Thermochimica Acta 487 (2009) 54–59

Contents lists available at ScienceDirect

Thermochimica Acta

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

Chemical preparation and thermal behavior of neodymium cyclotriphosphate pentahydrate $NdP_3O_9{\cdot}5H_2O$: A study by Controlled Rate Thermal Analysis (CRTA)

Kais Nahdi [a,*], Mokhtar Férid [b], Malika Trabelsi Ayadi [b]

[a] *Laboratoire d'Application de la Chimie aux Ressources et Substances Naturelles et à l'Environnement, Faculté des Sciences de Bizerte, Département de Chimie, 7021 Zarzouna, Bizerte, Tunisie*

[b] *Unité de Matériaux de Terres Rares, Centre National de Recherches en Sciences des Matériaux, BP 95, Hammam-Lif, 2050, Tunisie*

ARTICLE INFO

Article history:
Received 27 October 2008
Received in revised form 15 December 2008
Accepted 14 January 2009
Available online 22 January 2009

Keywords:
Neodymium cyclotriphosphate
Controlled Rate Thermal Analysis
XRD
IR

ABSTRACT

A new neodymium cyclotriphosphate pentahydrate powder, $NdP_3O_9{\cdot}5H_2O$, has been prepared using a classical chemistry method and characterized by X-ray diffraction and infrared spectroscopy techniques. The IR spectrum shows the characteristic bands of cyclotriphosphates as the triplet in the range 1055–1007–917 cm^{-1}.

The thermal behavior of the titled compound was also carried out using conventional thermal analysis techniques (TG and DSC) under air atmosphere and Controlled transformation Rate Thermal Analysis (CRTA) technique under constant water vapour pressure of 5 hPa. It was shown that thermal treatment in air, with linear heating rate of 10 K min^{-1}, favourites the structure breakdown as soon as the release of water molecules starts. In this case an amorphous compound is obtained, which then crystallizes at 1073 K and gives the polyphosphate $Nd(PO_3)_3$. However, by CRTA technique at $P_{H_2O} = 5$ hPa, the water molecules are eliminated with a lower rate which permits to save the initial structure up to an advanced dehydration step. The breakdown of the initial structure is immediately followed by the crystallization of the anhydrous polyphosphate $Nd(PO_3)_3$ phase in the temperature range 455 K < T < 793 K.

1. Introduction

Rare-earth phosphates are important in several applications such as ceramic materials, catalysts, photoluminescence materials, dielectric substances, metal surface treatment agents, optical materials, etc. Such phosphates play an important role as light emitters due to their well-defined transitions within the 4f shell [1,2]. Trivalent cation cyclotriphosphates are worth studying. Nevertheless, they are poorly investigated owing to the fact that only a few of them have been well characterized. In the rare-earth cyclotriphosphate field a series of three $LnP_3O_9{\cdot}3H_2O$ compounds, with Ln: La, Ce and Pr were prepared by Bagieu-Beucher and Durif [3] in order to determine their crystal data, in fact the cerium salt's crystal structure was identified by Bagieu et al. [4]. The thermal behavior of $LnP_3O_9{\cdot}3H_2O$ (Ln = La, Ce and Pr) was carefully investigated by Simonot and Gobled [5]. Then, the chemical preparation and thermal behavior of $PrP_3O_9{\cdot}4H_2O$, $LaP_3O_9{\cdot}4H_2O$ and $ErP_3O_9{\cdot}4H_2O$ were studied by Birke and Kempe [6]. Horchani et al. [7,8] have prepared and characterized two cyclotriphosphates $NdP_3O_9{\cdot}4H_2O$ and $Na_3Nd_3(P_3O_9)_4{\cdot}13H_2O$ by X-ray diffraction, IR spectroscopy and thermal analysis techniques (DTA-TG and DSC). In addition to the compounds listed above, Bagieu [9] gave only the X-ray diagrams of rare-earth cyclotriphosphates $LnP_3O_9{\cdot}5H_2O$ (Ln = Nd and Sm). Jemal et al. [10] have achieved the characterization of $SmP_3O_9{\cdot}5H_2O$.

Thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the thermal methods that have always been accepted as useful techniques for studying the thermal stabilities of solids. With conventional thermal analysis, the temperature of the sample follows some predetermined program as a function of time, which can has a major influence on the information content of the TG curve and on the properties of the heat treated products. A new approach of thermal analysis technique called Constant Rate transformation Thermal Analysis (CRTA) [11,12] has been developed. It offers significant advantages over conventional methods [13–16]. As far as this new approach is concerned, the heating control algorithm receives a feedback from the sample, which is a signal related to any physical property influenced by the thermal transformation of the sample. What is programmed here is not any more the temperature (whose profile is unknown in advance) but the rate of the thermal transformation.

