THERMAL BEHAVIOR OF ZINC γ-ZIRCONIUM PHOSPHATE INTERCALATION COMPOUNDS
Synthesis and X-ray characterization

C. Ferragina[1], R. Di Rocco[1] and L. Petrilli[2]*

[1]CNR, IMIP, via Salaria Km 29.300, 00016 Monterotondo (Roma), Italy
[2]CNR, ISM, via Salaria Km 29.300, 00016 Monterotondo (Roma), Italy

The layered ion-exchangers γ-zirconium phosphate and γ-zirconium phosphate containing intercalated diamines, obtained by exchanging zinc ions, have been synthesized and characterized. Zinc ions are able to form coordination compounds between the layers of the host matrix and consequently form zinc complexes formed in situ. The zinc ions uptake, the thermal behavior and the structural characterization of the compounds obtained have also been examined. The thermal stability and X-ray spectra of these compounds depend on the type of isomeric diamine precursor. The zinc fully exchanged γ-zirconium phosphate is able to form ZnS particles in the host matrix. The X-ray spectra of this obtained material matched those of the initial γ-zirconium phosphate precursor.

Introduction

Only in the last few years the inorganic ion-exchangers of the dihydrogen phosphates class of tetravalent elements (Zr, Ti, Sn, Ge, etc.) with a layered structure have revealed their potentiality both as ion-exchangers and as an intercalating support. The host matrix intercalates organic bases that in turn act as ligands with transition metal ions, forming coordination compounds in situ between the layers [1]. These molecular intercalates are 'new' [3–5] inclusion compounds. Due to their non-rigid structure like in the case of three-dimensional zeolites compounds, these ion-exchangers have an interlayer distance d that can be adjusted according to the nature of the intercalated species. The gamma phase of zirconium dihydrogen phosphate [γ-Zr(PO$_4$)(H$_2$PO$_4$)·2H$_2$O, denoted as γ-ZrP], one of the most studied ion-exchanger, has renewed researcher's interest in the intercalation of organic and inorganic molecules [2, 6] because of its chemical and thermal stability and its wider d with respect to its analogue α-phase (12.27 *vs*. 7.60 Å respectively). In this paper we describe the well–defined compounds obtained from the intercalation into γ-ZrP of aromatic diamines (L), isomeric as far as is concerned the nitrogen position in their molecule and their complexes formed in situ with the zinc ions. The materials thus obtained can be utilized in heterogeneous catalysis such as in oxidative reactions. Like in the case of sol–gel (SG) zirconium phosphate with the encapsulated ZnS [9] we

also wanted to study the γ-ZrP host with encapsulated particles of the semiconductor ZnS. Many methods have been applied to prepare semiconductor clusters and the best method for the formation of this semiconductor is the encapsulation in zeolites [10] because of the three-dimensional structure of the host matrix. The advantages of semiconductor clusters encapsulated in zeolites is their homogeneity and stability. The insertion in a two dimensional structure such as layered γ-ZrP is of increasing importance as a way of controlling the structure of chemical reactions.

Experimental

Chemicals

The zinc acetate, iron sulfide and isomeric diamines were purchased reagent grade from Aldrich and used without further purification. All the other reagents were Merck pro analyze products.

Materials

γ-zirconium phosphate was prepared as indicated in [11]. The intercalation compounds obtained with the isomeric diamines: 2,2'-bipyridyl (2,2'-bipy); 2,4'-bipyridyl (2,4'-bipy); 4,4'-bipyridyl (4,4'-bipy) were prepared by batch as indicated in [12] choosing the solvent ratio ethanol:water=1:2 for their solution, and the exchanger:diamine=1:1 for their intercalation

---

in the host matrix. The zinc diamine complexes were prepared in situ by ion-exchange, by equilibrating the diamine intercalation compounds with zinc acetate solution. All the batches were thermostatted at 45°C for a week; the suspensions were then filtered and the solutions analyzed for metal content and final pH. The solids were washed with distilled water and air dried. Zinc γ-zirconium phosphate was prepared by ion-exchange, following two methods: the batch procedure [1] and the hydrothermal synthesis method, by putting a sample of γ-ZrP phase sealed in a Pyrex tube with a zinc acetate solution so as to obtain a fully exchanged form. The tube was put into a hydrothermal bomb and heated in a oven at 120°C for 72 h. The zinc sulfide γ-ZrP material was obtained by flowing anhydrous H_2S [6–9] over the anhydrous (420°C) zinc γ-zirconium phosphate, for a week.

Physical measurements and chemical analysis

Zinc ions were analyzed on a GBC 903 A.A. spectrophotometer by studying the concentration changes which took place in the supernatant solutions, before and after contact, with the exchangers. The phosphate content was determined colorimetrically [13]. The contents of water and of diamines and the thermal behavior were determined with a simultaneous TG-DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 10 K min^{-1}, heated up to 1100°C to constant mass in an air flow. An X-ray powder diffractometer was used to study phase changes in the materials. This was done by monitoring the *d* reflection and its harmonics. A Philips diffractometer (model PW 1130/00) was used with Ni-filtered CuK$_\alpha$ radiation (λ=1.541 Å). The content of sulfur, carbon, nitrogen and hydrogen in the materials was determined using a Fisions 1108 elemental microanalyser.

