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THERMAL DEHYDRATION OF $CeP_3O_9 \cdot 3H_2O$ BY CONTROLLED RATE THERMAL ANALYSIS

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The aim of this work is to highlight the importance of controlling the residual water vapour pressure above the sample as well as the rate of the thermal decomposition during the thermal dehydration of cerium cyclotriphosphate trihydrate $CeP_3O_9 \cdot 3H_2O$.

For this reason, the dehydration of the titled compound was followed by both techniques: the constant rate thermal analysis at P_{H_2O}=5 hPa and the conventional TG-DTA in air.

It has been shown that the pathway of the thermal dehydration depends strongly on the nature of atmosphere above the sample.

However, in air atmosphere $CeP_3O_9 \cdot 3H_2O$ decomposes in two well defined steps to give first an amorphous, phase in the temperature range 440–632 K, then the cerium polyphosphate $Ce(PO_3)_3$ crystallizing in orthorhombic system ($C222_1$) at $T>632$ K. Whereas decomposition carried out at 5 hPa water vapour pressure, also occurring in two steps, leads first to a crystallized intermediate monohydrate at $259<T<343$ K and second to a crystallized anhydrous cerium polyphosphate, at $343<T<791$ K, with a structure different from those of all lanthanide polyphosphate known actually and particularly from that of $Ce(PO_3)_3$ obtained in air.

The activation energy corresponding to the dehydration of the initial phosphate was also measured experimentally by means of two CRTA curves and was found equal to 81±5 kJ mol^{-1}.

Keywords: *activation energy, cerium phosphate, controlled rate thermal analysis, TG-DTA*

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]. Besides, they also exhibit unique optical properties based on rare earth doped lanthanum phosphate [3, 4]. Furthermore, rare earth phosphates showed catalytic activity in the oxidative dehydrogenation of iso-butane to iso-butene [5], decomposition of CF4 [6], highly enantioselective hetero-Diels–Alder reaction [7], dehydration reaction of 2-propanol and cracking of cumene [8], vapour phase *o*-alkylation of α- and β-naphthols with methanol [9], isomerization of styrene epoxide [10] and NO decomposition [11].

The cyclotriphosphates of the monovalent or bivalent cations such as $M^{II}(NH_4)_4(P_3O_9)_2 \cdot 4H_2O$ [12] and $NiNa_4(P_3O_9)_2 \cdot 6H_2O$ [13] are largely studied. Investigations dealing with hydrated lanthanide cyclotriphosphates $LnP_3O_9 \cdot nH_2O$ (where *Ln*=rare earth) are relatively scarce. The synthesis of trihydrate cyclotriphosphates with *Ln*=La, Ce and Pr was first described in 1968, by Serra *et al.* [14]. Then, Bagieu-Beucher *et al.* identified the same series by X-ray analysis [15] and determined the structure of $CeP_3O_9 \cdot 3H_2O$ crystalline powder [16]. Simonot-Grange *et al.* studied the thermal dehydration of $LnP_3O_9 \cdot 3H_2O$ (where *Ln*=La, Ce and Pr) [17, 18] which remained poorly documented.

It is widely accepted that conventional thermogravimetry which subjects samples to a linear heating rate can have a major influence on the information content of the TG curve and on the properties of the heat treated products. This can be a source of irreproducibility and highlights the importance that constant transformation rate thermal analysis (CRTA) can have [19, 20]. CRTA permits a constant reaction rate slow enough to minimise the temperature and pressure gradients within the reacting sample and thus results in a more reproducible experiment [21]. It gives generally better separation of intermediate stages in thermal decomposition. CRTA can also be used for kinetic studies of transformations [22]. Besides, CRTA has been employed with success in the study of the stability and thermal decomposition

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pathways of minerals such as attapulgite [23], hydromagnesite [24], hydrozincite and smithsonite [25].

The aim of this work is first to best to deepen the study of the thermal behaviour of cerium cyclotriphosphate trihydrate powder and second to highlight the importance of controlling the residual water vapour pressure above the sample as well as the rate of the thermal dehydration during its thermal decomposition. This was realised using conventional thermal analysis techniques (DTA-TG) in air atmosphere and controlled rate thermal analysis technique under 5 hPa water vapour pressure. The intermediate and final products were analysed by XRD and FTIR techniques.