It has been reported that CRTA technique has a higher sensitivity and resolution than conventional thermoanalytical methods (TG, DSC, etc.) [17,18]. It minimizes the influence of heat and mass transfer phenomena since it allows keeping, if desired, both the rate of reaction and the pressure of the gaseous products at a low value.

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[*] Corresponding author. Tel.: +216 23 98 77 60; fax: +216 72 590 566.
E-mail address: k_nahdi@yahoo.fr (K. Nahdi).

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doi:10.1016/j.tca.2009.01.014

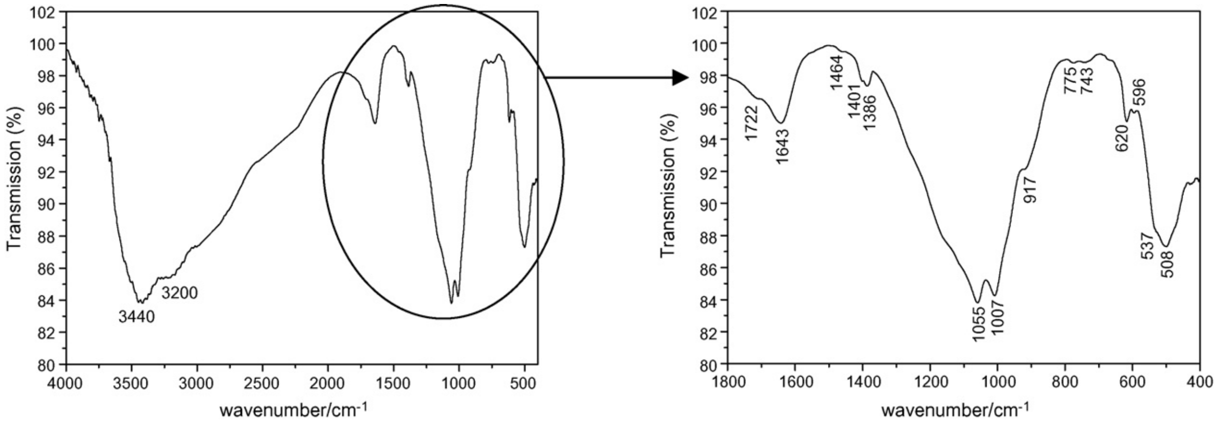

Fig. 1. IR spectrum of $NdP_3O_9{\cdot}5H_2O$.

CRTA, also, allows a good control of pressure not only surrounding but also within the sample. Moreover, it permits a constant reaction rate slow enough to minimize the temperature and pressure gradients within the reacting sample and thus results in a more reproducible experiments [19,20].

The CRTA technique has been used for the synthesis of many materials with controlled texture and structure in order to characterize processes of thermal preparation of solids [21–27], and also for kinetic study of thermal decomposition [28,29].

Besides, CRTA has been employed with success in the study of the stability and thermal decomposition pathways of minerals such as attapulgite [30], hydromagnesite [31], hydrozincite and smithsonite [32], aurichalcite [33], hydrotalcite [34], hydrated borates [35], sepiolites and palygorskytes [36], nontronite [37] and modified minerals such as mechanochemically activated and intercalated kaolinites [38–40].

Our aim is the research of new condensed rare-earth phosphates being able to present powerful optical properties. The present work deals with the synthesis and the characterization of $NdP_3O_9{\cdot}5H_2O$. A deepened study of the thermal behavior of neodymium cyclotriphosphate pentahydrate powder by conventional thermal analysis techniques (TG and DSC) in air and by Controlled transformation Rate Thermal Analysis (CRTA) technique at $P_{H_2O} = 5$ hPa was also carried out. The intermediates and final products were analyzed by XRD and FT-IR techniques.

2. Experimental procedure

2.1. Synthesis

$NdP_3O_9{\cdot}5H_2O$ was prepared at room temperature by adding in the proper ratio, an aqueous solution of $NdCl_3{\cdot}6H_2O$ (0.1 M) to an aqueous solution of $Na_3P_3O_9$ of the same concentration. The resulting product has a pale violet colour; it is insoluble in the water; it was filtered, washed with water and air dried. The chemical reaction is as follows:

$$Na_3P_3O_9 + NdCl_3{\cdot}6H_2O \rightarrow NdP_3O_9{\cdot}5H_2O(sd) + H_2O + 3NaCl \quad (1)$$

2.2. Methods of characterization

Powder X-ray diffraction measurements (XRD) were recorded using a Bruker X-ray diffraction unit with Cu Kα radiation ($\lambda = 1.5406$ Å) at room temperature in 40 kV and 30 mA at a scan speed of 1.2°/min.