Results and discussion

Zinc materials derived by γ-ZrP

By using the batch method, samples of 1 mmol of γ-ZrP were contacted with an appropriate volume of $4.5 \cdot 10^{-2}$ mol dm^{-3} of zinc acetate solution, at 45°C, for a week, in order to obtain the fully exchanged γ-ZrZn(PO$_4$)$_2$·4H$_2$O, denoted as γ-ZrPZn. The solid was recovered by centrifugation and air dried. The fully exchanged zinc form was only obtained by renewing the acetate solution for three times or by modifying the starting pH [6–9] as ascertained by A. Clearfield *et al*. [14], due to the relationship between the pH of the zinc acetate solution and the ion-exchange with the γ-ZrP. Besides the fully exchanged

**Table 1** Chemical composition and interlayer distance *d* (Å) of the intercalated compounds γ-ZrPL and γ-ZrPLZn

Intercalated compounds	*d*/Å
γ-Zr(PO$_4$)(H$_2$PO$_4$)2,2'-bipy$_{0.30}$·1.42H$_2$O	14.25
γ-Zr(PO$_4$)(H$_{1.46}$PO$_4$)2,2'-bipy$_{0.27}$Zn$_{0.27}$·1.65H$_2$O	16.24
γ-Zr(PO$_4$)(H$_2$PO$_4$)2,4'-bipy$_{0.28}$·1.47H$_2$O	14.21
γ-Zr(PO$_4$)(H$_{1.70}$PO$_4$)2,4'-bipy$_{0.15}$Zn$_{0.15}$·1.78H$_2$O	13.61
γ-Zr(PO$_4$)(H$_2$PO$_4$)4,4'-bipy$_{0.16}$·1.35H$_2$O	12.28
γ-Zr(PO$_4$)(H$_{1.74}$PO$_4$)4,4'-bipy$_{0.13}$Zn$_{0.13}$·1.70H$_2$O	12.28

material was obtained by performing the synthesis using the hydrothermal method, as in the case of SG [9], by contacting 1 mmol of γ-ZrP and 22 mL of $4.5 \cdot 10^{-2}$ mol dm^{-3} zinc acetate solution, at 120°C for three days. All the characterizations were performed on the zinc material obtained using the hydrothermal synthesis because this method is faster and easier. A form with 50% of Zn^{2+} exchanged was been also prepared by contacting 1 mmol of γ-ZrP and 11 mL of $4.5 \cdot 10^{-2}$ mol dm^{-3} zinc acetate solution, with the hydrothermal method. Its chemical formula is γ-ZrZn$_{0.50}$(HPO$_4$)(PO$_4$)·2H$_2$O, denoted as γ-ZrPZn$_{0.50}$.
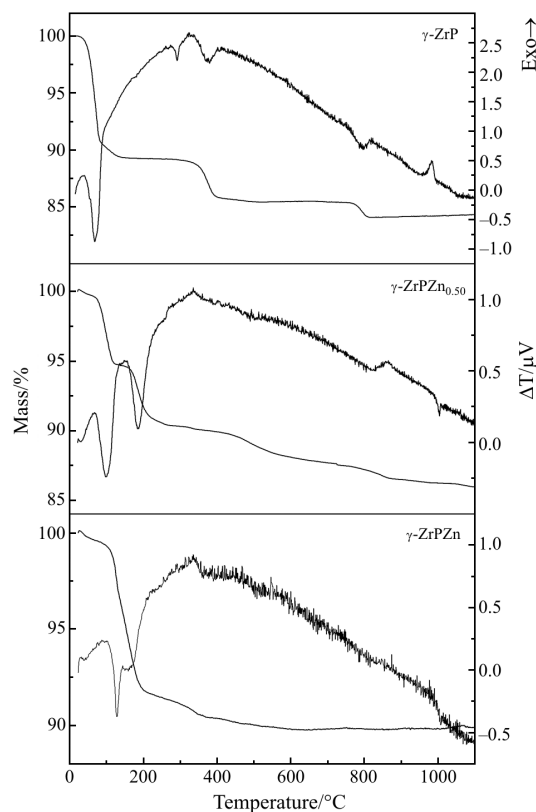
Fig. 1 TG-DTA curves of: γ-ZrP; γ-ZrPZn$_{0.50}$; γ-ZrPZn
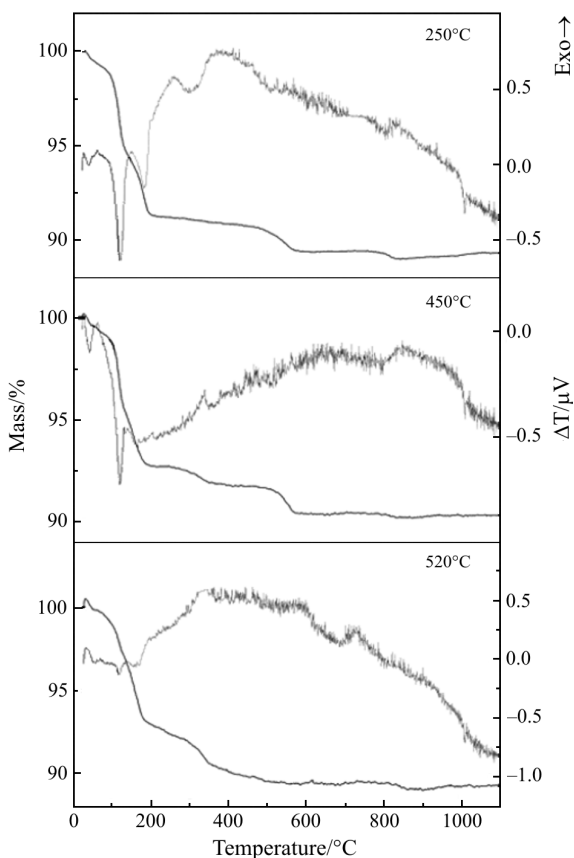
Fig. 2 TG-DTA of the γ-ZrPZn material (heated at 250–450–520°C), after the rehydration