Experimental

Synthesis

Powder of $CeP_3O_9{\cdot}3H_2O$ were synthesized by slowly mixing $CeCl_3{\cdot}6H_2O$ (0.1 M) and $Na_3P_3O_9$ (0.1 M) solutions at room temperature in a 1:1 mole ratio. The chemical reaction is as follows:

$$Na_3P_3O_9+CeCl_3{\cdot}6H_2O \rightarrow CeP_3O_9{\cdot}3H_2O(sd)+ \\ +3H_2O+3NaCl \quad (1)$$

The sodium cyclotriphosphate $Na_3P_3O_9$ was prepared as reported in [26] by heating $NaH_2PO_4{\cdot}2H_2O$ at 1073 K for 1 h then grounding the obtained vitreous phase and finely after annealing at 673K for 12 h.

After 2 days, powder of $CeP_3O_9{\cdot}3H_2O$ may be isolated from the resulting precipitate after filtering, washing with water and drying in air.

Experimental conditions

Powder X-ray diffraction measurements (XRD) were recorded using a Bruker X-ray diffraction unit with CuKα radiation (λ= 1.5406 Å) at room temperature in 40 kV and 20 mA at a scan speed of 1.2° min^{-1}.

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.

Conventional thermal analysis techniques (TG-DTA) were performed with a thermobalance SETSYS Evolution 1750 Setaram. Sample was heated from ambient up to 1173 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.

CRTA experiments were carried out on an apparatus built in house. The experiments were carried out on 50 mg samples weighed in a silica-cell in the temperature range from 248 up to 873 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 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 a preset value the vapour pressure generated by the sample [19, 20].

Results and discussion

Characterisation of the initial material

The starting material gave XRD pattern in general agreement with the result reported in the JCPDS data card (74-0057) of trihydrate cerium cyclotriphosphate $CeP_3O_9{\cdot}3H_2O$ which will be indicated CEP3p.

The structure of CEP3p belongs to the hexagonal system with space group $P\bar{6}$ (C^1_{3h}) [27]. The $P_3O_9^{3-}$ ring is planar with C_{3h} symmetry. Ce^{3+} ions occupy sites with C_{3h} symmetry. The nearest neighbours of the rare earth ion are six oxygen atoms belonging to the $P_3O_9^{3-}$ anion. These oxygen atoms are located at the corners of two parallel equilateral triangles forming a right prism, with its center occupied by the rare earth ion. Moreover, three oxygen atoms belonging to the water molecules form another equilateral triangle, which is antiparallel to the two others and located in the same plane as the rare earth ion.

In Table 1 are presented the attributions of the absorption bands observed in the infrared (IR) spectrum of a KBr-pressed pellet of the powdered sample.

One of the most noteworthy features of the IR spectrum is the presence of O–H stretching bands in the 3700–3200 cm^{-1} region and O–H bending band peaking at 1629 cm^{-1}. The vibration modes of phosphate anions usually occur in the 1400–400 cm^{-1} area. The strong absorption bands peaking near 1293 and 1032 cm^{-1} usually appear in the spectra of

Table 1 IR absorption frequencies of CEP3p

Assignment	Absorption frequencies/cm^{-1}
$\nu_{(OH)}$	3220–3502–3624–3776
$\delta_{(OH)}$	1629
$\nu_{as(OPO)}$	1293
$\nu_{s(OPO)}$	1112
$\nu_{as(POP)}$	1032
$\nu_{s(POP)}$	763
$\delta_{(OPO)}$	501

cyclophosphates [26, 28, 29]. They are assigned to $\nu_{as(OPO)}$ and $\nu_{as(POP)}$ vibrations, respectively. The observation of these bands is a good criterion to differentiate cyclophosphates from chain structure polyphosphates [30]. Yet another characteristic feature of cyclophosphate IR spectrum is the occurrence of two strong absorption peaks at 763 and 501 cm^{-1}, assigned to $\nu_{s(POP)}$ and $\delta_{(OPO)}$ vibrations, respectively.

Thermal behaviour under air atmosphere

This study was carried out by means of conventional thermal analysis techniques: TG-DTA. Figure 1 shows the TG-DTG and DTA curves of CEP3p carried out in air and at heating rate of 10 K min^{-1}. The DTA peaks, centred at 440 and 632 K, closely correspond to the mass changes observed on the TG curves. The total mass loss is about 14.86%.