The infrared absorption spectra of a KBr pressed pellet of the powdered sample was studied in the range 4000–400 cm^{-1} using a Nicolet 560 spectrophotometer.

Thermogravimetry measurement was performed with a thermobalance TGDTA 92 type SETARAM. Sample was heated from ambient up to 1273 K at a rate of 10 K min^{-1} in air atmosphere. The sample mass in the Pt cell of the thermogravimetric analyzer was kept at about 20 mg in all experiments.

The DSC analysis was performed on a Mettler–Toledo DSC822e (Switzerland). Sample mass of 5 mg was analyzed at a heating rate of 10 K min^{-1} in air. The reference pan was pure aluminum pan. The temperature and energy of instrument were calibrated by standard metal In, before all measures.

The Controlled Rate Thermal Analysis (CRTA) experiments were carried out on an apparatus built in house and on 100 mg samples weighed in a silica-cell in the temperature range from 248 K up to 1273 K. Once the equilibrium temperature is reached, the pressure above the sample is lowered using vacuum pumping system from 1 bar to the desired value (5 hPa in our case). The pressure is continuously followed using a Pirani gauge (PID control) placed in proximity of the sample. The pressure signal produced by the Pirani gauge is sent to the furnace-heating controller. The heating of the sample then takes place in such a way as to keep constant, at the preset value, the water vapour pressure generated by the sample [41,42].

3. Results and discussion

3.1. Characterization of the initial material

The XRD pattern shows that $NdP_3O_9{\cdot}5H_2O$ is well crystallized. The observed inter-reticular distances as well as the relative intensities of $NdP_3O_9{\cdot}5H_2O$ reflections are given in Table 1.

Fig. 1 shows the characteristic spectrum of the neodymium cyclotriphosphate pentahydrate. Table 2 presents the wavenum-

Table 1
The observed inter-reticular distances and the relative intensities of powder X-ray diffraction of $NdP_3O_9{\cdot}5H_2O$.

d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}	d_{obs} (Å)	I_{obs}
8.20	17	4.050	50	2.884	23
6.92	30	4.009	12	2.803	24
6.58	38	3.951	6	2.609	15
6.05	14	3.810	17	2.585	6
5.39	19	3.745	26	2.553	7
4.620	100	3.578	16	2.236	11
4.497	15	3.450	32	1.974	9
4.442	14	3.382	23	1.921	10
4.318	35	3.371	8	1.906	7
4.249	22	3.226	16	1.893	6
4.232	11	3.052	15	1.856	7
4.101	51	3.021	50		

Table 2
IR absorption wavenumbers of NDP3p and their assignments.

Assignment	Absorption wavenumbers (cm^{-1})
ν(OH)	3440–3200
δ(OH)	1722–1643
ν_{as}(OPO)	1464–1401
ν_{s}(OPO)	1386
ν_{as}(POP)	1055–1007–917
ν_{s}(POP)	775–743
δ(OPO)	620–596
δ(POP)	537–508

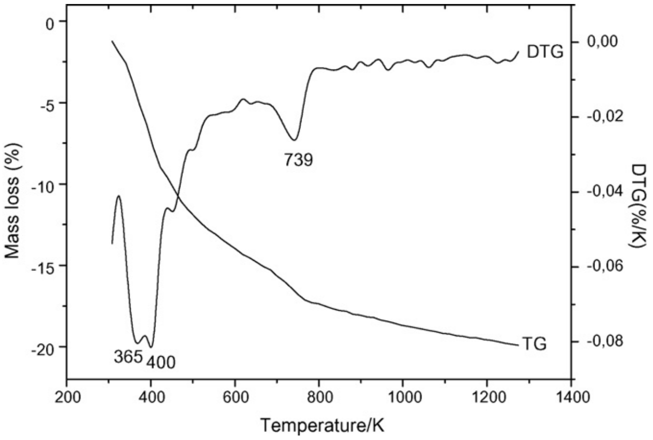

Fig. 2. TG curve of $NdP_3O_9 \cdot 5H_2O$ in air.

bers of the absorption bands and their attributions. These attributions are based on works given in Refs. [7,43–46]. The water of crystallization of $NdP_3O_9 \cdot 5H_2O$ absorbs in the 3440 cm^{-1} and 1643 cm^{-1} regions which presumably correspond to O—H stretching and O—H bending vibrations, respectively. The most noteworthy features being the appearance of very strong absorption bands of triplet, in the 900–1100 cm^{-1} area which are assigned to the ν_{as}(POP) stretching modes.