Fig. 3 XRPD of: γ-ZrP; γ-ZrPZn$_{0.50}$; γ-ZrPZn

Zinc materials derived by γ-ZrPdiamines

Samples of 1 mmol of γ-ZrPdiamines: γ-Zr(PO$_4$)(H$_2$PO$_4$)2,2'-bipy$_{0.30}$·1.42H$_2$O; γ-Zr(PO$_4$) (H$_2$PO$_4$)2,4'-bipy$_{0.28}$·1.47H$_2$O and γ-Zr(PO$_4$) (H$_2$PO$_4$)4,4'-bipy$_{0.16}$·1.35H$_2$O, denoted as γ-ZrP2,2'-bipy; γ-ZrP2.4'-bipy and γ-ZrP4,4'-bipy respectively, were contacted with an amount of 4.5·10^{-2} mol dm^{-3} zinc acetate solution so that [Zn^{2+}]:[intercalated diamine]=1:1. The 1:1 molar ratio was chosen in order to favor the 1:1=LZn complex species between the layers of the exchanger. Table 1 reports the chemical composition of the zinc materials and their *d* compared with those of their precursors. It can be stated that the total amount of the zinc exchanged in the γ-ZrPL is in the order of γ-ZrP2,2'-bipy>γ-ZrP2,4'-bipy≥γ-ZrP4,4'-bipy. The zinc exchanged compounds obtained are due to the –N– position between the layers of the host matrix forming N–Zn bonds. In the case of γ-ZrP2,4'-bipy and γ-ZrP4,4'-bipy the unfavorable position of –N– between the layers of the host matrix to form N–Zn bonds, gives rise to a competition between the Zn^{2+} exchange and the diamines present hindrance. The re-

sult is a diamine elution and a lower Zn^{2+} uptake during the process. As far as the γ-ZrP2,2'-bipy material is concerned that the two –N– positions are more favorable, the competition is negligible and the formation of the γ-ZrP2,2'-bipyZn complex is easier.
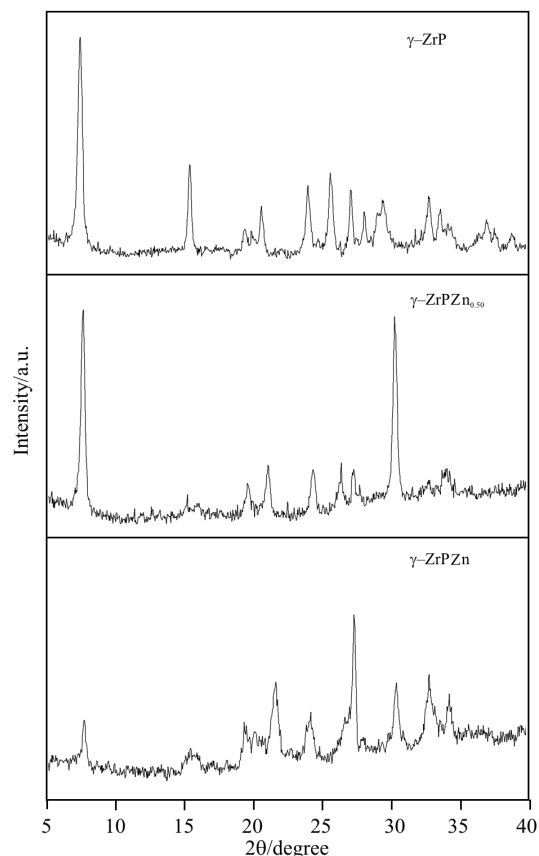
Thermal behavior and XRPD of γ-ZrPZn

