Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 183–189

PECTIN BASED CERIUM (IV) AND THORIUM (IV) PHOSPHATES AS NOVEL HYBRID FIBROUS ION EXCHANGERS
Synthesis, characterization and thermal behaviour

K. G. Varshney [1], *A. Agrawal* [1] *and S. C. Mojundar* [2*]

[1]Department of Applied Chemistry, Aligarh Muslim University, Aligarh-202002, India
[2]Institute for Research in Construction, National Research Council Canada, M-20, 1200 Montreal Road, Ottawa, ON, K1A 0R6 Canada

Pectin based cerium (IV) and thorium (IV) phosphates have been synthesized as new phases of hybrid fibrous ion exchangers. Both materials were characterized using X-ray diffraction, infrared (IR) spectra, thermogravimetric analysis (TG), differntial thermogravimetry (DTG), differntial thermal analysis (DTA) and scanning electron microscopy (SEM), as well as the determination of their ion exchange capacity, elution and pH titration. The X-ray study reveals the amorphous nature of the materials, while SEM studies confirm the fibrous nature of the materials. The thermal studies of these materials indicate that both of them are highly stable on heating as they retain about 97% of their ion-exchange capacity (i.e.c.) on heating up to 100°C and about 81% on heating up to 200°C.

Keywords: *cerium (IV), DTG and DTA studies, ion exchangers, IR, pectin, SEM, TG, thorium (IV), X-ray*

Introduction

Materials containing both organic and inorganic parts in their structure are termed as organic-inorganic ion exchangers, generally known as hybrid ion exchangers. These materials have attained an important status in analytical chemistry in the recent past, because of their improved ion exchange characteristics compared to both inorganic and organic ion exchangers. They contain polymeric species, such as polyacrylonitrile, polystyrene, polyacrylamide, pectin, etc., in their structure. These materials are expected to have high radiation and thermal stabilities. Because of their reproducible behaviour and ion exchange properties, their utility has been demonstrated for the separation of various metal ions [1]. The fibrous nature of these materials has also been confirmed by SEM studies [1]. Fibrous ion exchangers open a new land of opportunities in industrial and environmental applications, as they can offer wide range of interesting properties and can be obtained in different convenient forms, such as cloth, conveyor belts, nets etc.

The reveal of the relationship between the thermal behaviour and structure of coordination compounds, and the study of the influence of metal and ligand nature on the process of thermal decomposition are of a great interest. Therefore, many authors have investigated the metal and ligand nature in coordination compounds of several central atoms, and also studied their thermal, spectral and structural properties [2–29].

Recently we have produced acrylonitrile based cerium (IV) phosphate (ANCeP) [30], polyacrylonitrile based thorium (IV) phosphate (PANCeP) [31], polystyrene thorium (IV) phosphate (PStThP) [32], acrylamide based thorium (IV) phosphate (AAThP) [33] and acrylamide based cerium (IV) phosphate (AACeP) [34], which have shown selectivity for Hg(II), Pb(II), Cd(II) and Hg(II), respectively.

In continuation of such studies we have synthesized pectin based cerium (IV) phosphate (PcCeP) and pectin based thorium (IV) phosphate (PcThP), which possess a fibrous structure. This paper summarizes the synthesis, ion exchange characteristics and thermal behaviour of these new materials.

Experimental

Reagents and Chemicals

All the reagents and chemicals were of analytical reagent grade obtained from Central Drug House, India [$Ce(SO_4)_2 \cdot 4H_2O$, $Th(NO_3)_4 \cdot 5H_2O$, Pectin, LiCl, LiOH, $Mg(NO_3)_2$, $Ca(NO_3)_2$], Merck, India [H_2SO_4, HNO_3, $NaNO_3$, NaCl, $BaCl_2$] and Qualigens, India [NaOH, KCl, KOH, $Sr(NO_3)_2$].