The bands of doublet observed at 775 cm^{-1} and 743 cm^{-1} can be assigned to the ν_s(POP) stretching modes. The band which absorbs at 1386 cm^{-1} is assigned to the stretching mode of the ν_s(OPO) whereas those absorbing at 1464 cm^{-1} and 1401 cm^{-1} are assigned to the stretching modes of the ν_{as}(OPO). The bending modes of the δ(OPO) and δ(POP) have two absorption bands of doublets observed at 620–596 cm^{-1} and 537–508 cm^{-1}, respectively.

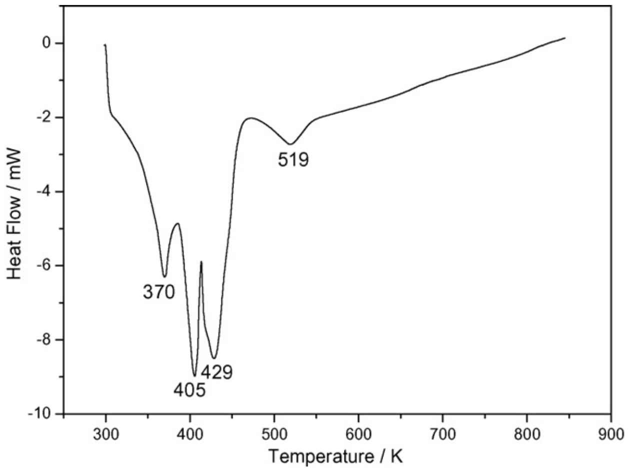

Fig. 3. DSC curve of $NdP_3O_9 \cdot 5H_2O$ in air.

Table 3
The data for the DSC peaks of thermal decomposition of $NdP_3O_9 \cdot 5H_2O$ in air.

Thermal step	Peak temperature (K)	ΔH (kJ mol^{-1})
1	370	23.82
2	405	28.81
3	429	53.43
4	519	22.61

3.2. Thermal behavior of $NdP_3O_9 \cdot 5H_2O$ in air

3.2.1. TG-DSC analysis

Figs. 2 and 3 show, respectively, the TG-DTG and DSC curves of the titled compound. The TG curve exhibits a total mass loss equal to 19.15% which corresponds to the release of five moles of H_2O per formula unit. The DTG curve shows three main dehydration steps at 365 K, 400 K and 739 K whereas the DSC curve shows four endothermic peaks which are attributed to the dehydration process. The enthalpies of average molecular weight corresponding to the four endothermic peaks are given in Table 3.

3.2.2. X-ray diffraction and IR spectroscopy analysis

The characteristic parts of X-ray powder diffraction patterns of the initial compound and its calcined products at 473 K, 623 K, 823 K, 1073 K and 1273 K are demonstrated in Fig. 4.

When heating at 473 K (Fig. 4b) the reflections related to $NdP_3O_9 \cdot 5H_2O$ disappear completely and the product becomes and stay amorphous up to 823 K. In the diffractogram of the isolated product at 1073 K one observes the appearance of new patterns. Their intensities increase after heating at 1273 K. These new patterns are attributed to the anhydrous neodymium polyphosphate $Nd(PO_3)_3$ (JCPDS 27-0322) which crystallizes in the orthorhombic system with $C222_1$ space group.

The IR spectra of untreated compound and the intermediate products calcined at 473 K, 623 K, 823 K, 1073 K and 1273 K are illustrated in Fig. 5. While heating $NdP_3O_9 \cdot 5H_2O$, the water vibrational bands in the IR spectra (Fig. 5a) disappear progressively and the compound becomes amorphous. IR absorption bands specific to P_3O_9 ring anions, observed in Fig. 1 at 1055–1007–917 cm^{-1}, disappear after heating at 473 K which indicates the breakdown of the cyclic structure of P_3O_9 anion. The characteristic bands of neodymium polyphosphate $Nd(PO_3)_3$ appear clearly from 1073 K. The assignment of the absorption bands of the final product obtained at 1273 K is presented in Table 4.

At this stage, both techniques DRX and IR permit to conclude that the thermal decomposition in air of neodymium cyclotriphos-

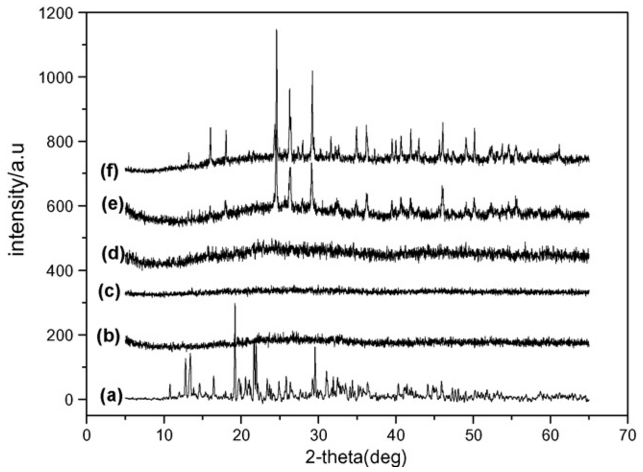

Fig. 4. Characteristic parts of XRD patterns of $NdP_3O_9 \cdot 5H_2O$ (a) and its calcined products at 473 K (b), 623 K (c), 823 K (d), 1073 K (e) and 1273 K (f).