The fully exchanged γ-ZrPZn material submitted to thermal analysis shows in the TG curve mass losses, in three distinct stages, between 25–520°C, related to the water (Fig. 1). As in the case of the SG zinc zirconium phosphate (SGZrPZn) [9] the maximum water loss is evident between 25–250°C, where 3.25 molecules of the coordination water are lost in two subsequent steps: 25–150°C (2H$_2$O) and 150–250°C (1.25H$_2$O). A third small loss slowly occurs between 250–520°C (0.75H$_2$O). The DTA curve is in accordance with the TG data showing the endothermic peaks, related to the water losses. At 1000°C a sharp endothermic peak, without mass variation, due to the phase transition (synterization) [9] is evident. The material, submitted to thermal treatment up to 520°C, rehydrates in air in two days: ~100–85% (for the γ-ZrPZn material heated from 150 up to 350°C); ~80–70% (from 400 up to 480°C); ~30% (at 520°C)
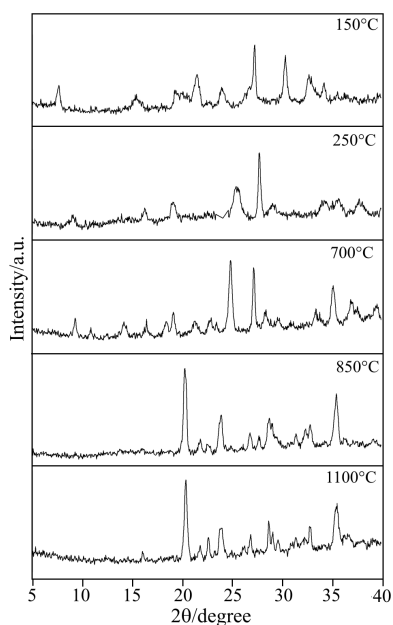
**Fig. 4** XRPD of the γ-ZrPZn at various temperatures

(Fig. 2). When the material is heated at T°>520°C the water loss is not recouped.

In the case of the γ-ZrPZn$_{0.50}$ (Fig. 1) the thermal behavior is similar to that of the fully exchanged material: 1.20H$_2$O is lost between 25–130°C and 0.60H$_2$O between 130–350°C. From 350°C up to 600°C, the loss of the second coordination water overlaps with the water derived from the condensation of the phosphate groups, not involved in the zinc ion-exchange, giving pyrophosphates.

The XRPD pattern of the γ-ZrPZn is similar to that reported in [14]. Unlike the case of SGZrPZn [9], there is a little decrease in *d*, with respect to the precursor γ-ZrP (11.50Å *vs.*12.30Å) (Fig. 3). This diffractogram is maintained up to~150°C. At 250 and 350°C (in correspondence with water losses) a small decrease in *d* is evident (9.82 and 9.61 Å respectively) and the diffractograms are different one from the other. All the XRPD spectra of the material heated from 350 up to 730°C are the same. It can be affirmed that the material maintains a layered structure up to 730°C. From 730 up to 1000°C the XRPD spectra are the same with reflection related to the Zn zirconium double phosphate [15]. At 1100°C, when the salt synthesization is evident, the diffractogram is similar to the previous one (heated from 730 up to 1000°C) but a shift of 1° or 0.5° is shown, between 2ϑ=24/34, as in the case of SGZrPZn [9] (Fig. 4). The material heated from 150 up to 450°C and left in air to rehydrate for two days, shows that X-rays pattern resembles the original one and are similar to that of the material recorded at room temperature (*rt*). The material heated at 520°C, left in air for two days, maintains the diffractogram with amorphization of the first reflection (Fig. 5). Even if the TG-DTA curves show rehydration (see above) the X-ray diffractogram is different showing a greater degree of amorphization and does not change. As regards γ-ZrPZn$_{0.50}$ the diffractogram is very similar to that of the fully exchanged material. Some differences take place in the range 2θ=20–30 and the first reflection appears more intense and crystalline with respect to the fully exchanged form (Fig. 3). At higher temperatures,
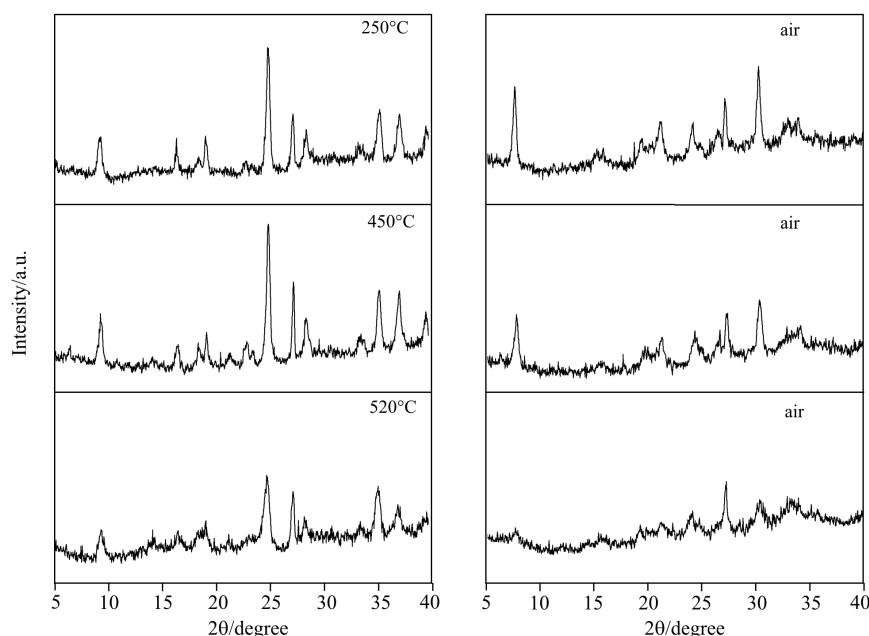
Fig. 5 XRPD of γ-ZrPZn [dehydration (left)–rehydration (right)]