* subhash.mojumdar@nrc-cnrc.gc.ca

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Synthesis of the ion-exchange materials

A number of sample of PcCeP and PcThP were prepared by adding one volume of 0.05M $Ce(SO_4)_2{\cdot}4H_2O$ (in case of PcCeP) and 0.1M $Th(NO_3)_4{\cdot}5H_2O$ (in case of PcThP) solutions in two volumes of (1:1) mixture of 6M H_3PO_4 (in case of PcCeP) and 2M H_3PO_4 (in case of PcThP) and pectin (varying % age). The solutions were added dropwise with constant stirring using magnetic stirrer, at a temperature of 70±5°C (in case of PcCeP) and 90±5°C (in case of PcThP). The resulting slurry obtained under these conditions was stirred for 4 h at these temperatures, filtered and then washed free of sulphate ions with demineralized water (pH~4). Finally, the slurry of PcCeP and PcThP were dried at room temperature, resulting in fibrous shiny sheets. These sheets were cut into small pieces and converted into H^+ form by treating them with 1M HNO_3 for 24 h with occasional shaking and intermittently replacing the supernatant liquid with 1M HNO_3. The materials thus obtained were then washed with demineralized water to remove the excess acid before finally drying at 45°C. The ion-exchange capacity of PcCeP and PcThP, were found to be maximum for sample PcCeP-2 (Table 1) and PcThP-11 (Table 2), respectively. These two samples were selected for further studies.

Table 1 Synthesis of various samples of pectin based cerium (IV) phosphate

Sample number	Pectin added/%	Na^+ ion exchanged capacity/meq(dry g)$^{-1}$
PcCeP-1	0	1.40
PcCeP-2	1	1.78
PcCeP-3	2	0.60
PcCeP-4	3	1.00
PcCeP-5	5	1.20
PcCeP-6	10	1.50
PcCeP-7	11	1.01
PcCeP-8	12	1.00

Results

Ion-exchange capacity (i.e. c.), elution and concentration behaviour

The ion exchange capacity for Na^+ ion and other metal ions were determined by the column process as described earlier [3], for both PcCeP and PcThP. The results are summarized in Table 3.

The elution and concentration behaviour were also studied on these materials by a similar method described earlier [30]. Table 4 summarizes the results of concentration behaviour.

Table 2 Synthesis of various samples of pectin based thorium (IV) phosphate

Sample number	Pectin added/%	Na^+ ion exchanged capacity/meq(dry g)$^{-1}$
PcThP-1	0	0.80
PcThP-2	1	0.85
PcThP-3	2	0.91
PcThP-4	3	1.08
PcThP-5	5	1.10
PcThP-6	7	1.53
PcThP-7	10	1.57
PcThP-8	11	1.60
PcThP-9	12	1.91
PcThP-10	13	1.96
PcThP-11	15	2.15
PcThP-12	17	1.75
PcThP-13	19	1.65
PcThP-14	20	1.60
PcThP-15	22	1.57
PcThP-16	24	1.50

Table 3 Ion exchange capacity of pectin based cerium (IV) and thorium (IV) phosphates for various metal solutions

Metal solution	Ion-exchange capacity/meq(dry g)$^{-1}$	
	PcCeP	PcThP
LiCl	1.65	1.80
$NaNO_3$	1.78	2.15
KCl	1.80	2.20
$Mg(NO_3)_2$	1.95	2.60
$Ca(NO_3)_2$	2.15	2.80
$Sr(NO_3)_2$	2.23	3.00
$BaCl_2$	2.50	3.10

Table 4 Concentration behaviour of pectin based cerium (IV) and thorium (IV) phosphates

Concentration of $NaNO_3$/M	Ion-exchange capacity/meq(dry g)$^{-1}$	
	PcCeP	PcThP
0.2	0.61	0.85
0.4	0.80	1.25
0.6	1.21	1.50
0.8	1.52	1.80
1.0	1.78	2.15
1.2	1.70	2.13

Recycling studies

1 g of material was loaded on the column of internal diameter ~1 cm, fitted with a glass wool at its bottom. The ion-exchange capacity was determined by col-

Table 5 Values of ion exchange capacity of pectin based cerium (IV) and thorium (IV) phosphates on recycling

Sample no.	No. of recycles	Mass of material load/ g	Ion-exchange capacity/meq(dry g)$^{-1}$		Retention of ion exchange capacity/%	
			PcCeP	PcThP	PcCeP	PcThP
1	0	1	1.78	2.15	100.00	100.00
2	1	"	1.67	1.72	93.82	80.00
3	2	"	1.55	1.62	87.08	73.35
4	3	"	1.42	1.51	79.78	70.23
5	4	"	1.10	1.31	61.79	61.10
6	5	"	0.91	0.74	51.12	34.42
7	6	"	0.53	0.33	29.78	15.35
8	7	"	0.20	0.07	11.24	3.26

umn process [30], using 1M $NaNO_3$ as eluant. The conversion of material in H^+ form was done by passing 250 mL of 1M HNO_3, maintaining a very slow flow rate of ~0.5 mL min^{-1}, then washed the excess of acid with DMW (pH~7). Table 5 shows the result of this study on PcCeP and PcThP.

pH Titrations

pH measurements were performed using an Elico Model LI-10 pH meter. pH titrations were performed by the Topp and Pepper's method [35] on both PcCeP and PcThP. Figures 1 and 2 show the results of this study on PcCeP and PcThP, respectively.

