ISSN 2347 - 3983
Volume 8, No. 1 January 2020
International Journal of Emerging Trends in Engineering Research
Available Online at http://www.warse.org/IJETER/static/pdf/file/ijeter30812020.pdf
https://doi.org/10.30534/ijeter/2020/30812020

Engineering Techniques applied for studies by Infrared vibration, crystallographic characterization and Thermal Behavior of two new cyclotriphosphates

Hamza Marouani [1], Malika Tridane [2], El Mehdi Majdi[1], Soufiane Zerraf [1], Mustafa Belhabra[1], Said Belaaouad[1]

[1] Laboratory of Chemistry-Physics of Materials, Faculty of Sciences Ben M'Sik B. P. 7955, Hassan II Universityof Casablanca, Casablanca, Morocco

[2]Centre Régional des métiers d'éducation et de formation Rabat, Maroc.

ABSTRACT

Chemical preparation, crystallographic characterization, thermal behavior, and IR vibration spectrometry studies are given for the cyclotriphosphate decahydrate of manganese and dicalcium $MnCa_2(P_3O_9)_2.10H_2O$ and its anhydrous form $MnCa_2(P_3O_9)_2$.$MnCa_2(P_3O_9)_2.10H_2O$ is monoclinic P21/n with the following unit-cell dimensions: a = 9.631 (5) Å, b = 18.173 (7) Å, c = 7.976 (4) Å, β = 109.438 (4) °, Z = 2. The thermal dehydration study of the title compound $MnCa_2(P_3O_9)_2.10H_2O$ was made by X-Ray diffraction, IR vibration spectrometry and thermal analyses TGA (TG,DTG), DTA and DSC to identify and characterize $MnCa_2(P_3O_9)_2.10H_2O$, the intermediate and final phases. The total thermal dehydration of $MnCa_2(P_3O_9)_2.10H_2O$ leads to its corresponding anhydrous new cyclotriphosphate $MnCa_2(P_3O_9)_2$ as an intermediate cyclotriphosphate. $MnCa_2(P_3O_9)_2$ was also chraracterized by X-ray diffraction and found to crystallize in the hexagonal system, space group P3 with the following unit-cell dimensions a =b = 7.392 Å (9) and c = 20.134 (2) Å. $MnCa_2(P_3O_9)_2.10H_2O$ and $MnCa_2(P_3O_9)_2$ were also characterized by infrared vibration spectrometry IR and Raman spectroscopy.

Key words: Engineering Techniques, Chemical preparation, chemical analyses, crystallographic characteriozation, thermal behavior, infrared spectrometry, thermal analyses TGA (TG,DTG), DTA and DSC

1. INTRODUCTION

Cyclotriphosphates associated to two divalent cations are rare, in fact, the only one well characterized till now by A. Durif and al [1] is $ZnBa_2(P_3O_9)_2.10H_2O$. That's why we made our research on such cyclotriphosphates. During a systematic investigation on the series of $M^{II}M'^{II}_2(P_3O_9)_2.nH_2O$ (M^{II} and M'II alkaline earth and transition metals) we found a new cyclotriphosphate associated to calcium and manganese $MnCa_2(P_3O_9)_2.10H_2O$. This Cyclotriphosphate decahydrate of manganese and calcium is a compound that has never been seen before. To our knowledge, it has not been the subject of any physico-chemical or radiocristallographic studies. We propose, in the present paper, to characterize it and study its thermal behavior under atmospheric pressure by X-Ray diffraction, infrared vibration spectrometry IR, Raman spectroscopy, TGA thermogravimetric analysis (TG and DTG), differential thermal analysis (DTA) and differential calorimetric analysis (DSC). The dehydration of hydrated cyclotriphosphates leads in some cases to their corresponding anhydrous compounds. This possibility exists in our case because the title compound is a new one and this thermal study permits us to identify the intermediate and final phases of the dehydration and decomposition under the effect of temperature for $MnCa_2(P_3O_9)_2.10H_2O$.

2. CHEMICAL PREPARATION OF CYCLOTRIPHOSPHATE DECAHYDRATE OF MANGANESE AND DICALCIUM $MNCA_2(P_3O_9)_2.10H_2O$ AND ANHYDROUS CYCLOTRIPHOSPHATE OF MANGANESE AND DICALCIUM $MNCA_2(P_3O_9)_2$

2.1 $MnCa_2(P_3O_9)_2.10H_2O$

The cyclotriphosphate decahydrate of manganese and dicalcium, $MnCa_2(P_3O_9)_2.10H_2O$ was prepared by using nitrates of manganese and calcium. To an aqueous solution of anhydrous sodium cyclotriphosphate (3.059g of $Na_3P_3O_9$ in 60 ml of distilled water) is added in stoichiometric quantities and with mechanical stirring, a mixture in aqueous solution containing calcium nitrate tetrahydrate (2.362 g of $Ca(NO_3)_2.4H_2O$), the manganese nitrate tetrahydrate (1.255 g of $Mn(NO_3)_2.4H_2O$) and 60 ml of distilled water

