-based inorganic-organic hybrid compounds have recently attracted a great interest not only for their variety of architectures and topologies, but also for their potential applications in many fields such as catalysis, magnetism, electrochemistry, photochemistry, and biochemistry [1–3]. It is well known that the crystal structure of materials is strongly connected to their properties and the band theory provides a way to establish their relationship. In this regard, the design of novel materials led to the generation of new band diagrams and consequently to various properties and applications [4,5].

Recently, many POM-based compounds have been obtained by employing POMs as inorganic linkers. In most works on POM-based inorganic- organic systems, flexible organo-nitrogen ligands (including pyridyl, pyrazine, triazole, etc.) are employed [6–8]. However, to our knowledge 1-H-1, 2, 4-triazole has not been widely used, due to its short bridging length and easy tendency to form insoluble products [9]. In addition, it is rather rigid and exhibits a typical coordination ability to give polynuclear clusters with unusual structures [10]. In the last years, only few papers on POM-based hybrid materials with triazole as organic ligand were reported in the literature and the relationship with their properties are less studied. Therefore, we thought of studying the properties of Keggin-triazole hybrid compounds, prepared by hydrothermal route.

In the current work, we report on the hydrothermal synthesis of a new semiconductor hybrid compound $[(Htrz)_3][PW_{12}O_{40}].6H_2O$. It has been characterized by the techniques used in solid-state chemistry. A band diagram of the junction semiconductor/electrolyte was constructed on the basis of physical and photoelectrochemical characterizations.

2. Experimental

2.1. Synthesis

$[(Htrz)_3][PW_{12}O_{40}].6H_2O$ has been synthesized hydrothermally, by dissolving $H_3PW_{12}O_{40}$ (2.88 g, 1 mmol) and 1H-1,2,4-triazole (0.07 g, 1 mmol) in 10 mL of distilled water. The mixture was stirred for 3 h at room temperature (pH ~ 2) and then transferred into 23 mL-Teflon-lined stainless steel autoclave. The crystallisation was carried out under autogenous pressure at 180 °C during 72 h. After cooling to ambient temperature, white transparent crystals were recovered by filtration, washed with distilled water and dried at 60 °C (60% yield based on W atoms). The chemical analysis of $[(Htrz)_3][PW_{12}O_{40}].6H_2O$ (3195.34): (wt%) Calc.: P, 0.97; W, 69.05, was close to the experimental composition: P, 0.68; W, 69.33.

---

* Corresponding author.
E-mail address: mtrari@usthb.dz (M. Trari).

https://doi.org/10.1016/j.ica.2018.05.019
Received 24 March 2018; Received in revised form 13 May 2018; Accepted 14 May 2018

2.2. Materials and methods

The X-ray powder diffraction (XRD) pattern was recorded with a Philips X'Pert Pro MDP diffractometer with Cu K_α radiation (λ = 1.54056 Å). Scanning electron microscopy (SEM) images were taken with a JSM-6700F (field emission) microscope, operating at 5 kV. The FT-IR spectrum was plotted using the KBr technique on a Nicolet avatar 330-FTIR spectrometer over the range (400–4000 cm^{-1}). The Raman spectrum was recorded in the range (50–1550 cm^{-1}) with backscattering mode using SENTERRA Version R200 Olympus BX51. The compound was excited with Neon ion laser (λ = 532 nm) and collected through 100 objective with an intensity of (~20 mW). The diffuse reflectance spectrum was recorded in the region (200–900 nm) on a Jasco V-650 spectrophotometer, $BaSO_4$ was used as reference. The thermal analysis (TG) was carried out under N_2 atmosphere at a heating rate of 10 °C min^{-1} thanks to a Perkin Elmer STA 6000 instrument. The electrochemical study was done on a PGZ 301 potentiostat (Radiometer analytical) at 25 °C in a Pyrex cell containing a neutral solution (Na_2SO_4, 0.5 M). A platinum foil was used as counter electrode and a saturated calomel electrode (SCE) as reference.

2.3. Crystal structure determination

The intensities of a suitable single crystal selected under a polarized microscope, were collected on a Bruker APEXII diffractometer working with Mo Kα mono-chromatic radiation (λ = 0.71073 Å) at 150 K. The multiscan absorption corrections were performed with SADABS program [11]. The structure was resolved with a sir 2002 software [12] and refined by the full-matrix least-squares methods on F^2 using the SHELX-97 package [11]. Anisotropic thermal parameters were used for the refinement of non-hydrogen atoms. The hydrogen atoms attached to C and N atoms were placed geometrically and constrained with C-H length of 0.93 Å and N-H length of 0.87 Å and refined with U_{iso} (H) 1.2 = U_{eq} (C, N). The crystallographic data and structure refinements are gathered in Table 1.

3. Results and discussion

3.1. Structure description

The X-ray diffraction on a single-crystal of $[(Htrz)_3][\alpha\text{-}PW_{12}O_{40}].6H_2O$ revealed that the compound consists of one third of α-Keggin type polyoxoanion and one protonated ligand $(Htrz)^{1+}$ with two H_2O molecules in the asymmetric unit, crystallizing with the space group $R\bar{3}$. As a result, there are one Keggin anion $[PW_{12}O_{40}]^{3-}$ whose charge is balanced by three protonated ligands $(Htrz)^{1+}$ and six water molecules in the motif, with six formula weights per unit cell. (Fig. S1).