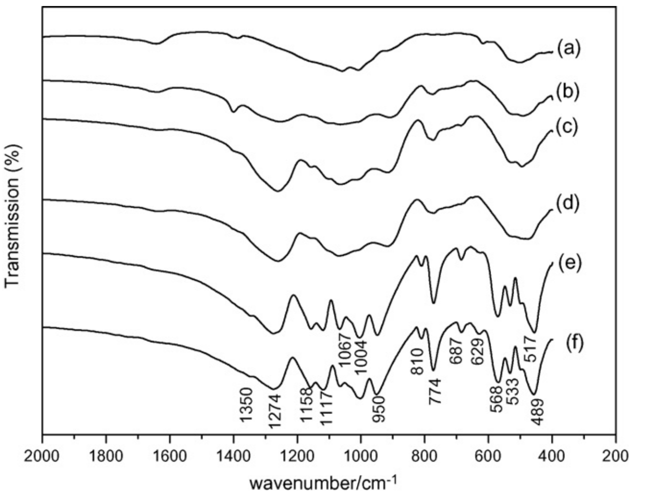

Fig. 5. IR spectra of $NdP_3O_9{\cdot}5H_2O$ (a) and its calcined products at 473 K (b), 623 K (c), 823 K (d), 1073 K (e) and 1273 K (f).

Table 4
IR absorption wavenumbers of $Nd(PO_3)_3$.

Assignment	Absorption wavenumbers (cm^{-1})
ν_{as}(OPO)	1350–1274
ν_s(OPO)	1117–1158
ν_{as}(POP)	810–950–1004–1067
ν_s(POP)	629–687–774
δ(OPO)	517–533–568
δ(POP)	489

phate pentahydrate leads first to an amorphous phase then to the neodymium polyphosphate. A proposed decomposition pathway is indicated in the equations below:

$$NdP_3O_9{\cdot}5H_2O(sd) \rightarrow \text{amorphousphase}(sd) \quad 298\,K < T \leq 823\,K$$

$$\text{amorphousphase}(sd) \rightarrow Nd(PO_3)_3(sd) \quad 823\,K < T \leq 1273\,K$$

3.3. *Thermal behavior of $NdP_3O_9{\cdot}5H_2O$ at $P_{H_2O} = 5$ hPa by CRTA technique*

3.3.1. *CRTA analysis*

The CRTA curves of $NdP_3O_9{\cdot}5H_2O$, shown in Fig. 6, were obtained by thermolysis of 100 mg of sample under 5 hPa water vapour pressure from 248 K up to 1273 K. Under these conditions the total thermolysis occurs within 57 h. The final mass loss is 19.20% which corresponds to the theoretical loss (19.09%) of five water molecules from the initial phosphate. So, the rate of the thermal decomposition is equal to 0.3368 mg h^{-1}. The CRTA curves show the sample temperature (curve I) variation with time, controlled so as to keep constant the pressure (curve II) above the sample. In case the gas composition above the sample does not change (water vapour in our case), the vapour pressure is kept in a state of quasi-equilibrium: its rate of production during the dehydration is maintained constantly equal to its rate of elimination which is itself kept constant with time. Under these conditions, the length of each dehydration step varies proportionally with the mass of water loss and the plot of temperature vs. time obtained by CRTA is analogue to a thermogravimetric curve.

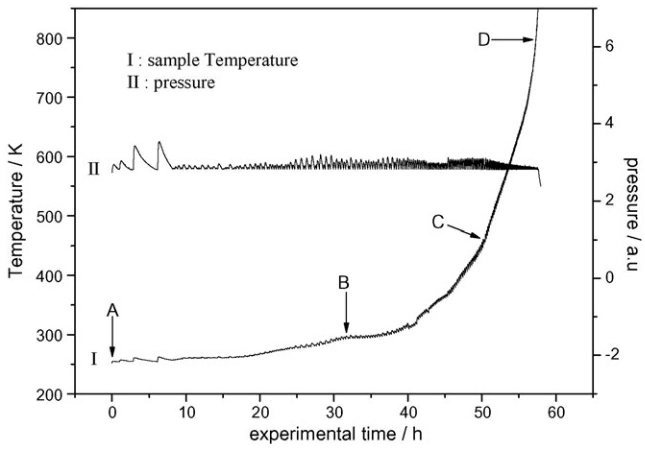

Fig. 6. CRTA curves of thermal decomposition of $NdP_3O_9{\cdot}5H_2O$ at $P_{H_2O} = 5$ hPa.