The mixture of the aqueous solution of nitrates has a pink color. Mechanical stirring is maintained for twenty-four hours at room temperature. After filtration, the solution thus obtained can be treated in two different ways either evaporated slowly at room temperature, or addition of ethyl alcohol dropwise while maintaining strong mechanical agitation. In the first case, a well crystallized product is obtained, but it is not possible to grow monocrystals of a suitable size for a structural study. In the second case, after a

few minutes at room temperature, a well crystallized, light pink powder is obtained. The equation of the chemical reaction is the following:

$$2Na_3P_3O_9 + Mn(NO_3)_2.4H_2O + 2\ Ca(NO_3)_2.4H_2O \longrightarrow MnCa_2(P_3O_9)_2.l0H_2O + 6NaNO_3 \quad (1)$$

$MnCa_2(P_3O_9)_2$.$l0H_2O$ will be studied by the following techniques: X-Ray diffraction, infrared vibration spectrometry IR,TGA thermogravimetric analysis (TG and DTG), differential thermal analysis (DTA) and differential calorimetric analysis (DSC), in order to determine the number of water molecules and characterize the intermediate and final phases of its dehydration and decomposition

2.2 $MnCa_2(P_3O_9)_2$

We have prepared the anhydrous cyclotriphosphate of manganese and dicalcium, $MnCa_2(P_3O_9)_2$, directly by the method of THILO et al [1] in the dry form powder. The diammonium mono hydrogenomonophosphate, $(NH_4)_2HPO_4$, in excess and the calcium and manganese carbonates respectively $CaCO_3$ and $MnCO_3$ are intimately ground and heated at 500°C, under atmospheric pressure, in a porcelain crucible, according to the following chemical reaction:

$$MnCO_3C(s) + 2CaCO_3(s) + 6(NH_4)_2HPO_4(s) \longrightarrow MnCa_2(P_3O_9)_2\ (s) + 3CO_2\ (g) + 12NH_3\ (g) + 6H_2O\ (g). \quad (2)$$

The heat treatment was done for 5 days with frequent grindings. The product thus obtained was characterized by its X-ray diffractograms and its absorption IR spectrum, such as anhydrous cyclotriphosphate of manganese and dicalcium, $MnCa_2(P_3O_9)_2$, pure with hexagonal symmetry.The X-ray Diffractogram and the IR absorption spectrum of $MnCa_2(P_3O_9)_2$ obtained by dry route are identical to those of the product resulting from the total thermal dehydration $MnCa_2(P_3O_9)_2.10H_2O$ between 400 and 450°C. The results described previously show that $MnCa_2(P_3O_9)_2$ was obtained from two different ways. The first being the total thermal dehydration of $MnCa_2(P_3O_9)_2$ between 400 and 450°C and the second is the direct synthesis by the method of THILO et al [1].

3. CHARACTERIZATION TECHNIQUES

3.1 Chemical analyses

The chemical analysis was made by atomic absorption using a spectrophotometer type VARIAN AA-475.

3.2 X-Ray Diffraction

Powder diffraction patterns for title compound were collected with a Diffractometer system type D 5000 using Cu Kα1 radiation (λ = 1.5406 Å). The experimental 2θ range was from 5 to 70° 2θ with a step size of 0.01° and a counting time of 15 s per step.

3.3 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

3.4 Thermal analyses

- TGA-DTA

TGA and 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 in atmospheric pressure with sample mass: 7.25mg, at heating rate 10°C/min.

- DSC

Differential scanning calorimetry (DSC) was carried out with a Setaram DSC 92 apparatus.

4. RESULTS AND DISCUSSION

4.1 Chemical analyses and determination of the water molecules number contained in the prepared hydrate

The chemical analyses were performed by atomic absorption using a spectrophotometer type VARIAN AA-475. The results of the chemical analysis are in agreement with the formula $MnCa_2(P_3O_9)_2.10H_2O$ for both powder and crystal samples, the results of the chemical analysis are the same and are in a ratio of 1, 2 and 6 for Mn, Ca and P respectively (Table 1).

A thermal dehydration conducted at 600°C under atmospheric pressure makes it possible to allocate ten water molecules to the cyclotriphosphate decahydrate of manganese and dicalcium both in powder and in the form of crystals. The cyclotriphosphate formula is therefore $MnCa_2(P_3O_9)_2.10H_2O$

Table 1: Results of chemical analyzes

P/Mn		P/Ca		Ca/Mn	
Theo	Exp	Theo	Exp	Theo	Exp
6	5,902	3	2,995	2	1,971

Theo =theoretical, Exp= experimental

4.2 Stability

The cyclotriphosphate decahydrate of manganese and dicalcium, $MnCa_2(P_3O_9)_2.10H_2O$, is stable under ambient conditions of temperature and pressure. We followed its evolution, by infrared vibration spectrometry, X-ray diffraction and thermogravimetry, periodically for 7 months, until the strains were exhausted and no evolution was observed over time.