Table 2 C(%) and N(%) of the intercalated compounds γ-ZrPL at the appropriate temperature of mass loss

$T/°C$	γ-ZrP2,2'-bipy		γ-ZrP2,4'-bipy		γ-ZrP4,4'-bipy	
	C	N	C	N	C	N
180	11.24	2.31	9.82	2.33	5.03	1.26
	(0.30)		(0.28)		(0.16)	
400	9.07	1.91	10.55	2.32	5.76	1.24
	(0.23)		(0.27)		(0.14)	
650	3.85	0.89	4.12	0.99	3.34	0.68
	(0.099)		(0.104)		(0.076)	

*dark numbers are diamines content at established temperatures

1100°C, mixed phases of zirconium pyrophosphate and zinc zirconium double phosphate phases are evident (Fig. 6a).

Thermal behavior and XRPD of γ-ZrPLZn

Figure 7 shows the TG-DTA curves of the γ-ZrPLZn materials compared to those of their precursors. Tables 2, 3 show the ligand content at set temperatures for the γ-ZrPL and γ-ZrPLZn materials. From the TG-DTA curves of both the γ-ZrPLZn materials and of those of their precursors, it can be seen that: a) the zinc presence stabilizes the ligand in the host matrix and so the organic combustion occurs at a higher temperature; b) the pyrophosphate formation occurs at a lower temperature; c) the synthesization is evident. The TG-DTA curves of the γ-ZrPL materials show losses related to the hydration water (25–280°C), to

Fig. 6 XRPD at 1100°C of: a. γ-ZrPZn$_{0.50}$ and c. γ-ZrPZn; b. zirconium pyrophosphate for comparison