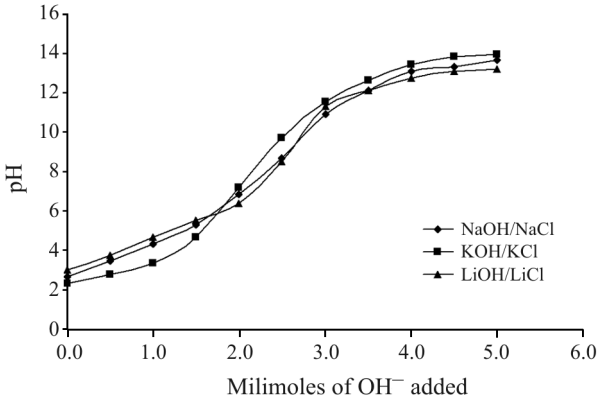

Fig. 1 Equilibrium pH titration curves of pectin based cerium (IV) phosphate

Thermal studies

One g samples of the material were heated at various temperatures for 1 h each in a muffle furnace, and their ion exchange capacity was determined by the column process after cooling them to room temperature. Table 6 summarizes the results of this study on PcCeP and PcThP.

TG/DTG/DTA studies

TG/DTG/DTA studies were carried out by using a PerkinElmer instrument, Pyric Diamond model. Figures 3 and 4 show the TG/DTG/DTA curves for PcCeP and PcThP, respectively.

Table 6 Thermal stability of pectin based cerium (IV) and thorium (IV) phosphates after heating to various temperatures for 1 h

Sample no.	Drying temp/°C	PcCeP			PcThP		
		Ion-exchange capacity/ meq(dry g)$^{-1}$	Change in colour	Retention of i.e.c./%	Ion-exchange capacity/ meq(dry g)$^{-1}$	Change in colour	Retention of i.e.c./%
1	45	1.78	Greenish yellow	100	2.15	Lemon yellow	100
2	100	1.73	Greenish yellow	97.19	2.07	Lemon yellow	96.28
3	200	1.45	Greenish yellow	81.46	1.80	Brown	83.72
4	400	1.33	Off white	74.72	1.38	Light brown	64.19
5	600	1.15	Off white	64.61	0.71	Grey	33.02
6	800	0.51	White	28.65	0.13	Light grey	6.05