$MnCa_2(P_3O_9)_2.10H_2O$ is also stable when heated under atmospheric pressure between room temperature and 50°C.

4.3 Crystallographic characterization of anhydrous cyclotriphosphate of manganese and dicalcium $MnCa_2(P_3O_9)_2.10H_2O$ and $MnCa_2(P_3O_9)_2$

- $MnCa_2(P_3O_9)_2.10H_2O$

The purity of the product obtained was controlled by its X-ray diffraction spectrum (Figure 1, Table II). $MnCa_2(P_3O_9)_2.10H_2O$ crystallizes in the monoclinic system. It is isotype to three cyclotriphosphates cadmium decahydrate $Cd_3(P_3O_9)_2.10H_2O$ [2], calcium $Ca_3(P_3O_9)_2.10H_2O$ [4] and manganese $Mn_3(P_3O_9)_2.10H_2O$ [3]. We calculated and refined the unit-cell parameters of $MnCa_2(P_3O_9)_2.10H_2O$ by isotopy with $Cd_3(P_3O_9)_2.10H_2O$ [2], $Ca_3(P_3O_9)_2.10H_2O$ [4] and

manganese $Mn_3(P_3O_9)_2.10H_2O$ [3]. .The unit-cell parameters are: a = 9.631 (5) Å, b = 18.173 (7) Å, c = 7.976 (4) Å, β = 109.438 (4), Z = 2 and the space group is P21/n.

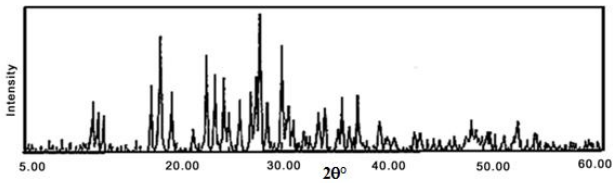

Figure 1: X-ray diffraction pattern of $MnCa_2(P_3O_9)_2.10H_2O$

Table 2: X-ray diffraction pattern of cyclotriphosphate decahydrate of manganese and dicalcium, $MnCa_2(P_3O_9)_2.10H_2O$

hkl	d_{cal} (Å)	d_{obs} (Å)	$100I/I_0$	Hkl	d_{cal}(Å)	d_{obs}(Å)	$100I/I_0$
101	7,02	7,02	37	132	2,780	2,787	15
001	6,95	6,95	29	241	"2,727	2,747	11
111	6,67	6,69	26	330	2,695	2,688	28
130	5,02	5,02	48	10-3	2,650	2,643	32
111	4,85	4,80	83	21-3	2,553	2,550	17
040	4,53	4,54	44	301	2,526	2,525	39
221	4,09	4,11	17	22-3	2,480	2,479	18
041	3,883	3,883	70	13-3	2,427	2,427	41
002	3,764	3,748	56	072	2,134	2,134	14
122	3,630	3,627	54	25-3	2,102	2,106	13
202	3,510	3,564	28	153	1,904	1,905	22
212	3,434	3,421	38	31-4	1,887	1,887	15
222	3,271	3,290	44	182	1,836	1,839	14
241	3,224	3,231	55	441	1,824	1,824	12
032	3,195	3,195	100	510	1,797	1,797	11
311	3,127	3,116	36	47-1	1,756	1,758	22
231	2,972	2,974	76	402	1,707	1,709	13
042	2,900	2,911	33	124	1,703	1,703	12
042	2,890	2,875	23				

- $MnCa_2(P_3O_9)_2$

The X-ray diffraction pattern of $MnCa_2(P_3O_9)_2$ (Figure 2) shows that it is isotype to $CaTl_4(P_3O_9)_2$ [8] of trigonal

Symmetry and the structure was solved on that of $MgTl_4(P_3O_9)_2$ [8]. $MnCa_2(P_3O_9)2$ is of hexagonal symmetry with Z = 2, its space group is P3.The unit-cell parameters that we calculated and affined for $MnCa_2(P_3O_9)_2$ by isotopy with $MgTl_4(P_3O_9)_2$ [8] are as follows: a = b = 7.392 Å (9) and c = 20.134 (2) Å. This isotopy could be schematized as follows

$$M^{II}M^{I}_4(P_3O_9)_2 <=> M^{II}\ M''^{II}2(P_3O_9)_2$$

$$M^{II} <=> M''^{II}$$

$$4M^{I} <=> 2M''^{II}$$

$$2M^{I} <=> M''^{II}$$

In this particular isomorphism, the substitution of two cations of the structure $CaTl_4(P_3O_9)_2$ by a cation M^{II} of $MnCa_2(P_3O_9)_2$, which respects electroneutrality with half of the unoccupied sites, should be accepted.