the ligand combustion and to the water derived from the phosphate condensation (280–600°C). The thermal behavior is similar both in the case of γ-ZrP2,2'-bipy and γ-ZrP2,4'-bipy, whereas in the case of γ-ZrP4,4'-bipy the ligand combustion occurs at a temperature increased by ~50°C. In the case of γ-ZrPLZn the TG-DTA curves of γ-ZrP2,2'-bipyZn and γ-ZrP2,4'-bipyZn show losses related to water (25–280°C). The ligand combustion occurs at ~600°C with a sharp or broad peak respectively. The loss of water due to phosphate condensation is also present. At 820 and 900°C respectively, a very sharp peak due to the last ligand loss and to the pyrophosphate formation is evident. At 1000°C it can be noted the endothermic peak due to the synthesization. In the case of γ-ZrP4,4'-bipyZn the thermal behavior is similar to that of its precursor, the only differences being the sharp peak at 870°C (last ligand combustion and pyrophosphate formation) and the endothermic peak at 1000°C (see above). From the microanalysis values in Table 2 is shown that at 400°C the stability of the materials γ-ZrPL is in the order of γ-ZrP2,4'-bipy>γ-ZrP4,4'-bipy>γ-ZrP2,2'-bipy the loss of ligands being 3.5–12,5–23% respectively. At 650°C the thermal stability is in the order of 4,4'-*bipy*>2,4'-*bipy*=2,2'-bipy the loss of ligands being 46–61–61% respectively. These facts are clearly evident from both the TG and the DTA curves. In Table 3 (microanalyses values and the ligand content of the γ-ZrPLZn at set temperatures) is shown a ligand stability at 400°C for all the γ-ZrPLZn; at 650°C for ZrP2,4'-bipyZn and γ-ZrP4,4'-bipyZn.
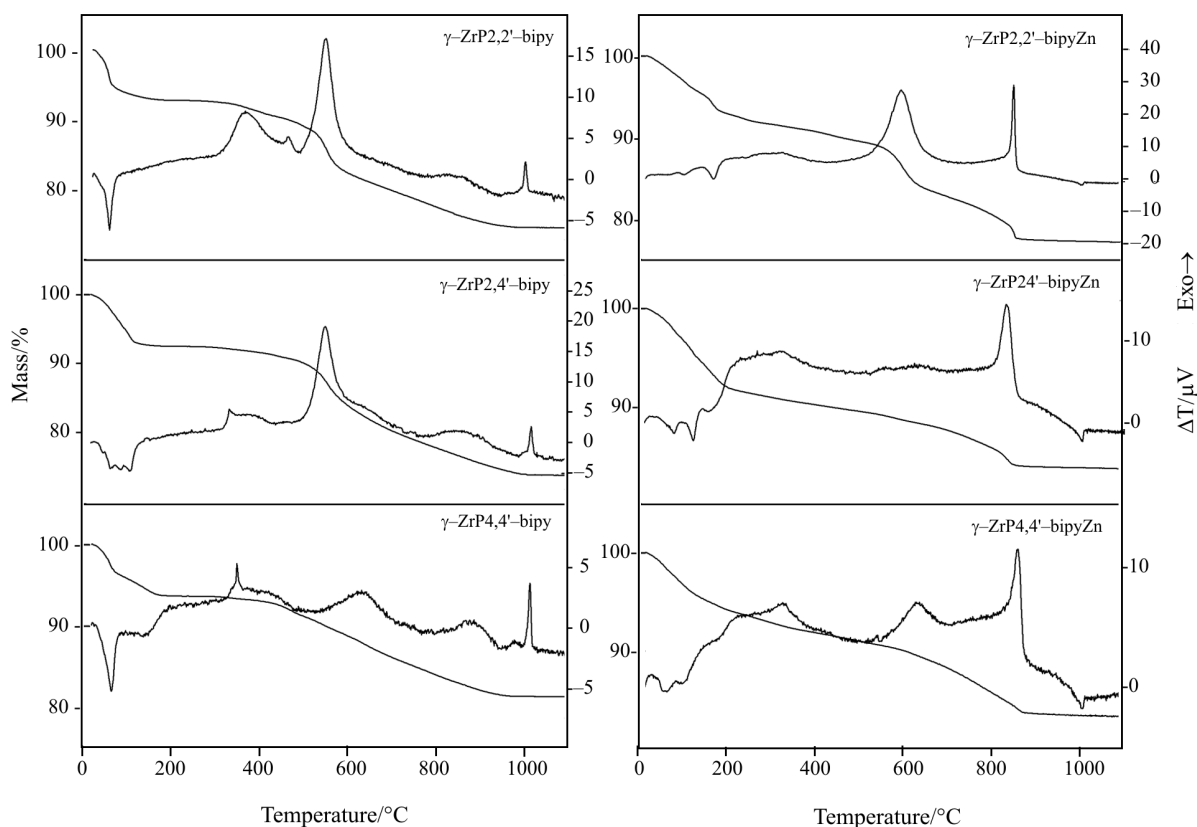
In the XRPD it is evident that in the case of γ-ZrPLZn compounds the *d* increases only for γ-ZrP2,2'-bipyZn (16.24 Å *vs*. 14.25 Å). For all the other materials listed in Table 1 there is no variation of the *d* value (Fig. 8).

Zinc sulfide materials derived by γ-ZrPZn

To obtain the ZnS particles in the γ-ZrP the same procedure was used as in the case of SGZrP [9]. Anhy-
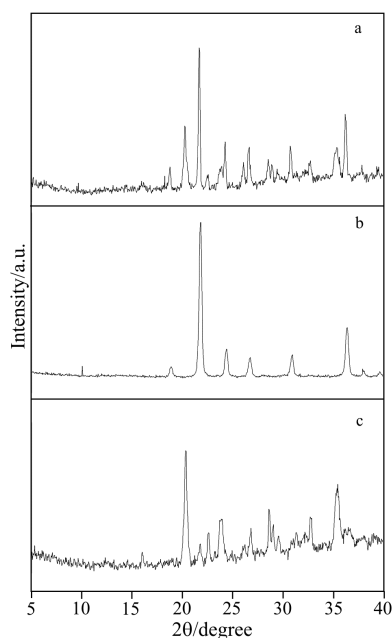
Fig. 7 TG-DTA of γ-ZrPL and γ-ZrPLZn for comparison

Table 3 C(%) and N(%) of the intercalated γ-ZrPLZn compounds at the appropriate temperature of mass loss

T/°C	γ-ZrP2,2'-bipyZn		γ-ZrP2,4'-bipyZn		γ-ZrP4,4'-bipyZn	
	C	N	C	N	C	N
180	9.52	2.09	5.99	1.25	5.56	1.11
	(0.27)		(0.15)		(0.13)	
400	9.25	2.04	5.47	1.08	5.08	1.06
	(0.269)		(0.14)		(0.12)	
650	3.69	0.85	4.87	1.02	4.47	0.93
	(0.09)		(0.12)		(0.11)	