Here, we have considered that, under 5 hPa, dehydration starts at 259 K which is the temperature at which the constant pressure regime, required for CRTA, is reached. At around 793 K, a rapid drop in the pressure signal is observed indicating the end of the dehydration of the initial phosphate.

The variation in slope of the temperature curve as well as the regulation changes that appear in the pressure curve allow the delimitation of three essential decomposition steps occurring, respectively, between 259 K and 298 K (A–B), 298 and 455 K (B–C) and 455 and 793 K (C–D). As the only gas generated in the reaction is water and the reaction rate is kept constant the length ratio of steps (AB), (BC) and (CD) is the same that the amount of loss water 2.75/1.5/0.75, respectively.

Thus, the first decomposition step (A–B), can be attributed to the removal of 2.75 water molecules from the pentahydrate. The second decomposition step (B–C) corresponds to the release of 1.5 water molecules and the last decomposition step (C–D) corresponds to the leaving of the remained 0.75 water molecule.

3.3.2. *X-ray diffraction and IR spectroscopy analysis*

To characterize the products obtained at the end of each dehydration step, the CRTA experiment is restarted under identical conditions of rate and pressure; and the reaction is stopped at the temperatures determined from the initial curve. The obtained intermediate products are immediately submitted to IR and X-ray powder diffraction studies.

Fig. 7 shows the X-ray diffraction patterns of the initial cyclotriphosphate (point A), the intermediates products isolated at 298 K (point B), 455 K (point C), 793 K (point D) and 1223 K. According to the CRTA curve, the product isolated at 298 K (point B) would

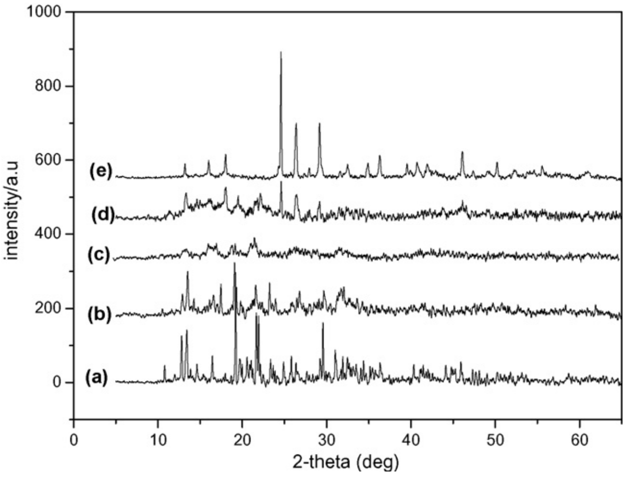

Fig. 7. X-ray diffraction patterns of $NdP_3O_9{\cdot}5H_2O$ (a) and products obtained at 298 K (b); 455 K (c); 793 K (d) and 1223 K (e) at 5 hPa water vapour pressure.

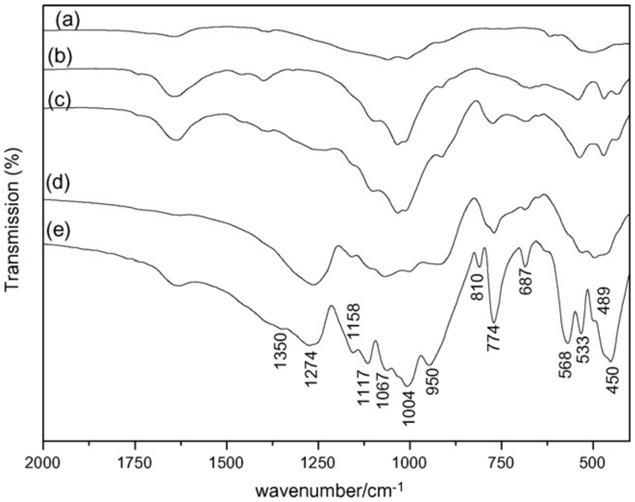

Fig. 8. IR spectra of $NdP_3O_9{\cdot}5H_2O$ (a) and products obtained at 298 K (b); 455 K (c); 793 K (d) and 1223 K (e) at 5 hPa water vapour pressure.

seem to be that of the 2.25 hydrated phosphate whereas the X-ray diffraction pattern would suggest the pentahydrated salt. However, the XRD peaks are slightly shifted to larger angles. This result suggests that the removal of the first 2.75 water molecules from the initial cyclotriphosphate, under the chosen conditions, takes place without any lattice transformation. This is confirmed by the IR spectroscopy technique (Fig. 8b) since the strong absorption bands specific to P_3O_9 ring anions, observed at 1055–1007–917 cm^{-1}, persist yet with slight shift to higher wavenumbers.