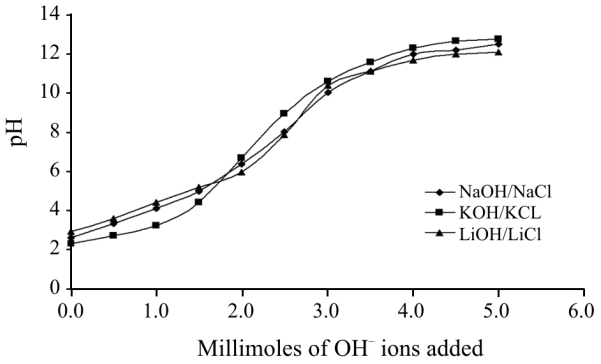

Fig. 2 Equilibrium pH titration curves of pectin based thorium (IV) phosphate

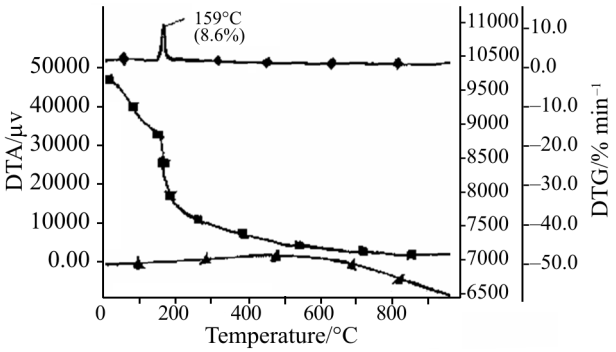

Fig. 3 TG, DTG (top) and DTA curves of pectin based cerium (IV) phosphate

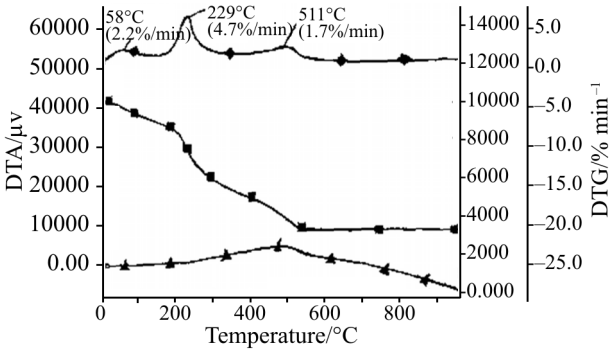

Fig. 4 TG, DTG (top) and DTA curves of pectin based thorium (IV) phosphate

SEM studies

SEM studies were done with LEO 435 VP scanning electron microscope. Scanning electron micrograph of PcCeP and PcThP were taken at 1000× and 2000× magnification, respectively, as shown in Figs 5 and 6.

IR spectral studies

IR studies were carried out by the KBr disc method using PerkinElmer FTIR spectrometer RX-I. Figures

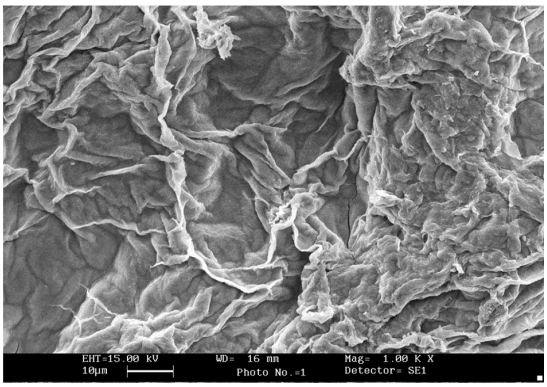

Fig. 5 Electron micrograph of pectin based cerium (IV) phosphate at 1000× magnification.

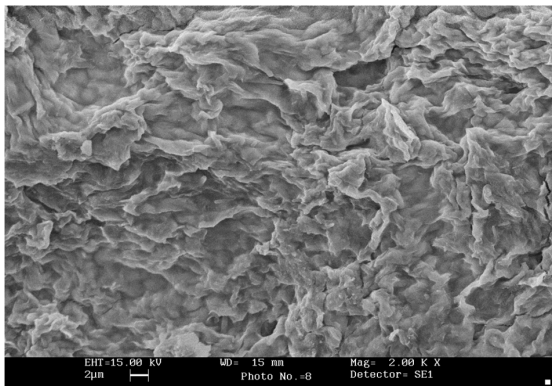

Fig. 6 Electron micrograph of pectin based thorium (IV) phosphate at 2000× magnification

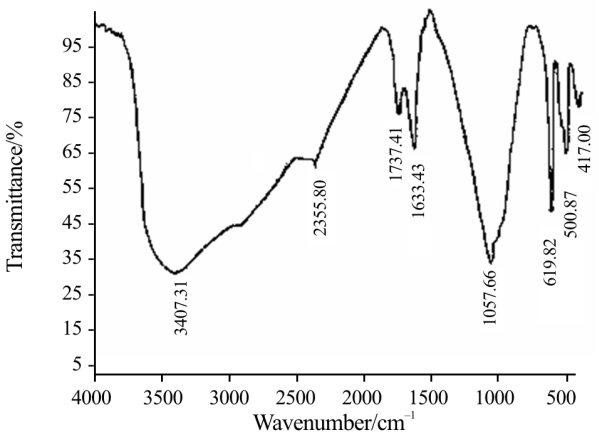

Fig. 7 Infrared spectrum of pectin based cerium (IV) phosphate

7 and 8 show the IR spectra of PcCeP and PcThP, respectively.