This value is slightly higher compared to the theoretical loss of three water molecules (12.52%). This can be explained by the existence of adsorbed water in the initial sample, purchased at temperature below 413 K, origin of the little dissymmetry observed in the first DTA peak.

The DTG curve shows that, the thermal decomposition of CEP3p at temperatures below 1173 K occurs in two well-defined steps AB and BC. The first step (AB) starts at about 413 K and is accompanied by a mass loss of 8.37% at 610 K. This corresponds to the release of two water molecules. The second step (BC) starts at 610 K and is accompanied by a mass loss of 4.20% at 1173 K which correspond to the release of one water molecule.

To characterize the products obtained at the end of each decomposition step, samples prepared after calcination of CEP3p, in an electric oven, at 598 K and 698 K with a heating rate of 10 K min^{-1} in air were immediately submitted to IR and DRX studies.

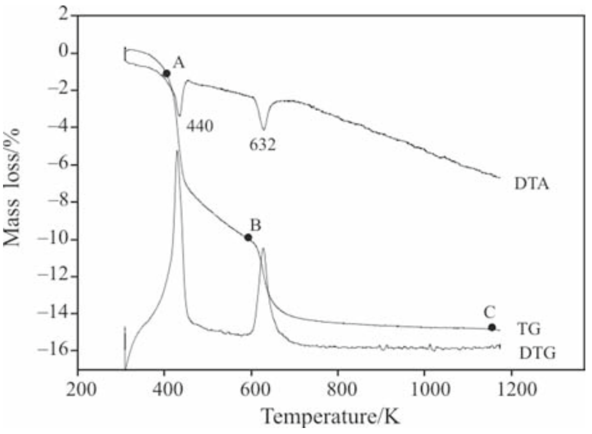

Fig. 1 TG-DTG and DTA curves of CEP3p under air

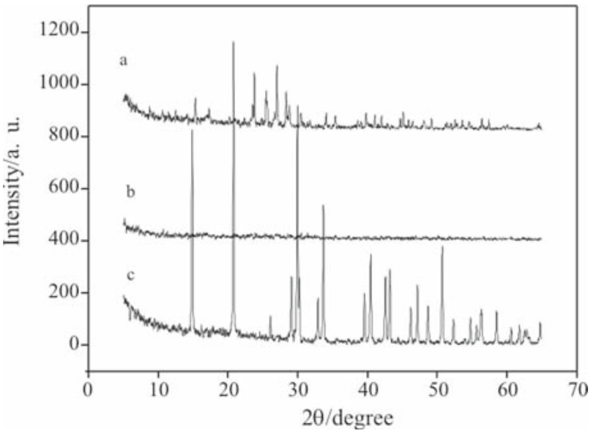

Fig. 2 X-ray diffraction patterns of a – CEP3p and of intermediate products obtained at b – 598 and c – 698 K

In Fig. 2 are presented the X-ray diffraction patterns of the untreated compound and the intermediate products. When heating at 598 K (Fig. 2b) the reflexions related to $CeP_3O_9{\cdot}3H_2O$ disappear completely and the product becomes amorphous. In the diffractogram of the isolated product at 698 K one observes the appearance of new patterns, which correspond to the anhydrous cerium polyphosphate $Ce(PO_3)_3$ (JCPDS 33-0336) crystallizing in orthorhombic system ($C222_1$).

The IR spectra of the untreated compound and the intermediate products calcined at 598 and 698 K are illustrated in Fig. 3. While heating $CeP_3O_9{\cdot}3H_2O$, the water vibrational bands in the IR spectra disappear completely at 698 K. IR absorption bands specific to P_3O_9 ring anions, observed in Fig. 3a at 1293–1032–763 cm^{-1}, disappear after heating at 598 K and the characteristic bands of cerium polyphosphate $Ce(PO_3)_3$ appear clearly at 698 K. The assignment of the absorption bands for the final product obtained at 698 K is presented in Table 2.

