

Chemical Preparation, Thermal Behavior and IR Studies of the New Chromium Diphosphate Hydrate and Crystal Structure of its Corresponding Anhydrous

Soufiane Zerraf^{1*}, Mustafa Belhabra², Malika Tridane³, Said Belaaouad⁴

¹ Laboratory of Physical Chemistry of Materials, FSBM, Hassan II University of Casablanca, Morocco; soufiane.zerraf@gmail.com (S.F.);

² Laboratory of Physical Chemistry of Materials, FSBM, Hassan II University of Casablanca, Morocco; mustapha.belhabra@gmail.com (M.B.);

³ Regional Center of the education and training trades Casablanca. Morocco; tridane.malika@gmail.com (M.T.);

⁴ Laboratory of Physical Chemistry of Materials, FSBM, Hassan II University of Casablanca, Morocco; sbelaouad@yahoo.fr (S.B.)

* Correspondence: soufiane.zerraf@gmail.com (S.Z.);

Scopus Author ID 57196034559

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Abstract: Chemical preparation, thermal behavior, and IR studies are given for the diphosphate $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$ and its anhydrous form $\text{Cr}_4(\text{P}_2\text{O}_7)_3$. $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$, is monoclinic P2/m with the following unit-cell dimensions : $a = 16.169(1)\text{\AA}$, $b = 9.336(5)\text{\AA}$, $c = 9.446(4)\text{\AA}$, $\beta = 124.796(5)^\circ$, and $Z = 4$. The total dehydration of $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$, between 90°C and 450°C , leads to its anhydrous form, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$. $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ is isotopic to $\text{V}_4(\text{P}_2\text{O}_7)_3$, crystallizing in the orthorhombic system, space group Pmcn, $Z = 4$ with the following unit-cell dimensions: $a = 7.25(2)$, $b = 9.38(1)\text{\AA}$ and $c = 21.00(4)\text{\AA}$. $\text{Cr}_4(\text{P}_2\text{O}_7)_3$ is stable until its melting point at 1050°C . The thermal behavior of $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$ has been investigated and interpreted by comparison with IR absorption spectrometry and X-ray diffraction experiments.

Keywords: chemical preparation; thermal behavior; infrared spectrometry; X-ray diffraction.

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1. Introduction

Today there is current interest in the chemistry of materials containing diphosphates. They are involved in bioenergetics [1-3] and catalytic processes [4]. The existence of acidic diphosphate anions, such as $(\text{P}_2\text{O}_7)^{4-}$, $(\text{HP}_2\text{O}_7)^{3-}$, $(\text{H}_2\text{P}_2\text{O}_7)^{2-}$ and $(\text{H}_3\text{P}_2\text{O}_7)^{-}$, has been well established for a long time [5]. Such anions, interconnected by strong hydrogen bonds, have geometric characteristics showing infinite networks of varied geometries ranging from chains to three-dimensional networks [6-10].

This paper describes the chemical preparation, thermal behavior, and vibration properties of the new diphosphates $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$.

2. Materials and Methods

2.1 Synthesis.

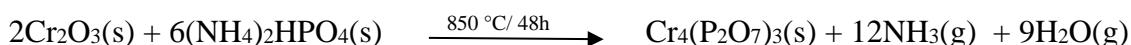
2.1.1. Chemical preparation of Cr₄(P₂O₇)₃.28H₂O.

Polycrystalline Sample of the title compound, Cr₄(P₂O₇)₃.28H₂O was prepared by slowly adding dilute diphosphoric acid to aqueous solutions of chrome carbonate according to the following chemical reaction:



The so-obtained solution was then slowly evaporated at room temperature until a polycrystalline sample of Cr₄(P₂O₇)₃.28H₂O was obtained. The diphosphoric acid used in this reaction was prepared from an aqueous solution of Na₄P₂O₇ passed through an ion-exchange resin, "Amberlite IR 120" [11].