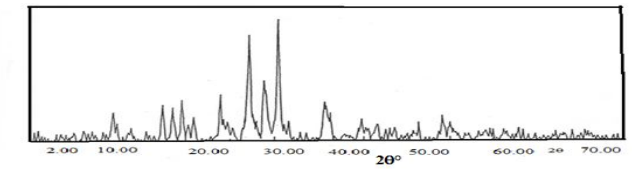

Figure 2: X-ray diffraction pattern of $MnCa_2(P_3O_9)_2$

Table 3: X-Ray diffraction pattern of the anhydrous cyclotriphosphate of Manganese and dicalcium, $MnCa_2(P_3O_9)_2$

Hkl	d_{cal} (Å)	d_{obs} (Å)	$100I/I_0$	hkl	d_{cal} (Å)	d_{obs} (Å)	$100I/I_0$
100	6,40	6,40	11	017	2,628	-	-
101	6,10	-	-	008	2,522	-	-
102	5,41	-	-	025	2,510	2,513	32
004	5,05	5,06	30	116	2,487	2,470	23
103	4,64	4,66	28	211	2,402	-	-
104	3,960	-	-	212	2,353	-	-
110	3,700	3,714	38	018	2,347	-	-
112	3,470	3,510	11	206	2,319	-	-
015	3,414	-	-	213	2,267	2,263	18
006	3,363	3,363	11	214	2,182	2,223	10
200	3,221	3,275	87	214	2,180	2,170	14
201	3,161	3,177	10	302	2,088	2,090	10
202	3,051	3,060	35	215	2,075	2,074	11
114	2,981	-	-	304	1,964	1,957	15
016	2,977	2,940	100	217	1,853	1,855	21
203	2,890	2,873	14	209	1,836	1,820	15
204	2,703	"	-				

4.4 Characterization by infrared vibration spectrometry of cyclotriphosphate decahydrate of manganese and dicalcium,$MnCa_2(P_3O_9)_2.10H_2O$

The packaging used for the $MnCa_2(P_3O_9)_2.10H_2O$ IR absorption spectrum is 1mg of product in 200 mg of KBr

intimately ground for the manufacture of a pellet at room temperature under atmospheric pressure. Before giving this characterization of cyclotriphosphate hexahydrate of manganese and calcium by IR vibration spectrometry, it is worth noticing that the structure of $MnCa_2(P_3O_9)_2.10H_2O$.

The absorption spectrum IR of $MnCa_2(P_3O_9)_2.10H_2O$ (Figure 3) contains:

- In the spectral region 4000-3000 cm-1, characteristic of OH valence bands, a single wide band around 3450 cm-1 accompanied by a shoulder at 3290 cm^{-1}.
- In the range, 1700-1600 cm^{-1} characteristic of water deformation bands, a strong intensity band at 1671 cm-1, accompanied by a shoulder at 1690 cm-1
- between 1400 and 640 cm-1, the characteristic domain of the valence bands of the $P_3O_9^{3-}$ cycle, possibly of the water-cycle interaction and rotations of the water molecules, seven bands are observed. Four broad bands of high intensity all appear as a doublet of frequency: (1280, 1264 cm^{-1}), (1132, 1105 cm^{-1}), (1025, 987 cm^{-1} and (791, 753 cm^{-1}). All the other bands are fine and of average intensity, one appears doubled at 685 cm^{-1} - 645 cm^{-1} and two others are observed at 1162 cm-1 and 868 cm^{-1}. The symmetry of the $P_3O_9^{3-}$ cm^{-1} ring in this compound is lower than the symmetry C3h or D3h [6,7].
- Between 640 and 400 cm^{-1}, the domain characterizing the deformation vibrations of oxygen atoms outside the cycle (δOPO- + δPOP) exist two frequencies respectively located at 522 cm^{-1} and at 476 cm^{-1}.

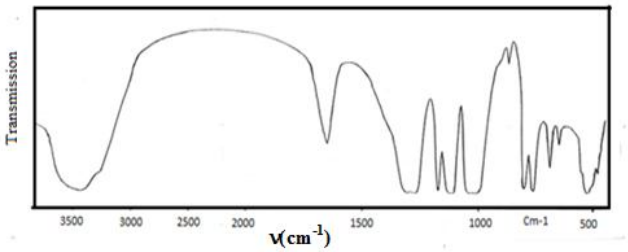

Figure 3: IR absorption spectrum of $MnCa_2(P_3O_9)_2.10H_2O$

These are the fine bands observed at 1162 cm^{-1} and at 683 cm^{-1}. All these bands are typical of a C_{3V} pseudo-symmetry cycle in agreement with the results of X-ray diffraction indicating that the symmetry of the cycle is C_{3V}. The method of K.SBAI [6] relating to the determination of the ring symmetry $P_3O_9^{3-}$, contained in $MnCa_2(P_3O_9)_2.10H_2O$, on the basis of its IR spectrum is in agreement with the X-ray diffraction results of its isotype $Cd_3(P_3O_9)_2.10H_2O$ [4] whose cycle $P_3O_9^{3-}$ is of approximate symmetry C_{3V}.