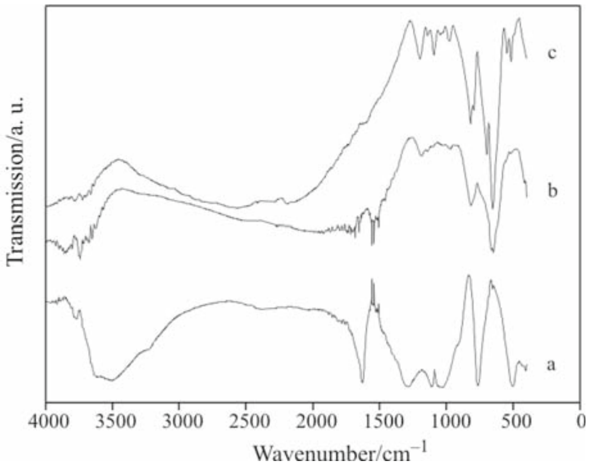

Fig. 3 IR spectra of the a – CEP3p and intermediate products obtained at b – 598 and c – 698 K

Table 2 IR absorption frequencies of $Ce(PO_3)_3$

Assignment	Absorption frequencies/cm^{-1}
$\nu_{as(OPO)}$	1200
$\nu_{s(OPO)}$	1093–1139
$\nu_{as(POP)}$	820–978–1027–1046
$\nu_{s(POP)}$	696–793
$\delta_{(OPO)}$	517–545–652
$\delta_{(POP)}$	489

At this stage, both techniques DRX and IR permit to conclude that the thermal decomposition of cerium cyclotriphosphate trihydrate in air leads first to an amorphous phase then to the cerium polyphosphate. A proposed decomposition pathway is indicated in the equations below:

$$CeP_3O_9{\cdot}3H_2O(sd) \rightarrow \text{amorphous phase}(sd) + 2H_2O(g)$$

$$\text{amorphous phase} \rightarrow Ce(PO_3)_3(sd) + H_2O(g)$$

Thermal behaviour by CRTA technique at P_{H_2O}=5 hPa

CRTA analysis

The CRTA curves of CEP3p, shown in Fig. 4, were obtained by thermolysis of 50 mg of sample under 5 hPa water vapour pressure from 248 to 873 K. The final mass loss at 873 K is 13.2% which corresponds to the theoretical loss (12.52%) of three water molecules from the initial phosphate.

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 the case where 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. The plot of temperature *vs.* time thus obtained by CRTA is analogue to a TG curve. Thus, the time is directly related to a given mass loss and a direct comparison between curves obtained via CRTA and conventional TG can be made.

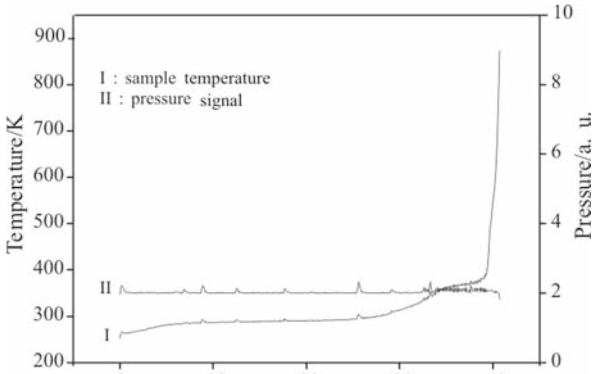

Fig. 4 CRTA curves of thermal decomposition of CEP3p at P_{H_2O}=5 hPa

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 791 K, a rapid drop in the pressure signal is observed indicating the end of the dehydration of the initial phosphate.

In Fig. 5 are shown the sample temperature curve and its derivative. It is clear that the decomposition occurs in two main steps noted AB and BC which can be related to the two steps observed in the conventional TG curve of Fig. 1. However, step AB is in the temperature range 259<T<343 K and occurs within 27.5 h where as step BC is in the temperature range 343<T<791 K and occurs within 13.5 h.

If one considers that the three water molecules of the initial phosphate need 41 h to be completely released it is possible to conclude that the first step (AB) corresponds to the release of two water molecules and that the second step (BC) corresponds to the release of one water molecule. This is in agreement with that obtained by TG analysis.