2.1.2. Chemical preparation of Cr₄(P₂O₇)₃.



Powder diffraction patterns for the title compound were collected with a Diffractometer system=XPERT-PRO using Cu K α 1 radiation ($\lambda = 1.5406 \text{ \AA}$). The experimental 2θ range was from 5 to $70^\circ 2\theta$ with a step size of 0.01° and a counting time of 15 s per step.

2.1.3. IR absorption studies.

Spectra were recorded in the range 4000-400 cm⁻¹ with a "Bio-Red FTS 6000" spectrometer, using samples dispersed in spectroscopically pure KBr pellets.

2.1.4. Thermal analysis.

TGA-DTA coupled were performed using the SETARAM model TG-DTA 92 (GMI-IPCMS) operating from room temperature up to 600°C, in a platinum crucible and atmospheric pressure with sample mass: 7.25mg, at a heating rate 10°C/min.

3. Results and Discussion

3.1. Crystallographic characterization.

3.1.1. Crystallographic data of Cr₄(P₂O₇)₃.28H₂O.

Cr₄(P₂O₇)₃.28H₂O has a powder diffraction pattern plotted in (Figure 1) Cr₄(P₂O₇)₃.28H₂O crystallizes in the monoclinic P2/m with the following unit-cell dimensions: $a = 16.169(1)\text{\AA}$, $b = 9.336(5)\text{\AA}$, $c = 9.446(4)\text{\AA}$, $\beta = 124.796(5)^\circ$, and $Z = 4$ and $V = 587.98 (1)\text{\AA}^3$. The figures of merit are $M(20) = 93.3$ and $F(20) = 263.3(0.0025, 31)$. The lattice parameters and the merit figures, M and F, were calculated using the computer programs Dicvol and Treor [12, 13].

The powder diffraction data of Cr₄(P₂O₇)₃.28H₂O is reported in Table 1, and chemical analysis in Table 2.

3.1.2. Crystallographic data of Cr₄(P₂O₇)₃.

The crystallographic data and the final atomic positions of the non-hydrogen atoms of the Cr₄(P₂O₇)₃ [14] structure are given in Tables 3 and 4. A projection of the Cr₄(P₂O₇)₃ atomic arrangement along the b-axis is illustrated in Figure 2. It shows that all the atomic arrangement components are located around axis 2 to form networks delimiting large channels parallel to direction b. Each anion is connected to its neighbor by a strong hydrogen bond, giving rise to infinite ribbons extending along with the b axis Figure 3.

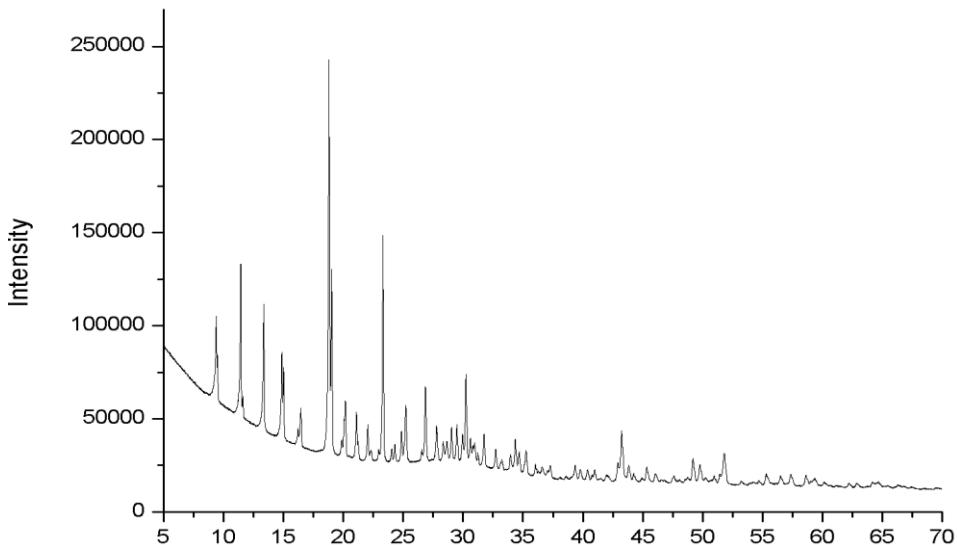


Figure 1. X-ray powder diffractogram of the phosphate Cr₄(P₂O₇)₃.28H₂O.