4.5Characterization of anhydrous cyclotriplibsphate of manganese and dicalcium, $MnCa_2(P_3O_9)_2$, by vibration spectrometry IR

The product resulting from the total thermal dehydration under atmospheric pressure of

$MnCa_2(P_3O_9)_2.10H_2O$ between 400 and 450°C is the anhydrous cyclotriphosphate of manganese and dicalcium, $MnCa_2(P_3O_9)_2$, pure and with hexagonal symmetry. The IR vibration spectrum of $MnCa_2(P_3O_9)_2$ (Table 4, Figure 4) comprises:

-between 1350 and 600 cm^{-1}, 6 bands of which 4 are doubled and which are all characteristic of the cycles $P_3O_9^{3-}$

-in the range 600-400 cm^{-1}, characteristic of the deformation vibrations of the oxygen atoms outside the $P_3O_9^{3-}$ cycle, a high intensity band appears in the form of a quadruplet of frequencies: 580, 545, 520 and 480 cm^{-1}.

- Symmetry of the cycle $P_3O_9^{3-}$ contained in $MnCa_2(P_3O_9)_2$

The IR absorption spectrum of $MnCa_2(P_3O_9)_2$ contains: Four valence bands of the $P_3O_9^{3-}$ cycles, whose frequencies are respectively at 1290, 1100, 1024 and 780 cm^{-1}. In addition to these bands, there is also the existence of a band of average intensity at 750 cm^{-1} .

- three bands of average intensity, which are characteristic of any lowering of symmetry relative to C3h observed at 1160 and 680 cm^{-1}

-A very intense band that appears as a quadruplet of frequencies: 580, 545, 520 and 480 cm^{-1} . All the spectral characteristics of a $P_3O_9^{3-}$ deformed cycle, of pseudo-symmetry C_{3V}, defined by K. SBAI [4], are found in the absorption spectrum IR of $MnCa_2(P_3O_9)_2$

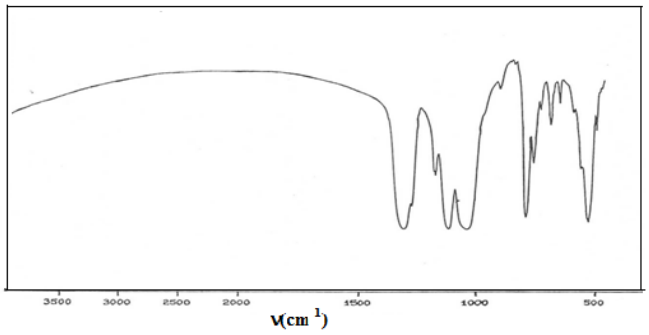

Figure 4: IR absorption spectrum of $MnCa_2(P_3O_9)_2$

Table 4: IR Frequency Assignments and movements of the Cyclotriphosphates $MnCa_2(P_3O_9)_2.10H_2O$ and $MnCa_2(P_3O_9)_2$ with approximate symmetry C3v

Movements and assignments		$MnCa_2(P_3O_9)_2.10H_2O$ ν (cm^{-1})		$MnCa_2(P_3O_9)_2$ ν (cm^{-1})	
ν OH		3450	VS		
ν OH		3290	SH		
VδHOH		1690	SH		
VδHOH		1671	S		
V_{aS} OPO^-	modeE	1280	S	1290	VS
	mode A1	1264	VS	1255 VS	
V_S OPO^-	mode A1	1162	S	1160	A
V_S OPO^-	mode E	1132	S		
V_S OPO^-	mode E	1105	S	1100	VS
V_{as} POP	mode E	1025	VS	1024	VS
V_{as} POP		987	VS	965	SH
	mode A_1	868	VS	890	VS
	ModeE	791	VS	780	VS
		753	VS	750	S
V_S POP	mode A_1	683	A	680	A
V_SPOP	mode A_1	645	VS		
				580	VS
		550	SH	545	VS
δ OPO-		522	S	520	VS
		492	SH		
δ POP		476	VS	480	S

The signification of the used symbols: S: strong, VS: very strong, A: average SH: shoulder.

▪ $MnCa_2(P_3O_9)_2$:

The C_{3V} pseudo-symmetry of the $P_3O_9^{3-}$ cycle contained in $MnCa_2(P_3O_9)_2$ is also confirmed in the light of the crystalline structure resolved by X-ray diffraction, its isotype $CaTl_4(P_3O_9)_2$ [8] whose $P_3O_9^{3-}$ cycle is of C_3 local symmetry or of C_{3V} approximated symmetry.