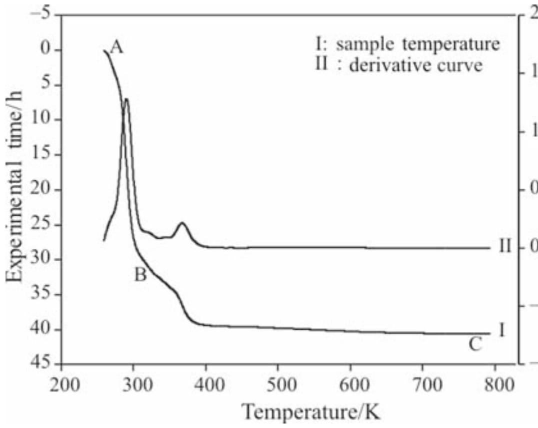

Fig. 5 CRTA curve of the thermal decomposition of CEP3p and its derivative

Activation energy measurement

The rate equation for the thermal decomposition of solids carried out by means of CRTA technique is often written in the form:

$$\frac{d\alpha}{dt} = C = Af(\alpha)\exp\left(\frac{-E_a}{RT}\right) \qquad (1)$$

where $d\alpha/dt$ is the rate of the solid decomposition maintained constant, equal to C, along the total thermolysis, A is the pre-exponential factor, E_a is the activation energy and $f(\alpha)$ is the conversion function.

Thus for a single value of α during a reaction, without any presumption of the reaction mechanism, an expression of the activation energy, at a given value of α, can be obtained :

$$E_a = \frac{RT_1T_2}{T_2-T_1}\ln\left(\frac{C_2}{C_1}\right) \qquad (2)$$

where T_1 and T_2 are the temperatures corresponding to the rates C_1 and C_2 for the same degree of reaction.

In our case, the activation energy was measured using two CRTA curves [31] obtained under the same residual water vapor pressure and at two different rates C_1 and C_2 in the ratio 1:3.

We have presented in Fig. 6, the variation of the apparent Arrhenius activation energies measured all along the steps AB and BC at 5 hPa *vs.* the degree of reaction α.

Figure 6 shows that the apparent Arrhenius activation energies are constant all along the decomposition process at 81 ± 5 kJ mol^{-1}. While water molecules were released in two steps one would expect to obtain two different activation energies which is not the case. It is, thus, possible to consider that after the first step of decomposition the structure of the solid change and the last water molecule take a position that lets it to be released easily and with the same activation energy.

The strength of binding of water molecules in the crystal lattice is different and, hence, results in different dehydration temperatures and kinetic parameters. The activation energy for the losing of crystal water lie in the range 60–80 kJ mol^{-1}, while the value for co-ordinately bounded one are within the range 130–160 kJ mol^{-1} [32]. The activation energy found here for the dehydration of CEP3p suggests that the water molecules are losely linked water.

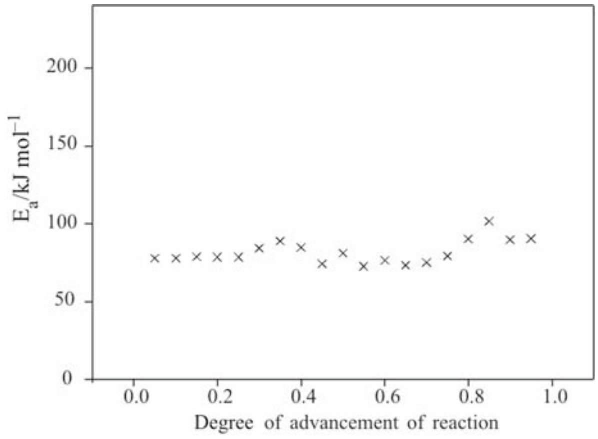

Fig. 6 Variation of activation energy along the decomposition process

Characterisation of the thermal decomposition pathway by XRD and FTIR

To investigate the decomposition pathway of CEP3p at 5 hPa water vapour pressure, XRD patterns of the initial sample, the intermediate sample isolated at 343 K (point B in Fig. 5) and the final product obtained at 791 K (point C in Fig. 5) were compared in Fig. 7.

The X-ray diffraction pattern of the intermediate prepared at 343 K (Fig. 7b), identified as the monohydrate according to the CRTA analysis, shows the existence of diffraction peaks indicating the formation of a new crystallized product. This pattern is different to that of the initial cyclophosphate. This can be explained by a reorganisation in the structure occurring after the release of the two first water molecules which is in agreement with the result observed in activation energy measurement. The corresponding IR spectrum, presented in Fig. 8b, shows the disappearance of the absorption band at 1032 cm^{-1} specific to P_3O_9 ring anions and the appearance of new absorption bands at 988 and 1152 cm^{-1}. It is thus possible to consider that the structure reorganisation is a consequence of the destruction of the cyclophosphate and that this intermediate may be di- or tri- or polyphosphate monohydrate.