Table 1
Crystal data and structure refinement parameters.

Formula	$[(Htrz)_3][PW_{12}O_{40}].6H_2O$
FW/g mol^{-1}	3195.34
Temp/K	150
Crystal system	Hexagonal
Space group	*R*-3
a/Å	17.9536
b/Å	17.9536
c/Å	24.3510
α/°	90
β/°	90
γ/°	120
V/$Å^3$	6797.5
Z	6
R_{int}	0.0329
R_1[a][I > 2 sigma(I)]	0.0729
wR_2[b](all data)	0.0495
GOF	1.0570

[a] $R_1 = \sum^{|} |F_0|-|F_c||/|F_0|$.

[b] $wR_2 = [\sum^{w} (|F_0|^2-|F_c|^2)^2/(w|F_0|^2)^2]^{1/2}$.

The polyoxoanion $[PW_{12}O_{40}]^{3-}$ has a typical α-Keggin structure which consists of a central PO_4 with a disordered T_d symmetry enclosed by four vertex-sharing $\{W_3O_{13}\}$ trimers. Each trimer is composed by three $\{WO_6\}$ octahedra connected in a triangular symmetry sharing common edges. The oxygen atoms in the α-Keggin structure can be classified in four types on the basis of their coordination modes: central oxygen atoms (O_c), terminal oxygen atoms (O_t), bridging oxygen atoms between two octahedra sharing an edge (O_b) and bridging oxygen atoms between two octahedra sharing a corner ($O_{b'}$). The bond distances (Å) are in the range: W–O_t 1.691–1.699(6), W–O_c 2.438–2.449(5), W–O_b 1.901–1.919(5), W–O_b' 1.898–1.926(5) (Table S1). For the PO_4 groups, the O–P–O angles lie in the range {109.32–109.62(3)°} (Table S2) while the P–O_c length varies from 1.526 to 1.533(5) Å (Table S1). Hydrogen bond is an important interaction in the design of supramolecular networks; it allows the formation of materials with various architectural topologies and consequently enhances functional properties [13]. However, in the structure of $[(Htrz)_3][\alpha\text{-}PW_{12}O_{40}].6H_2O$, each α-Keggin is connected to six $(Htrz)^{1+}$ molecular ions by several hydrogen bonds formed by the C-H … O interactions from $(Htrz)^{1+}$ ligands to oxygen atoms of $[PW_{12}O_{40}]^{3-}$ (Fig. S3); these bond lengths vary from 2.41 to 2.54 Å.

The hydrogen bonds formed by water molecules play an important role in the stability of structures [14]. Many interactions exist between the lattice water molecules and $(Htrz)^{1+}$ and $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ ions in the compound; the distances are in the range (1.88–2.75 Å). As shown in Fig. 2, the $(Htrz)^{1+}$ ligands do not develop interactions between them, and the stability of the structure cannot be explained only by their interactions with Keggin ions but rather by hydrogen bonds formed with the lattice water molecules (Fig. S3).

The interactions between the water molecules and triazole ligands form a porous three-dimensional structure along the [0 0 1] direction, where the Keggin anions are wrapped and maintained in the pores through hydrogen bonding (Fig. 1).

3.2. Characterization

The XRD pattern was recorded on powder to ascertain the purity of the phase (Fig. 2). As compared to the simulated pattern, obtained from the X-ray single crystal diffraction, only a small difference between the intensities is observed and this is due to the preferred orientations during the data collection. The full width at half maximum (β, rd) permits to evaluate the crystalline size (D) through the relation [15]:

$$D= 0.94(\beta \cos \theta)^{-1} \tag{1}$$

where θ is the diffraction angle; D is found to be 60 nm, leading to a minimal average specific surface area of 33 m2 g − 1 (= 6/ρ D), ρ being the experimental density (= 3.04 g cm − 3).

The SEM micrograph of $[(Htrz)_3][\alpha\text{-}PW_{12}O_{40}].6H_2O$ (Fig. 3), shows regular crystals with cuboid shape (0.1–0.4 mm). Both form and size of the compound are suitable for single-crystal X-ray diffraction.

The TG curve (Fig. S4) clearly displays a three-step weight loss. The first one of 3.43% (calc 3.38%) in the temperature range (30–90 °C), corresponds to the release of six H_2O molecules. The second weight loss of 6.33% (calc 6.40%) in the range (390–500 °C) is due to the release of three triazole ligands while the last loss 2.72% (calc 2.97%) in the range (500–610 °C) is attributed to the liberation of PO_4 tetrahedron. The weight loss from the TG curve supports the molecular formula of the compound.

It is well known that the α-Keggin under T_d symmetry possesses 153 normal vibration modes ($\Gamma_{vib} = 9A_1 + 4A_2 + 13E + 16\,T_1 + 22\,T_2$) in which 44 are Raman active ($\Gamma_{Raman} = 9A_1 + 13E + 22\,T_2$) and 22 are IR active ($\Gamma_{IR} = 22\,T_2$) while [Htrz] has 21 normal vibration modes classified into 15A' and 6A" with respect to Cs symmetry. The FTIR and Raman spectra of the compound are shown in Fig. 4; the characteristic