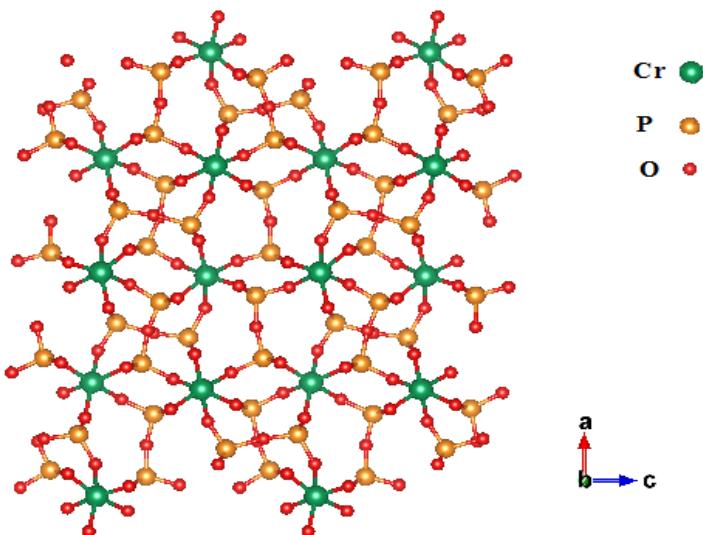


Figure 2. Projection along the b axis of the atomic arrangement in Cr₄(P₂O₇)₃.

Table 1. Powder diffraction data of Cr₄(P₂O₇)₃.28H₂O.

2θ _{obs} °	d _{obs} Å	I _{obs}	h k l	d _{cal} Å	2θ _{cal} °	Δ2θ°	2θ _{obs} °	d _{obs} Å	I _{obs}	h k l	d _{cal} Å	2θ _{cal} °	Δ2θ°
9.49	9.309	44	0 1 0	9.308	9.49	0.00	27.78	3.208	22	3 2 -2	3.209	27.78	0.00
11.42	7.736	56	0 0 1	7.738	11.43	0.01	28.65	3.112	20	0 3 0	3.109	28.69	-0.04
13.35	6.625	47	1 1 -1	6.626	13.35	0.00	29.95	2.981	32	0 2 2	2.980	29.97	-0.01
14.86	5.955	36	0 0 1	5.955	14.86	0.00	30.61	2.918	15	2 1 -3	2.918	30.61	0.00
16.20	5.464	24	1 0 1	5.464	16.21	0.01	30.96	2.885	18	0 3 1	2.886	30.96	0.01
18.80	4.716	100	1 1 1	4.715	18.81	0.01	31.24	2.861	12	1 0 -3	2.860	31.24	-0.01
19.86	4.466	26	1 0 -2	4.467	19.86	0.00	32.71	2.736	14	1 1 -3	2.735	32.72	-0.01
21.09	4.209	23	2 1 -2	4.208	21.09	0.00	33.94	2.639	11	5 2 -2	2.639	33.94	0.00
21.23	4.180	20	1 2 -1	4.179	21.24	0.01	34.68	2.584	18	0 0 3	2.584	34.69	0.00
23.30	3.814	62	2 2 0	3.814	23.30	0.00	36.04	2.490	9	0 1 3	2.490	36.04	0.00