X-ray studies

X-ray diffraction studies were made on Bruker Analytical X-ray diffractometer, model D8 advance. The

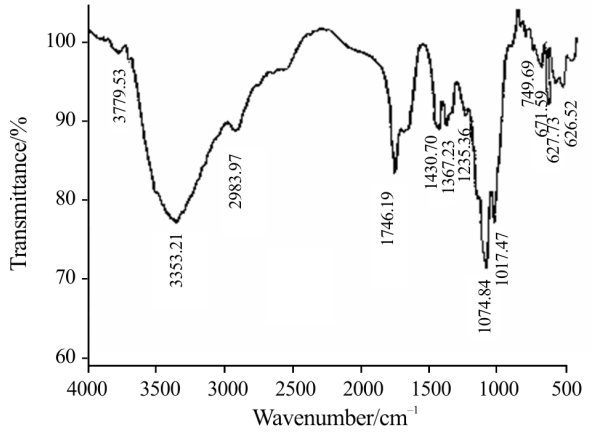

Fig. 8 Infrared spectrum of pectin based thorium (IV) phosphate

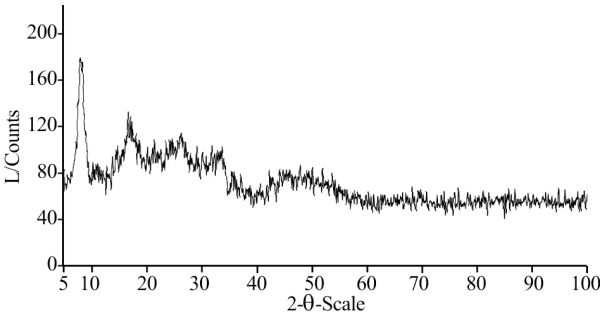

Fig. 9 X-ray diffraction pattern of pectin based cerium (IV) phosphate

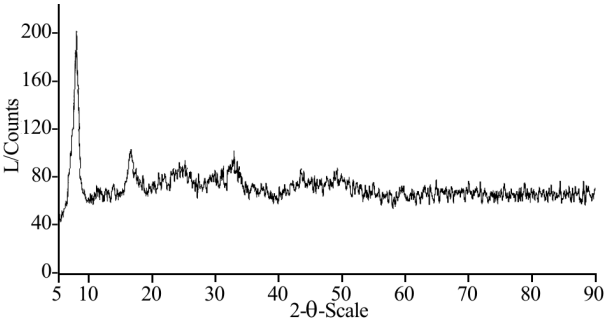

Fig. 10 X-ray diffraction pattern of pectin based thorium (IV) phosphate

X-ray patterns of materials were taken using Cu target, with wavelengths 1.54060 and 1.54439Å. The step size and smoothing width were 0.050 and 0.300°, respectively. The step times were 6.00 and 3.00 s for PcCeP and PcThP, respectively. Figures 9 and 10 show the X-ray diffraction patterns.

Conclusions

This study highlights certain interesting features of the pectin-based cerium (IV) and thorium (IV) phosphates as new fibrous ion exchangers obtained in the form of sheet. The SEM photographs of PcCeP (magnification 1000×) and PcThP (magnification 2000×) reveal their particle size as 10 and 2 μm, respectively.

The Na^+ ion exchange capacity was found to be 1.78 meq/dry g of PcCeP and 2.15 meq/dry g of PcThP. The ion-exchange capacity (i.e.c.) of alkali metals and alkaline earths on PcCeP and PcThP show the following trends: $Li^+<Na^+<K^+$ and $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$. It is in same order as the decreasing trend in the hydrated ionic radii of these metal ions.

A study of the elution behaviour reveals that the exchange is fast on both PcCeP and PcThP. Almost all the H^+ ions are eluted out in the first 150 mL of the effluent from a column of 1.0 g material. The optimum concentration for the eluant was found to be 1M (Table 4) for a complete removal of H^+ ions from the PcCeP and PcThP columns.

In recycling studies, ion-exchange columns containing these materials (PcCeP and PcThP) were regenerated repeatedly for many times to study the retention behaviour of their i.e.c. on recycling. Table 5 shows that the retention value decreases slowly with increasing number of recycles. PcCeP retains about 11% and PcThP retains about 3% of their i.e.c. upto 7 recycles.