* numbers in brackets are diamines content at established temperatures

drous H_2S was flowed several times (1–30 h), at *rt*, over a sample of 1 mmol of fully anhydrous (420°C) γ-ZrPZn. The best way to obtain a significant number of ZnS particles was to flow the H_2S gas for 30 h. The chemical composition of the white material obtained, after sulfuration, is γ-Zr(ZnS)$_{0.67}$Zn$_{0.33}$(PO$_4$) (H$_{1.48}$PO$_4$)·2.3 H$_2$O, denoted as γ-ZrPZnS (Table 4). An experiment with H_2S was also performed on γ-ZrPZn$_{0.50}$ material calcinated at 400°C: there is not evidence of S^{2-} ions as in the case of SGZnS [9].

Table 4 S(%) and H(%) of the zinc material submitted to the H_2S gas over the time

Material	5h		10h		20h		30h	
	S	H	S	H	S	H	S	H
γ-ZrPZn	0.55	0.88	1.25	1.03	2.63	1.09	6.19	0.69
(anhydrous at 420°C)	(0.05)		(0.13)		(0.25)		(0.67)	

* in brackets numbers are ZnS content over the time

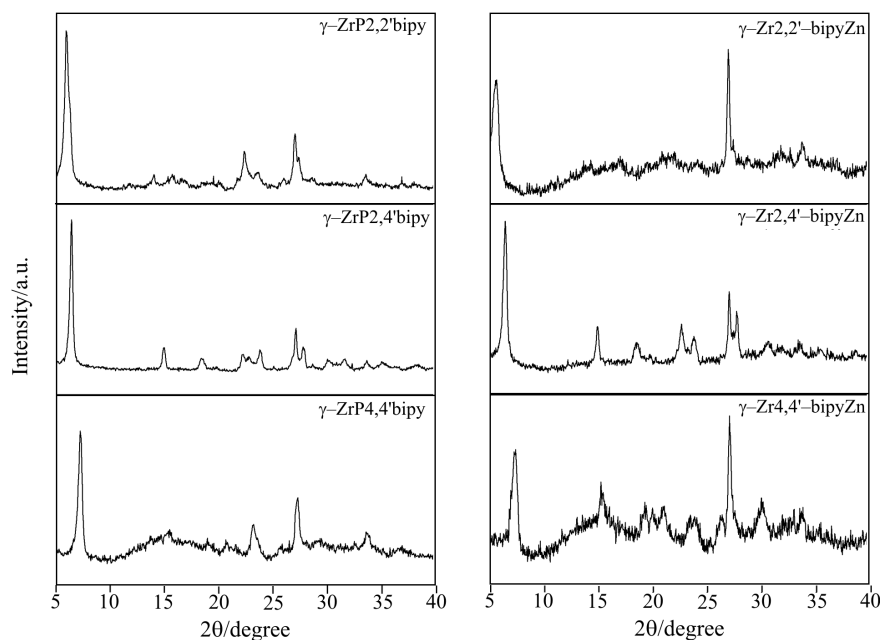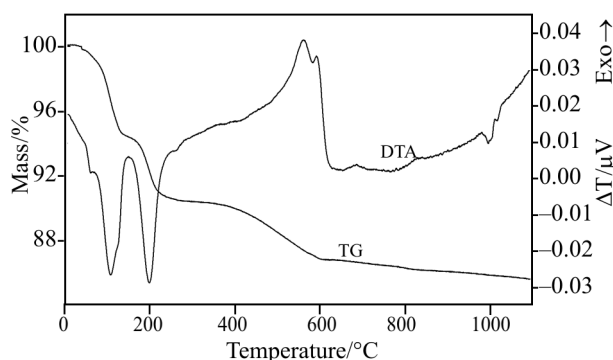**Fig. 8** XRPD of γ-ZrPL and γ-ZrPLZn for comparison