The two IR absorption spectra of $MnCa_2(P_3O_9)_2.10H_2O$ and its total thermal dehydration product, $MnCa_2(P_3O_9)_2$, show the spectral characteristics of an approximate C3V symmetry cycle given by K. SBAI [5]. Thus, the use of IR vibration spectrometry as a complementary technique for the characterization of the intermediate and final phases of the dehydration of $MnCa_2(P_3O_9)_2.10H_2O$, was found to be particularly important and effective and allowed us to characterize an unspecified cyclotriphosphate up to now, it is the anhydrous $MnCa_2(P_3O_9)_2$, well crystallized, pure and with hexagonal symmetry. To remove any ambiguity as to the purity of the intermediate $MnCa_2(P_3O_9)_2$ phase, obtained during the thermal dehydration of $MnCa_2(P_3O_9)_2.10H_2O$, we made the direct preparation of the anhydrous cyclotriphosphate of manganese and dicalcium, $MnCa_2(P_3O_9)_2$, by the method of THILO et al. [1].

4.6 Thermal dehydration of cyclotriphosphate decahydrate of manganese and dicalcium

ATG Thermogravimetric Analysis (TG and DTG)

▪ Thermogravimetric Analysis TGA (TG and DTG)

Differential thermal analysis, DTA, of $MnCa_2(P_3O_9)_2.10H_2O$, under atmospheric pressure, by linear temperature rise with a heating rate of 5°C/min (Figure 6), gives a relatively complicated thermogram. It is useful to examine this thermogram in the light of the TG-DTG thermogram obtained under the same conditions.

The DTA curve shows in the range, 50°C-441°C, where water was released, four endothermic peaks:

- In the first stage, dehydration, between 50°C and 123°C., the DTA curve has an endothermic peak at T = 76 °C which appears at exactly the same temperature where the dehydration rate is maximum. This endothermic peak is attributable to the departure of the first mole of water;

- In the second step, between 123°C and 190°C, the DTA thermogram has an endothermic peak, the peak of which is observed at a temperature of 172°C. This peak corresponds to that observed in DTG during the second stage of dehydration at 166°C. It is therefore from the beginning of 2 moles of water that leave the solid during the second step that the failure of the thermogram between 109°C and 172°C suggests an overlap of two phenomena, one of which is exothermic, which seems to be beginning, at 109°C, even before the first stage is completed

In this case, the highest point of the DTA thermogram could be mentioned between 109 and 172°C as an exothermic peak with an apex temperature of 161°C. This peak is due to the crystallization which occurs before the complete elimination of the first mole of water per unit formula. This hypothesis is supported by the DSC thermogram which indicates a very intense exothermic peak at 168°C and by X-ray diffraction, which shows, at 170°C the crystallization of the three-phase mixture δ $[Ca(PO_3)_2]\infty$, $Mn_2P_2O_7$, $Mn_2P_4O_{12}$.

- In the third step, between 190 and 292°C, the DTA thermogram has a wide and doubtful endothermic peak at 250°C which corresponds to that observed in the DTG thermogram at 250°C. This peak corresponds to the departure of 4.6 moles of water per unit formula.

- In the fourth stage, between 292 and 330°C, the DTA thermogram shows an endothermic peak, at T = 313°C, which appears in the DTG thermogram at the same temperature. This endothermic peak is attributable to the departure of one mole of water. It is followed by another exothermic peak of low intensity at 316°C which is relatively doubtful and would be due to the crystallization of $MnCa_2(P_3O_9)_2$ from the results of X-ray diffraction.

-In the fifth step, between 330 and 441°C, the DTA curve has no peak equivalent to that observed in the DTG thermogram at 352°C relative to the start of the remaining fraction of water.

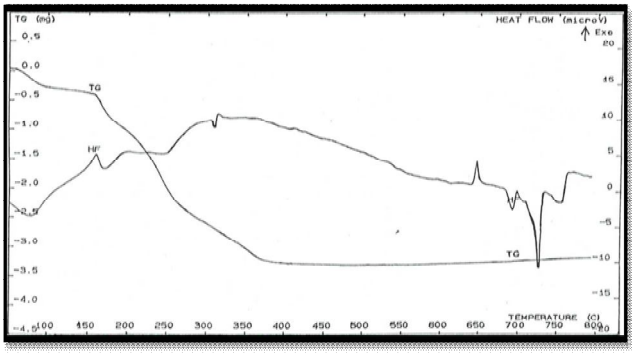

Figure 5: Coupled TG-DTA curves of $MnCa_2(P_3O_9)_2$ l0H_2O by linear temperature rise

Between 441°C and 800°C, the DTA thermogram showed an exothermic peak at T = 646°C, and three endothermic peaks observed at 694°C, 727°C and 754°C. According to the results of the X-ray diffraction, the exothermic peak, at T = 646°C, is due to the crystallization, one and/or the other of the constituents, of the mixture of infinite-chain polyphosphates $[Mn(PO_3)_2]\infty$ and $\beta[Ca(PO_3)_2]\infty$.