The X-ray pattern of the compound obtained at 791 K (Fig. 7c), identified as the anhydrous phosphate according to the CRTA curve, is different from those of the monohydrate and the trihydrate cerium cyclophosphate indicating a second reorganisation in the structure after the release of the last water molecule. This is confirmed by the examination of the corresponding IR spectrum presented in Fig. 8c

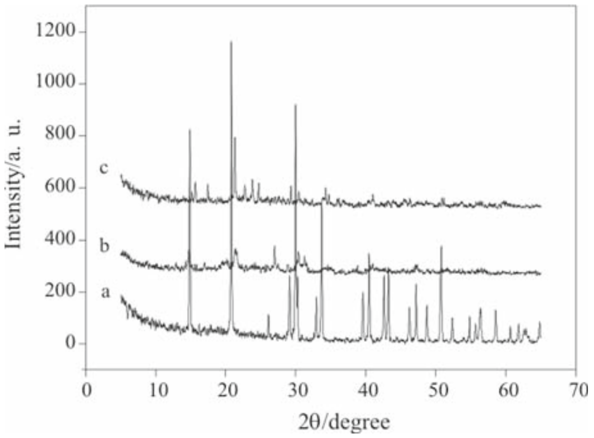

Fig. 7 X-ray diffraction patterns of a – CEP3p and products obtained at b – 343, c – 791 K at 5 hPa water vapour pressure

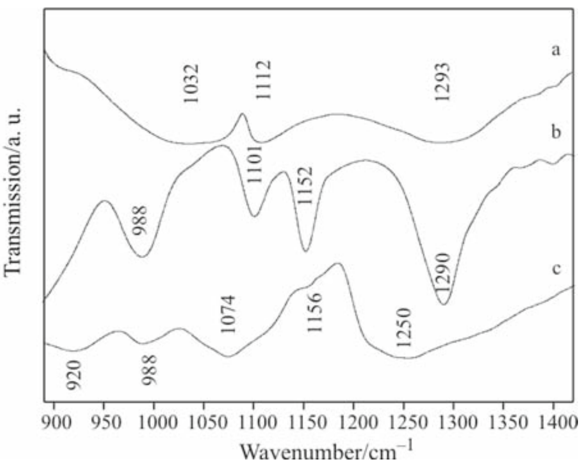

Fig. 8 IR spectra of a – CEP3p and intermediate products obtained by CRTA treatment at b – 343 and at c – 791 K

which is quite different from those of the intermediate obtained at 343 K (Fig. 8b) and the initial cyclophosphate (Fig. 8a). This spectrum shows absorption bands specific to polyphosphate.

Besides, the pattern of the final product is different from all lanthanide polyphosphate ($Ln(PO_3)_3$) actually known and particularly from that given by JCPDS No. 33-0336 of $Ce(PO_3)_3$ ($C222_1$) obtained in air.

Conclusions

This study highlights the influence of the residual water vapour pressure on the thermal decomposition of the cerium tricyclophosphate trihydrate.

By conventional thermal analysis techniques and under atmospheric air the thermal transformation observed for $CeP_3O_9\cdot3H_2O$ occurs in two steps leading first to an amorphous phase and second to the cerium polyphosphate with orthorhombic crystal system and space group $C222_1$.

Whereas by CRTA technique carried out under 5 hPa water vapour pressure and at constant rate of decomposition, the thermal transformation observed for $CeP_3O_9\cdot3H_2O$ occurs also in two steps but leading first to a crystallized intermediate monohydrate and second to a crystallized anhydrous polyphosphate with a structure different from those of all lanthanide polyphosphate known actually and particularly from that of $Ce(PO_3)_3$ ($C222_1$) obtained in air.

That activation energy was also measured experimentally by means of two CRTA curves and was found equal to 81±5 kJ mol^{-1}.

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), does not permit a crystalline rearrangement during the elimination of the two first water molecules. In this case a progressive disorganisation of this latter structure and the passage by an amorphous state is observed.

On the other hand, under controlled water vapour pressure of 5 hPa, the water molecules are eliminated with a lower rate (duration of the experiment: 40 h), presumably by diffusion in the zeolitic channels existing in the atomic arrangement of $CeP_3O_9\cdot3H_2O$. This low rate encourages the reorganization of the crystalline structure and leads to crystallized intermediate product at 343 K.

To give more information on the intermediate and the final products obtained at P_{H_2O}=5 hPa a further work on their structure will be carried by Rietvield method.

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