Fig. 9 TG-DTA of γ-ZrPZnS

Fig. 10 XRPD of γ-ZrP; γ-ZrPZnS; ZnS (from Aldrich) and γ-ZrPZn for comparison

Thermal behavior and XRPD of γ-ZrPZnS

The γ-ZrPZnS material submitted to thermal treatment with the TG-DTA simultaneous apparatus (Fig. 9) shows that in the TG curve water loss is evident between 25–350°C. A big loss occurs between 350–700°C due to the S^{2-} elimination. In the DTA curve, in accordance with the TG curve, endothermic peaks related to water loss and a couple of exothermic peak for the S^{2-} elimination at 575 and 600°C, are present. At 1100°C an endothermic sharp peak, without mass loss, indicates synthetization. Figure 10 shows the XRPD of the γ-ZrPZnS material compared with those of the host matrix γ-ZrP, the fully exchanged form γ-ZrPZn and ZnS (from Aldrich). The γ-ZrPZnS diffractogram shows a layered structure similar to that of the precursor γ-ZrP and reflections
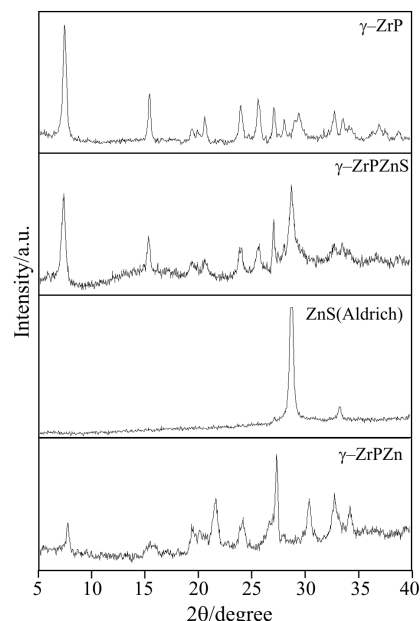
(2θ=27–28.70–33.10) related to the ZnS [16] or to the ZnS compound from Aldrich. As in the case of CdS particles inserted in SG zirconium phosphate and γ-ZrP [6, 7] and as in the case of ZnS particles inserted in SG zirconium phosphate [9], the ZnS formation is due to the ion-exchange between the H^+ of the H_2S gas and Zn^{2+} of the host matrix. The Zn^{2+} combine with the S^{2-} ions to form ZnS particles.

Conclusions

Zinc ions can be fully and half exchanged in γ-ZrP and in γ-ZrPL isomeric diamines. The uptake speed of the Zn^{2+} in γ-ZrPL and its content depends on the more or less favorable –N– position in the diamine molecule. γ-ZrP zinc material that underwent thermal treatment show a water loss up to 520°C. After dehydration they can be rehydrated. The γ-ZrPLZn materials show both water loss and ligand combustion whose temperature increases in the presence of zinc ions. The XRPD patterns of γ-ZrPZn show very little decrease in *d* with respect to its precursor. In the case of γ-ZrPLZn *d* increases only in the case of γ-ZrP2,2'-bipyZn. When H_2S is flowed over anhydrous γ-ZrPZn, S^{2-} combine with Zn^{2+} to form ZnS particles in the layers of the host matrix. The diffractogram of the γ-ZrPZnS shows a layered structure almost the same as its precursor γ-ZrP and there is evidence of the presence of ZnS particles, whereas the half exchanged form does not 'accept' the S^{2-}. The γ-ZrPZnS material submitted to thermal treatment shows the S^{2-} elimination with a couple of exothermic peaks in the DTA curve.

References

1 C. Ferragina, M. A. Massucci, A. A. G. Tomlinson, P. Patrono, A. La Ginestra and P. Cafarelli, Pillared Layered Structures, Ed. I. V. Mitchell, Elsevier Applied Science, London and New York 1990, 127.

2 C. Ferragina, R. Di Rocco, P. Giannoccaro and L. Petrilli, J. Therm. Anal. Cal., 76 (2004) 871.

3 J. Votinsky, J. Kalousova and L. Benes, J. Incl. Phen., 14 (1992) 19.

4 T. Cassagneau, G. B. Hix, D. J. Jones, P. Maireles-Torres, M. Rhomar and J. Roziere, J. Mat. Chem., 4 (1994) 189.

5 P. Olivera-Pastor, P. Maireles-Torres, E. Rodriguez-Castellon and A. Jmenez-Lopez, Chem. Mat., 8 (1996) 1758.

6 C. Ferragina and R. Di Rocco, Mat. Res.Bull., 34 (1999) 1981.

7 C. Ferragina, P. Cafarelli and R. Di Rocco, Thermochim. Acta, 363 (2000) 81.

8 C. Ferragina, P. Cafarelli and R. Di Rocco, J. Therm. Anal. Cal., 63 (2001) 709.

9 C. Ferragina, R. Di Rocco and L. Petrilli, Thermochim. Acta, 409 (2004) 177.

10 T. Bein, Supramolecular Architecture, Ed. American Chemical Society, Ch. 20, 1992, p. 274.

11 S. Yamanaka and M. Tanaka, J. Inorg. Nucl. Chem., 41 (1979) 45.

12 C. Ferragina, P. Cafarelli, A. De Stefanis and G. Mattei, Mat. Res. Bull., 34 (1999) 1039.

13 G. Alberti, U. Costantino and E. Torracca, J. Inorg. Nucl. Chem., 28 (1966) 225.

14 A. Clearfield and J. M. Kalnins, J. Inorg. Nucl. Chem., 40 (1978) 1933.

15 C. Bettinali, A. La Ginestra and M. Valigi, Atti Accad. Naz. Lincei, Sez. VIII, Ch. 88, 1962, p. 472.

16 Powder Diffraction File, JCPDS, in L.G. Berry (Ed.), File 36–1450, Philadelphia 1974.