$2\theta_{\text{obs}}^{\circ}$	$d_{\text{obs}} \text{ \AA}$	I_{obs}	$h \ k \ l$	$d_{\text{cal}} \text{ \AA}$	$2\theta_{\text{cal}}^{\circ}$	$\Delta 2\theta^{\circ}$	$2\theta_{\text{obs}}^{\circ}$	$d_{\text{obs}} \text{ \AA}$	I_{obs}	$h \ k \ l$	$d_{\text{cal}} \text{ \AA}$	$2\theta_{\text{cal}}^{\circ}$	$\Delta 2\theta^{\circ}$
24.04	3.699	15	2 1 1	3.698	24.04	0.00	39.34	2.288	7	4 1 -4	2.287	39.35	-0.01
24.30	3.659	18	4 1 -1	3.659	24.31	0.01	42.92	2.105	11	1 3 -3	2.106	42.91	0.01
24.86	3.578	26	0 1 2	3.578	24.87	-0.01	43.34	2.085	19	3 2 -4	2.084	43.37	-0.03
25.24	3.528	6	3 2 -1	3.525	25.22	-0.02	49.77	1.830	13	1 5 -1	1.831	49.76	-0.01
26.86	3.317	9	2 2 -2	3.316	26.86	0.00	51.82	1.763	14	3 5 -1	1.763	51.80	0.02

3.2. Chemical analyzes.

The chemical analysis was done by atomic absorption using a VARIAN AA-475 spectrometer. The results of the chemical analysis are consistent with the formula $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$. The table below summarizes the results of the chemical analysis of $\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$.

Table 2. Results of the chemical analyzes

Cr	P	H ₂ O			
Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
4	3.99	6	6.01	28	27.8

$\text{Cr}_4(\text{P}_2\text{O}_7)_3 \cdot 28\text{H}_2\text{O}$ is stable under ambient conditions of temperature and pressure. We monitored IR stability, X-ray diffraction, and thermogravimetric stability for about six months, and no changes or changes in the degree of hydration were observed over time.

Table 3. Crystal structure data for $\text{Cr}_4(\text{P}_2\text{O}_7)_3$.

Compound	2
Empirical Formula	$\text{Cr}_4(\text{P}_2\text{O}_7)_3$
molar mass	729.8144 g/mol
Crystal System / Space Group	orthorhombic / $P bnm$
a / Å	9.3850(1) Å
b / Å	21.0000(5) Å
c / Å	7.2600(2) Å
$\alpha / ^\circ$	90°
$\beta / ^\circ$	90°
$\gamma / ^\circ$	90°
V / Å ³	1430.07(6) Å ³
Z	4
D _{calc} (g/cm ³)	3.39 g/cm ³
μ (mm ⁻¹)	7.362
Crystal size (mm)	0.18 × 0.18 × 0.43 mm ³
Color / Shape	Colorless / Prism
Temp (K)	297(2)K
Theta range for collection	3.59° / 31.49°
Reflections collected	3278
Independent reflections	2895
Data/restraints/parameters	2448/0/147
Goodness of fit on F ²	1.113
Final R indices [I > 2σ(I)]	R ₁ = 0.0325, wR ₂ = 0.1166
R indices (all data)	R ₁ = 0.0329, wR ₂ = 0.1138
Largest difference peak / hole (Å ⁻³)	0.78/-1.40

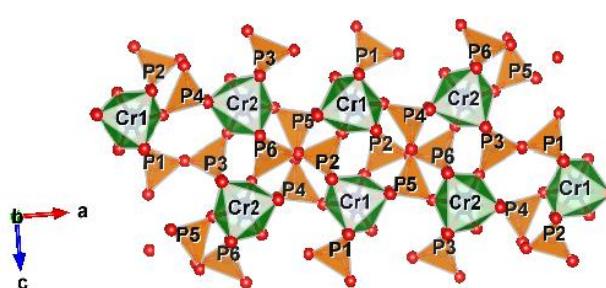


Figure 3. Projection along the b axis of the atomic arrangement in $\text{Cr}_4(\text{P}_2\text{O}_7)_3$.

Table 4. Final atomic coordinates and U equivalent temperature factors for Cr₄(P₂O₇)₃.