The X-ray diffraction pattern of the hydrate prepared at 455 K (point C), shows broad peaks with low intensities indicating the starting of the breakdown of the initial structure of the cyclotriphosphate.

The X-ray pattern of the compound obtained at 793 K (point D), identified as the anhydrous phosphate according to the CRTA results, shows the existence of new reflections indicating the formation of a new crystallized product. This is confirmed by IR technique since the strong absorption bands specific to P_3O_9 ring anions disappear completely at 793 K (point D). After heating at 1223 K, reflections of the new phase become fine and their intensities increase. The corresponding X-ray pattern (Fig. 7e) and IR spectrum (Fig. 8e) are similar to those observed in Figs. 4f and 5f which are previously attributed to the anhydrous neodymium polyphosphate $Nd(PO_3)_3$.

4. Conclusion

A new neodymium cyclotriphosphate pentahydrate powder, $NdP_3O_9{\cdot}5H_2O$, has been prepared using a classical chemistry method and characterized by X-ray diffraction and infrared spectroscopy techniques. Its thermal behavior has been deepened using conventional thermal analysis techniques (TG and DSC) in air and CRTA technique at $P_{H_2O} = 5$ hPa. This study highlights the influence of the nature of the thermal treatment on the thermal decomposition pathway of the neodymium cyclotriphosphate pentahydrate. In conventional thermal analysis conditions $NdP_3O_9{\cdot}5H_2O$ gives an amorphous phase while losing its five water molecules then crystallizes to anhydrous neodymium polyphosphate with orthorhombic crystal system and $C222_1$ space group.

Whereas in CRTA conditions, the thermal transformation observed for $NdP_3O_9{\cdot}5H_2O$ occurs in three steps without obtaining any amorphous phase and can be represented schematically by the following steps:

$$NdP_3O_9{\cdot}5H_2O(sd) \rightarrow NdP_3O_9{\cdot}2.25H_2O(sd) + 2.75H_2O(g) \quad 259\text{–}298\,K$$

$$NdP_3O_9{\cdot}2.25H_2O(sd) \rightarrow NdP_3O_9{\cdot}0.75H_2O(sd) + 1.5H_2O(g) \quad 298\text{–}455\,K$$

$$NdP_3O_9{\cdot}0.75H_2O(sd) \rightarrow Nd(PO_3)_3(sd) + 0.75H_2O(g) \quad 455\text{–}793\,K$$

It would seem from these results that under atmospheric pressure, thermal treatment with linear heating rate of 10 K min^{-1} (duration of the experiment ~2 h), favourites the structure breakdown as soon as the release of water molecule starts. In this case a passage by an amorphous state is observed. However, in CRTA conditions, the water molecules are eliminated with a lower rate (duration of the experiment: 57 h) which permits to save the initial structure up to an advanced dehydration step leading to a poorly crystalline cyclophosphate which decomposes in the last step to the corresponding anhydrous polyphosphate.