The endothermic peak at 694°C is probably the decomposition of the constituents of the mixture. The other two endothermic peaks with peaks at 727°C and 754°C respectively correspond to the melting of $[Mn(PO_3)_2]\infty$ and $\beta[Ca(PO_3)_2]\infty$.

▪ AnaLyse Differential Scanning Calorimetry (DSC)

The differential calorimetric analysis curve, DSC, of $MnCa_2(P_3O_9)_2.10H_2O$ obtained, by linear temperature rise, with a heating rate of 5°C/min, is shown in Figure 9. When examinated alone, independently of the TG-DTG curves, it rises sharply three peaks, one of which is endothermic at 116°C (ΔH = 42.44 kJ.mol'1) and the other two are exothermic and are located respectively at 168°C (ΔH = -23,96) and 400° C (ΔH = -32.04 kJ · mol1) (Table 5).

However, the examination of the DSC thermogram in the light of the TG-DTG thermograms makes it possible to take into account two other endothermic peaks, less pronounced than the other three, doubtful at 80°C, which manifests it self only by a shoulder and another relatively broad one at 316°C.

These last two peaks are easily attributable the first, observed at 80°C, corresponds to the departure of the first mole of water which leaves the solid during the first stage of the dehydration and the second corresponds to the loss of water which is in the fourth stage for the first and the fourth stage of water removal the DTG thermogram, obtained under the same conditions as the DSC thermogram, the peak temperatures are respectively 80 °C and 316 °C.

We still have to attribute the well pronounced peaks of the DSC thermograms. The endothermic peak observed in DSC at 116 ° C corresponds to the departure of the water.

For the exothermic peak, the peak which is observed in DSC at 168°C, dehydration between 180°C and 250°C and the thermal residues analyzed by X-ray diffraction showed that the thermal residues analyzed by X-ray diffraction is of a three-phase mixture δ$[Ca(PO_3)_2]\infty$, $Mn_2P_2O_7$ And $Mn_2P_4O_{12}$.

These phases have also been characterized by IR vibration spectrometry. The exothermic peak of the DSC curve therefore corresponds to the crystallization of the above-mentioned mixture or to one or two of these components.

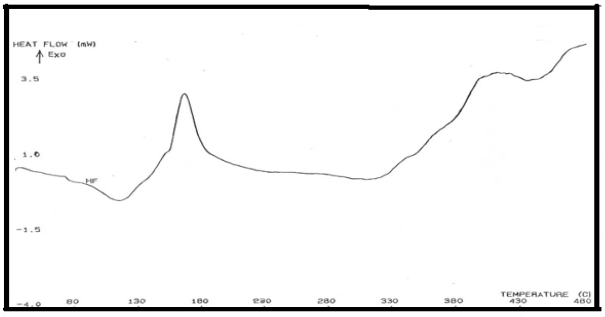

Figure 6: DSC Curve of $MnCa_2(P_3O_9)_2.10H_2O$ by Rise Linear temperature (v-5 °C/min, P = 1 atm)

At the temperature of 400 ° C., all X-ray diffraction lines and IR. Characteristics of anhydrous cyclotriphosphate, $MnCa_2(P_3O_9)_2$, were observed

The peak observed in DSC at 400°C can therefore be attribute to the crystallization of the anhydrous manganese and dicalcium cyclotriphosphate, $MnCa_2(P_3O_9)_2$, which has never been characterized.

Since the differential scanning calorimetry (DSC) apparatus, we have been working on, can not exceed the temperature of 480°C, we have not observed in DSC the crystallization of the infinite-chain polyphosphate mixture, $(2\beta\ [Ca(PO_3)_2]\infty + [Mn\ (PO_3)_2]\infty)$.

The results of thermogravimetric analysis TGA (TG and DTG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of $MnCa_2(P_3O_9)_2.10H_2O$ are concordant and are in agreement with the results obtained by diffraction of X-ray diffraction during the structural resolution of $Cd_3(P_3O_9)_2.10H_2O$ [1] isotype of $MnCa_2(P_3O_9)_2.10H_2O$. The ten water molecules of $Cd_3(P_3O_9)_2.10H_2O$ [1] occupy five different sites and the thermogravimetric analysis TGA (TG and DTG) of $MnCa_2\ (P_3O_9)_2\ .10H_2O$ shows the existence of five types of water in the latter.