Atoms	X	Y	Z	Site
Cr1	0.00364	0.05362	0.26062	8d
Cr2	0.24355	0.05333	0.77933	8d
P3	0.04777	0.75000	0.03233	4c
P4	0.06126	0.75000	0.47111	4c
P5	0.10934	0.25000	0.66728	4c
P6	0.14175	0.25000	0.34272	4c
P7	0.18918	0.75000	0.00152	4c
P8	0.19933	0.75000	0.55343	4c
O9	0.02730	0.58254	0.10192	8d
O10	0.05296	0.58173	0.39299	8d
O11	0.07399	0.08123	0.69721	8d
O12	0.17693	0.08248	0.30915	8d
O13	0.19961	0.58117	0.92262	8d
O14	0.21379	0.58082	0.62587	8d
O15	0.02276	0.75000	0.60554	4c
O16	0.03135	0.75000	0.87689	4c
O17	0.07781	0.25000	0.26730	4c
O18	0.11961	0.75000	0.04732	4c
O19	0.12746	0.25000	0.50629	4c
O20	0.12890	0.75000	0.52812	4c
O21	0.17087	0.25000	0.74974	4c
O22	0.22180	0.75000	0.14357	4c
O23	0.23115	0.75000	0.41052	4c

3.3. Vibrational studies

The pyrophosphate group has a quasi-eclipsed conformation, making it possible to consider the C_{2v} group as a molecular group of symmetry. The 21 fundamental vibrations of the P₂O₇ groups are thus distributed as follows [5]:

$$\Gamma_{\text{vib}}(\text{C}_{2v}) = 7 \text{ A}_1 \oplus 4 \text{ A}_2 \oplus 4 \text{ B}_1 \oplus 6 \text{ B}_2$$

Normal coordinate analysis performed a distribution of the 21 normal modes of internal vibration.

$$\Gamma_1 = 2\text{A}_1 \oplus \text{A}_2 \oplus \text{B}_1 \oplus 2\text{B}_2 \quad \text{Valence vibration of PO}_3 \text{ groups}$$

$$\Gamma_2 = \text{A}_1 \oplus \text{B}_2 \quad \text{POP bridge stretching vibration}$$

$$\Gamma_3 = 3\text{A}_1 \oplus 3\text{A}_2 \oplus 3\text{B}_1 \oplus +3\text{B}_2 \quad \text{Deformation vibration of PO}_3 \text{ groups}$$

$$\Gamma_4 = \text{A}_1 \quad \text{Vibration deformation of the POP bridge}$$

Table 5 gives the correlation diagram for the P₂O₇⁴⁻ ion. The enumeration of normal modes of vibration in the crystal realized using the method of the site [15] shows that the 84 vibrations of the ion P₂O₇⁴⁻ are distributed as follows:

$$\Gamma_{\text{vib}} = 21 \text{ A}_g \oplus 21 \text{ B}_g \oplus 21 \text{ A}_u \oplus 21 \text{ B}_u$$

Using the same method, the counting of the external vibrations in the crystal shows that the rotation vibrations of the group P₂O₇⁴⁻ are distributed as follows:

$$\Gamma_R = 3 \text{ A}_g \oplus 3 \text{ B}_g \oplus 3 \text{ A}_u \oplus 3 \text{ B}_u$$

Concerning the translation movements of the ions P₂O₇⁴⁻, A²⁺, M²⁺, they are distributed as follows:

$$\Gamma_T = 9 A_g \oplus 9 B_g \oplus 9 A_u \oplus 9 B_u$$

$$\text{and } \Gamma_{ac} = A_u \oplus 2B_u$$

The internal vibration distribution in terms of group vibration is as follows [16-19]:

$$\Gamma_{\text{valence}} (PO_3) = 6A_g \oplus 6B_g \oplus 6A_u \oplus 6B_u$$

$$\Gamma_{\text{valence}} (POP) = 2A_g \oplus 2B_g \oplus 2A_u \oplus 2B_u$$

$$\Gamma_{\text{deformation}} (PO_3) = 12A_g \oplus 12B_g \oplus 12A_u \oplus 12B_u$$

Table 5. Internal and External Vibration Modes of the P₂O₇ Group.