The pH titration curves of PcCeP (Fig. 1) and PcThP (Fig. 2) obtained under equilibrium conditions for LiOH/LiCl, NaOH/NaCl and KOH/KCl systems indicate a monofunctional exchange process for both materials. The materials release H^+ ions easily with the addition of metal salt solution containing no OH^- ions, showing a strong cation exchange behaviour. At low metal hydroxide concentration, the ion exchange for Li^+ ions is lower than those for Na^+ and K^+ ions, as is evident from the initial pH at a lower hydroxide concentration. Also, the H^+–Li^+ exchange rate is slower than those for the H^+–Na^+ and H^+–K^+ exchanges. The H^+–Li^+ exchange process is completed at higher OH^- concentration. This behaviour may be due to a larger hydrated radius of Li^+ ion than those of Na^+ and K^+ ions, thus accounting for a lower ion exchange capacity for Li^+ ion in the column process (dynamic condition) where the equilibrium is not fully established. The end point in the titration is not quite sharp which may be due to some alkaline hydrolysis of the ion exchanger. An overall higher ion-exchange capacity for all three metal ions in the batch process (static condition) than in the column process, as shown by the potentiometric curves was observed. This behaviour may be due to the presence of alkali hydroxides, which facilitates the ion exchange by the removal of H^+ ions from the external solution in accordance with the Le Chatelier's principle.

Thermal studies of these materials indicate certain very interesting results. Both of them are highly stable on heating as they retain about 97% of their i.e.c. on heating up to 100°C and about 81% on heat-

ing up to 200°C. On heating up to 400°C, however they show a significant difference in the retention capability of their i.e.c.. PcCeP showing retention of 74% while PcThP showing retention of 64%. Even on heating up to 600°C these materials show an appreciable i.e.c., PcCeP retaining about 64% and PcThP about 33%. PcCeP retains it i.e.c. upto 28% even on heating up to 800°C. However, the i.e.c. of PcThP sharply decreases on heating up to this temperature, showing only 6% retention. This is a unique behaviour of these materials as compared to the other ones of this class studied earlier [1]. AACeP(5) loses its i.e.c. about 60% at 200°C and 95% at 400°C, while AAThP(4) loses its i.e.c. almost totally beyond 200°C. The curves (Figs 3 and 4) show 9.04% mass loss up to 151°C in PcCeP and 13.2% mass loss up to 177°C in PcThP, which may be due to the removal of external water molecules from the exchanger. Beyond 151°C the condensation of PcCeP must have started, resulting in the dehydration due to the removal of strongly coordinated water molecules from the framework of the exchanger. The dehydration continues up to 1000°C, where the mass becomes almost constant. It also involves the production of CeO_2 at 450°C [36]. In PcThP, the condensation starts at 177°C as indicated by a mass loss up to ~415°C. On further heating an abrupt change was observed. At 561°C, ThO_2 horizontal starts [37], indicating the formation of pyrophosphate.

For elemental analysis, Heraeus Carlo Erba-1108 analyzer was used. The elemental analysis gave the molar ratio of C, H, N as 3: 77: 1 and 31: 80: 1 for PcCeP and PcThP, respectively.

The IR spectrum of PcCeP (Fig. 7) and PcThP (Fig. 8), confirms the presence of metal oxide and metal hydroxide bands in the material. The metal–oxygen and metal hydroxide bands are observed at 619.8 cm^{-1} in PcCeP, and 627.73 and 671.59 cm^{-1} in PcThP. The bands at 417.00, 500.87 and 1057.66 cm^{-1} in PcCeP, and 526.52 and 1074.84 cm^{-1} in PcThP indicate the presence of phosphate groups. The absorption bands at 1633.43 and 3407.31 cm^{-1} in PcCeP, and 3353.21 cm^{-1} in PcThP correspond to the water of crystallization. The bands at 2355.80 cm^{-1} in PcCeP and 1367.23, 1430.70 and 2933.97 cm^{-1} in PcThP indicate the C–H stretching of carbon. The C=O stretching of ester was observed at 1737.61 cm^{-1} in PcCeP and 1235.36 and 1746.14 cm^{-1} in PcThP. The absorption bands at 1017.47 and 1235.36 cm^{-1} in PcThP indicate C–O stretching in alcohols [38].

The X-ray diffraction patterns of PcCeP and PcThP show their amorphous nature.

Acknowledgements

Thanks are due to the Chairman, Department of Applied Chemistry, for research facilities and to the Institute Instrumentation Center, Indian Institute of Technology, Roorkee, All India Institute of Medical Science, New Delhi and Central Drug Research Institute, Lucknow, India, for technical assistance.