References

[1] P. Schuetz, F. Caruso, Chem. Mater. 14 (2002) 4509.
[2] O. Lehmann, H. Meyssamy, K. Kompe, H. Schnablegger, M. Haase, J. Phys. Chem. B 107 (2003) 7449.
[3] M. Bagieu-Beucher, A. Durif, Bull. Soc. fr. Mineĭral Cristallogr. 94 (1971) 440–441.
[4] M. Bagieu-Beucher, I. Tordjman, A. Durif, Revue de Chimie Minérale 8 (1971) 753.
[5] M.H. Simonot-Grange, D. Gobled, J. Less-Common Met. 38 (1974) 167.
[6] P. Birke, G. Kempe, Z. Chem. 13 (1973) 110.
[7] K. Horchani, M. Ferid, M. Trabelsi-Ayadi, Solid State Sci. 3 (2001) 347.
[8] K. Horchani, M. Ferid, M. Trabelsi-Ayadi, Mater. Res. Bull. 36 (2001) 897.
[9] M. Bagieu-Beucher, Thèse de doctorat d'Etat, Grenoble, 1980.
[10] M. Jemal, F. Khlissa, M. Férid, M. Trabelsi-Ayadi, J. Therm. Anal. Calorim. 78 (2004) 207.
[11] J. Rouquerol, J. Therm. Anal. 2 (1970) 123.
[12] J. Rouquerol, Thermochim. Acta 144 (1989) 209.
[13] J.M. Criado, F.J. Gotor, A. Ortega, C. Real, Thermochim. Acta 199 (1992) 235.
[14] F. Rouquerol, J. Rouquerol, G. Thevand, M. Triaca, Surf. Sci. 162 (1985) 239.
[15] J.M. Criado, F.J. Gotor, C. Real, F. Jimenez, S. Ramos, J. Del Cerro, Ferroelectrics I 15 (1991) 43.
[16] S. Bordère, F. Rouquerol, J. Rouquerol, J. Esfienne, A. Floreancig, J. Therm. Anal. 36 (1990) 1651.
[17] A. Ortega, Int. J. Chem. Kinet. 34 (2002) 223.
[18] S. Bordere, R. Fourcade, F. Rouquerol, A. Floreancig, J. Rouquerol, J. Chim. Phys. 87 (1990) 1233.
[19] J. Rouquerol, Thermochim. Acta 111 (1982) 209.
[20] J.M. Criado, F. Rouquerol, J. Rouquerol, Thermochim. Acta 38 (1980) 109.
[21] Perez-Maqueda, J.M. Criado, J. Subrt, C. Real, Catal. Lett. 60 (1999) 151.
[22] Perez-Maqueda, J.M. Criado, C. Real, J. Subrt, J. Boháek, J. Mater. Chem. 9 (1999) 1839.
[23] G.S. Chopra, C. Real, M.D. Alcalá, L.A. Pérez-Maqueda, J. Subrt, J.M. Criado, Chem. Mater. 11 (1999) 1128.
[24] J.M. Criado, F.J. Gotor, C. Real, F. Jimenez, S. Ramos, J. Del Cerro, Ferroelectrics 115 (1991) 43.
[25] J.M. Criado, M.J. Dianez, M. Macias, M.C. Paradas, Thermochim. Acta 171 (1990) 229.
[26] C. Real, M.D. Alcalá, J.M. Criado, J. Am. Ceram. Soc. 87 (2004) 75.
[27] A. Ortega, M.A. Roldan, C. Real, Int. J. Chem. Kinet. 38 (2006) 369.
[28] K. Nahdi, P. Llewellyn, F. Rouquerol, J. Rouquerol, N.K. Ariguib, M.T. Ayedi, Thermochim. Acta 390 (2002) 123.
[29] J.M. Criado, A. Ortega, F. Gotor, Thermochim. Acta 157 (1990) 171.
[30] V. Vagvolgyi, L.M. Daniel, C. Pinto, J. Kristof, R.L. Frost, E. Horvath, J. Therm. Anal. Calorim. 92 (2008) 589–594.
[31] V. Vagvolgyi, R.L. Frost, M. Hales, A. Locke, J. Kristof, E. Horvath, J. Therm. Anal. Calorim. 92 (2008) 893–897.
[32] V. Vagvolgyi, M. Hales, W. Martens, J. Kristof, E. Horvath, R.L. Frost, J. Therm. Anal. Calorim. 92 (2008) 911–916.
[33] V. Vagvolgyi, A. Locke, M. Hales, J. Kristof, R.L. Frost, E. Horvath, W.N. Martens, Thermochim. Acta 468 (2008) 81–86.
[34] V. Vagvolgyi, J. Palmer Sara, J. Kristof, L. Frost Ray, E. Horvath, J. Colloid Interface Sci. 318 (2008) 302–308.
[35] I. Waclawska, J. Therm. Anal. Calorim. 53 (1998) 519–532.

[36] R.L. Frost, Z. Ding, Thermochim. Acta 397 (2003) 119.
[37] Z. Ding, R.L. Frost, Thermochim. Acta 389 (2002) 185.
[38] L. Frost Ray, J. Kristof, E. Horvath, N. Martens Wayde, J.T. Kloprogge, J. Colloid Interface Sci. 251 (2002) 350.
[39] R.L. Frost, J. Kristof, E. Horvath, J.T. Kloprogge, J. Colloid Interface Sci. 239 (2001) 126.
[40] E. Horvath, L. Frost Ray, E. Mako, J. Kristof, T. Cseh, Thermochim. Acta 404 (2003) 227.
[41] J. Rouquerol, Thermochim. Acta 144 (1983) 203.
[42] O. Toft Sorensen, J. Rouquerol (Eds.), Sample Controlled Thermal Analysis: Origin, Goals, Multiple Forms, Applications and Future, Kluwer Acad. Publishers, Dordrecht, 2003.
[43] A. Jouini, J.-C. Gacon, A. Brenier, M. Férid, M. Trabelsi-Ayadi, J. Lumin. 99 (2002) 365.
[44] D.E.C. Corbridge, E.J. Lowe, J. Chem. Soc. (1954) 49.
[45] K. Sbai, A. Atibi, K. El Kababi, Thermochim. Acta 389 (2002) 153.
[46] K. Sbai, A. Atibi, A. Charaf, M. Radid et, A. Jouini, Ann. Chim. Sci. Mater. 26 (2001) 45.