Molecular group C _{2v}	Group of site C ₁	Factor group C _{2h}
Internal vibration modes		
7A ₁		21A _g
4A ₂		21A _u
4B ₁	21A(IR, R)	21B _g
6B ₂		21B _u
Rotation modes		
A ₁		3A _g
A ₂		3A _u
B ₁	3A(IR, R)	3B _g
B ₂		3B _u
Translation modes		
A ₁		3A _g
A ₂		3A _u
B ₁	3A(IR, R)	3B _g
B ₂		3B _u

By grouping the different modes of vibration, the total representation of crystals Cr₄(P₂O₇)₃.28H₂O is:

$$\Gamma_{\text{total}} = 27A_g \oplus 27B_g \oplus 27A_u \oplus 27B_u$$

The IR absorption spectra of Cr₄(P₂O₇)₃.28H₂O and Cr₄(P₂O₇)₃ are reported in Figure 4. In the 4000-1600 cm⁻¹ range, the spectra show bands that are allocated to valence and deformation vibrations of water molecules. The valence vibration bands of water molecules (vOH) are between 4000 and 3000 cm⁻¹. The water molecules' deformation vibration bands (δHOH) exist between 1700 and 1600 cm⁻¹ [20-22].

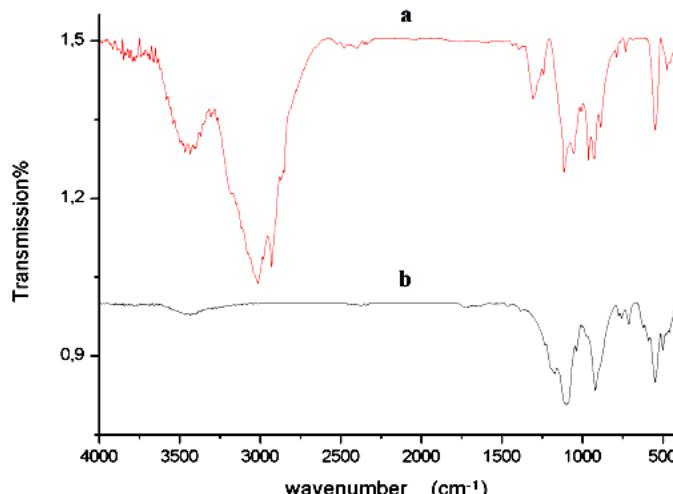


Figure 4. FT-IR spectra of (a) for Cr₄(P₂O₇)₃.28H₂O; (b) for Cr₄(P₂O₇)₃.

Between 1340 and 660 cm⁻¹, the IR absorption spectra of Cr₄(P₂O₇)₃.28H₂O and Cr₄(P₂O₇)₃ (Figure 4) show valence vibration bands characteristic of phosphates with P₂O₇⁴⁻ anions.

The vibrations corresponding to the different valence and deformation bands are grouped in Table 6.

Table 6. Frequencies (cm⁻¹) of IR absorption bands for Cr₄(P₂O₇)₃.28H₂O.

Frequencies v (cm ⁻¹)		Movements
Cr ₄ (P ₂ O ₇) ₃ .28H ₂ O	Cr ₄ (P ₂ O ₇) ₃	
3427	-	V O-H
2360	-	V _d H-O-H
1670	-	
1116	1270 1112	V _{as} PO ₃
996	980	V _s PO ₃
920	915	
735	740 680	V _{as} POP
572	550	δ _{as} PO ₃
485	490	δ _s PO ₃

3.4. Thermal behavior.

Figure 5 shows the thermogram of TGA-DTA coupled with thermal dehydration at atmospheric pressure of Cr₄(P₂O₇)₃.28H₂O by linear temperature rise with heating rate 10°C/min. The analysis is carried out shows that the temperature increases linearly between 25 and 600°C.