Table 5: Differential Scanning CalorimetryDSC (v = 5 °C/ min) from $MnCa_2(P_3O_9)_2.10H_2O$

	Ti(K)	Tmax (K)	Tf(K)	ΔH(KJ/mole)	nature of the peak
First peak	347	389	426	42,44	endothermic
Second peak	429	441	480	-23,96	Exothermic
Third peak	555	673	716	-32,04	Exothermic

5. CONCLUSION

A new cyclotriphosphate decahydrate of manganese and dicalcium, $MnCa_2(P_3O_9)_2.10H_2O$, was prepared by the nitrate method. This cyclotriphosphate was crystallographicaly characterized and found isotype of $Cd_3(P_3O_9)_2.10H_2O$. We calculated and refined the unit-cell parameters of $MnCa_2(P_3O_9)_2.10H_2O$ by its isotype $Cd_3(P_3O_9)2.10H_2O$. The unit-cell parameters are: a = 9.631 (5) Å, b = 18.173 (7) Å, c = 7.976 (4) Å, β = 109.438 (4) °, Z = 2 and the space group is P21/n. The study of the thermal dehydration of the cyclotriphosphate decahydrate of manganese and dicalcium, $MnCa_2(P_3O_9)_2.10H_2O$, was made by X-ray diffraction, IR vibration spectrometry, TGA (TG and DTG), DTA and DSC. By using X-ray diffraction and IR spectrometry we have identified and characterized the intermediate and final phases of the thermal dehydration of $MnCa_2(P_3O_9)_2.10H_2O$. $MnCa_2(P_3O_9)_2.10H_2O$ is stable between room temperature and 50°C. The total thermal dehydration of $MnCa_2(P_3O_9)_2.10H_2O$ leads to the anhydrous form $MnCa_2(P_3O_9)_2$. $MnCa_2(P_3O_9)_2.10H_2O$ can't be partially dehydrated without the disorganization of its structure and the decondensation of the cycles $P_3O_9^{3-}$. The departure of the water molecules takes place in five distinct stages. The IR absorption spectra of $MnCa_2(P_3O_9)_2.10H_2O$ and $MnCa_2(P_3O_9)_2$ were interpreted and all the frequencies were assigned.

REFERENCES

1. E. THILO et I. GRUNZE. Z. Anorg. Allgem. Chem., 290, **223-237,(1957);290(5-61.209-223,(1957).**doi.org/10.1002/zaac.201000028
2. Aziz Kheireddine, Malika Tridane and Said Belaaouad **Chemical preparation, kinetic of thermal behavior and infrared studies a of Pb3(P3O9)2.3H2O And Cd3(P3O9)2.3H2O** Mediterrean journal of chemistry 2013, 2(4), 549-568 [3] N. EL HORR et A. DURIF. C. R.Acad.Sc. Paris, 296, 1185-1187 (1983).
3. Bouchra Gourja, Mustafa Belhabra, Malika Tridane and Said Belaaouad **STUDY OF THE STRUCTURAL MODIFICATIONS OF CYCLOPHOSPHATES OF MANGANESE FROM Mn3(P3O9)2.10H2O TO Mn2P4O12 DURING THERMAL BEHAVIOR PROCESS BY INFRARED SPECTROSCOPY** International Journal of Recent Scientific Research Vol. 7, Issue, 9, pp. 13462-13473, September, 2016
4. Said Belaaouad, Malika Tridane, Hind Chennak, Rachid Tamani, Abdelkbir Kenz, Mohamed Moutaabid. **Chemical preparation, thermal behavior, kinetic and infrared studies and quantum chemical calculations of Ca3(P3O9)2.10H2O** Phosphorus research bulletin vol 21 (2007) pp 60-70
5. M. TRIDANE, S. BELAAOUAD and K. SBAl. **Solid State Sciences**., 2, 701-704, (2000).doi.org/10.1080/00387010600812574
6. K SBAI. **Thèse d'Etat. DIJON. FRANCE**. (1984).doi.org/10.1023/A:1019980327518
7. P.TARTRE, A. RULMONT, K.SBAI et M.H. SIMONOT-GRANGE. **Spectrochim. Acta., 43A (3), 337-343 (1987)**doi.org/10.1016/0584-8539(87)80114-9
8. E.RAKOTOMAHANINA-ROLAISOA, Y.HENRY, A. DURIF et C.RAHOLISON. Bull. Soc. Fr. Minér. Crist, 93, 43-51, (1970) doi.org/10.1007/10201585_19
9. AnghamHazim ,Ahmed Hashim, Hayder MAbduljalil **Novel (PMMA-ZrO_2-Ag) Nanocomposites: Structural, Electronic, Optical Properties as Antibacterial for Dental Industries** Volume 7, No.8 August 2019 International Journal of Emerging Trends in Engineering Research https://doi.org/10.30534/ ijeter /2019/01782019
10. Angham Hazim, Hayder M.Abduljalil and AhmedHashim **Structural,Electronic,OpticalProperties and Antibacterial Application of Novel (PMMA-Al_2O_3-Ag) Nanocomposites for Dental Industries Applications** Volume 7, No.8 August 2019 International Journal of

Emerging Trends in Engineering Research https://doi.org/10.30534/ijeter/2019/04782019

11. Basim Abbas, Ahmed Hashim **Novel X-rays attenuation by(PMMA-PS-WC)NewNanocompsites: Fabrication, Structural, Optical Characterizations and X-Ray Shielding Application** International Journal of Emerging Trends in Engineering Research, 7(8), August 2019, 131 – 144 https://doi.org/10.30534/ijeter/2019/06782019