References

1 K. G. Varshney, Solid State Phenomena, 90 (2003) 445.
2 D. Czakis-Sulikowska, A. Czylkowska and A. Malinowska, J. Therm. Anal. Cal., 67 (2002) 667.
3 E. Jóna, M. Kubranová, P. Šimon and J. Mroziñski, J. Therm. Anal. Cal., 46 (1996) 1325.
4 S. C. Mojumdar, L. Martiška, D. Valigura and M. Melník, J. Therm. Anal. Cal., 74 (2003) 905.
5 K. Kundu and M. A. H. Miah, Jahangirnagar Univ. J. Sci., 19 (1995) 49.
6 S. C. Mojumdar, M. Melník and E. Jóna, Thermochim. Acta, 352 (2000) 129.
7 R. N. Patel and K. B. Pandeya, Synth. React. Inorg. Met.-Org. Chem., 28 (1998) 23.
8 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
9 R. N. Patel and K. B. Pandeya, J. Inorg. Biochem., 72 (1998) 109.
10 D. Ondrušová, E. Jóna and P. Šimon, J. Therm. Anal. Cal., 67 (2002) 147.
11 E. Jóna, D. Ondrušová, M. Pajtášová, P. Šimon and J. Michálek, J. Appl. Polym. Sci., 81 (2001) 2936.
12 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 53 (2000) 149.
13 M. Pajtášová, E. Jóna, M. Koman and D. Ondrušová, Polish. J. Chem., 75 (2001) 1209.
14 E. Jóna, M. Pajtášová, D. Ondrušová and P. Šimon, J. Anal. Appl. Pyrolysis, 63 (2002) 17.
15 M. Kubranová, E. Jóna, E. Rudinská, K. Nemčeková, D. Ondrušová and M. Pajtášová, J. Therm. Anal. Cal., 74 (2003) 251.
16 E. Jóna, M. Hvastijová and J. Kohout, J. Thermal Anal., 41 (1994) 161.
17 S. C. Mojumdar, K. Lebrušková and D. Valigura, Chem. Papers, 57 (2003) 245.
18 S. C. Mojumdar, I. Ondrejkovičová, L. Neviďanská and M. Melník, J. Anal. Appl. Pyrolysis, 64 (2002) 59.
19 E. A. Ukraintseva, V. A. Logvinenko, D. V. Soldatov and T. A. Chingina, J. Therm. Anal. Cal., 75 (2004) 337.
20 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 541.
21 B. R. Srinivasan and S. C. Sawant, Thermochim. Acta, 402 (2003) 45.
22 D. Czakis-Sulikowska and A. Czylkowska, J. Therm. Anal. Cal., 71 (2003) 395.
23 E. Jóna and M. Jamnický, J. Thermal Anal., 27 (1983) 359.
24 E. Jóna, T. Šramko and J. Gažo, J. Thermal Anal., 16 (1979) 213.
25 A. Krutošíková, B. Mitasová, E. Jóna and M. Bobošíková, Chem. Papers, 55 (2001) 290.

26 S. C. Mojumdar, J. Therm. Anal. Cal., 64 (2001) 629.
27 S. Cakir, I. Bulut, E. Bicer, E. Coskun, and O. Cakir, J. Electroanalytical Chem., 511 (2001) 94.
28 D. Czakis-Sulikowska, A. Czylkowska, A. Malinowska, J. Therm. Anal. Cal., 65 (2001) 505.
29 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 46 (1998) 147.
30 K. G. Varshney, Namrata Tayal and U. Gupta, Colloids Surf. A Physicochem. Eng. Asp., 145 (1998) 71.
31 K. G. Varshney, Namrata Tayal, A. A. Khan and R. Niwas, Colloids Surf. A. Physicochem. Eng. Asp., 181 (2001) 123.
32 K. G. Varshney and Namrata Tayal, Langmuir, 17 (2001) 2589.
33 K. G. Varshney, P. Gupta and A. Agarwal, Proceedings of the National Symposium on Biochemical Sciences: health and Environmental Aspects, Allied Publisher, New Delhi, Oct 2–4, pp. 254-257 (2003).
34 K. G. Varshney, P. Gupta and N. Tayal, Indian J. Chem., 42(A) (2003) 89.
35 N. E. Topp and K. W. Pepper, J. Chem. Soc., 3299 (1949).
36 C. Duval, 'Inorganic Thermogravimetric Analysis', Elsevier, Amsterdam (1953), p. 403.
37 C. Duval, 'Inoganic Thermogravimetric Analysis', Elsevier, Amsterdam (1953), pp. 492, 497.
38 R. T. Morrison and R. N. Boyd, 'Organic Chemistry', Prentice Hall of India Pvt. Ltd., New Delhi (1998).

DOI: 10.1007/s10973-005-6995-y