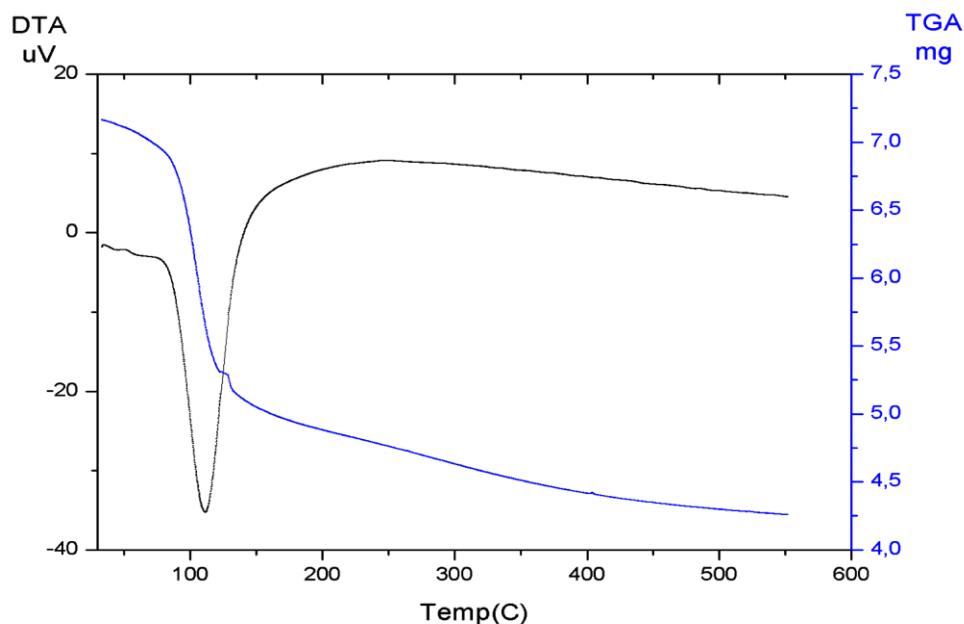


Figure 5. TGA-DTA coupled with thermal dehydration at atmospheric pressure of Cr₄(P₂O₇)₃.28H₂O with heating rate 10°C/min.

The TGA thermograms realized at different heating rates all have the same speed and two mass loss stages corresponding to twenty-eight water molecules perform unit. For the heating rate of 10°C/min, the ATG curve has two stages of loss of mass:

- The first step between 40°C and 120°C corresponds to the rapid elimination of water with a maximum dehydration rate at 110 °C with a very intense peak. At 120°C, the weight loss is 28% of the hydrate's molar mass and corresponds to the elimination of 18 H₂O.

- The second step between 120 and 500°C corresponds to a mass loss of 12% of the hydrate's molar mass and results in a continuous removal of 10 H₂O, with a maximum dewatering rate at 170°C.

4. Conclusions

The new chromium diphosphate hydrate has been prepared by the method of ion exchange resin. The title compound was characterized by crystallography using the computer programs Dicvol and Treor, and we found the same unit-cell parameters and good factors of merit. The unit-cell parameters are the following: $a = 16.169(1)\text{\AA}$, $b = 9.336(5)\text{\AA}$, $c = 9.446(4)\text{\AA}$, $\beta = 124.796(5)^\circ$, and $Z = 4$. The thermal behavior of chromium diphosphate hydrate has been studied by X-ray diffraction, infrared spectroscopy, and thermal analyses TGA-DTA. After partial dehydration, the new chromium diphosphate hydrate leads to an amorphous phase by X-ray diffraction and IR spectroscopy. The final product of the total thermal dehydration of Cr₄(P₂O₇)₃.28H₂O under atmospheric pressure is its corresponding anhydrous diphosphate of chromium. The structure of the diphosphate of chromium was reinvestigated by X-ray diffraction and IR spectroscopy. The vibrational spectra of chromium diphosphate hydrate and its corresponding anhydrous have been examined and interpreted in the domain of the stretching vibrations of the P₂O₇⁴⁻ anion.

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Conflicts of Interest

The authors declare no conflict of interest.

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