Thermal Behaviour of Germanium Bis(monohydrogenphosphate) Monohydrate and Characterization of derived Germanium Pyrophosphates

Aldo La Ginestra,* Paola Galli, and Maria L. Berardelli
Istituto di Chimica Generale ed Inorganica dell'Università di Roma, Rome, Italy
Maria A. Massucci
Istituto di Metodologie Avanzate Inorganiche del C.N.R., Area della Ricerca di Roma, C.P. 10 Monterotondo Scalo, Rome, Italy

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The preparation of crystalline layered $Ge(HPO_4)_2 \cdot H_2O$ is described and its thermal behaviour, with the phase changes observed between room temperature and 1 300 °C, reported. Three GeP_2O_7 phases can be characterized depending on temperature and heating rates. At lower temperatures (600—800 °C) a layered phase is obtained, and this then gives a monoclinic (slow heating rate) or cubic (fast heating rate) phase in the range 900—1 050 °C. The monoclinic and cubic phases then slightly decompose above 1 000 °C to give materials having P : Ge < 2 : 1. Above 1 050 °C a more drastic decomposition occurs with evolution of P_2O_5 and GeO_2. A comparison with the thermal behaviour of isostructural titanium and zirconium compounds is given.

The acid phosphates of tetravalent metals can be prepared either as amorphous or crystalline compounds.[1,2] They are mainly known as ion-exchangers with a generally high ion-exchange capacity and high resistance towards elevated temperatures and ionizing radiations. Many of the crystalline materials have a layered structure and among these the most studied is the α-zirconium acid phosphate, α-$Zr(HPO_4)_2 \cdot H_2O$.[1,2]

Recently attention has turned to possible uses of these materials in catalysis. Most papers are devoted to the catalytic properties of zirconium phosphate,[3] whereas the other compounds of the class have been almost completely neglected.

Given our interest in the catalytic field we describe some more unusual materials which may have interesting catalytic properties. This paper deals with germanium bis(monohydrogenphosphate), $Ge(HPO_4)_2 \cdot H_2O$, ' germanium acid phosphate ' the least known and studied compound of the class.

Previous studies on the preparation of germanium acid phosphate have been made by Everest,[4] Lelong,[5] and Winkler and Thilo.[6] In ref. 5 are reported thermogravimetric (t.g.) data and the *X*-ray powder spectra of $Ge(HPO_4)_2 \cdot H_2O$ and of two pyrophosphates, but the data seem to indicate that the materials are not pure compounds. Winkler and Thilo [6] obtained a germanium acid phosphate with a poor degree of crystallinity, nevertheless they were able to say that the compound is isostructural with the crystalline silicon, lead, zirconium, titanium, and tin analogues that they also prepared.

Avduevskaya and Tananaev [7,8] studied the reaction of GeO_2 with H_3PO_4 and found the conditions in which $Ge(HPO_4)_2 \cdot H_2O$ can be prepared. They produced *X*-ray patterns of the phases obtained at different temperatures corresponding to hydrated and anhydrous acid phosphates and to pyrophosphates. Their results depended on the P : Ge ratio of the samples, but generally, they are not clearly understandable, so we think that the compounds they dealt with do not correspond to pure phases.

In this paper we describe the best conditions for obtaining $Ge(HPO_4)_2 \cdot H_2O$ as a pure crystalline compound. A thermal study is made in order to settle the temperature ranges in which dehydration, condensation, and phase transitions take place in this material. Similarities and differences in the thermal behaviour of germanium, zirconium, and titanium acid phosphates are discussed.

Experimental

Chemicals.—All reagents were Merck ' pro analysi ' products.

Analytical Procedures.—The P : Ge ratio of crystalline germanium phosphate was determined as follows. The material (100 mg) was dissolved in weakly alkaline distilled water (25 cm^3).

Phosphate was determined as described in ref. 9 by measuring at 430 nm the absorbance of solutions obtained by adding to the unknown (2 cm^3) a solution containing ammonium heptamolybdate-acetone-sulphuric acid in the appropriate ratio,[9] up to 50 cm^3. Germanium does not interfere.

Germanium was determined as in ref. 10 by measuring at 440 nm the absorbance of solutions obtained by adding to the germanium solutions a solution containing 2.5% of ammonium heptamolybdate and glacial acetic acid as stabilizer. Since in these cases phosphate ions interfere positively with germanium, the addition method was used. Known amounts of germanium were added to fixed volumes of unknown and the measurements were made against a previously determined reference solution containing the same amount of phosphate as present in the unknown.

The water content of germanium acid phosphate was determined from the weight losses during heating up to 900 °C.

Germanium acid phosphate dried over P_4O_{10} and its derivatives obtained by heating at various temperatures [as defined by t.g. and d.t.a. (differential thermal analysis) curves] were subjected to *X*-ray diffraction analysis in order to follow the structural changes in the material.

Apparatus.—Phosphate and germanium determinations were made with a photoelectron model DL spectrophotometer.

T.g. and d.t.a. measurements were carried out on a Stanton model STA 781 simultaneous thermoanalyser, with a heating rate of 5 °C min^{-1}, Pt/Pt-Rh (87 : 13) thermocouples, and platinum crucibles.

X-Ray powder diffraction patterns were taken on a Philips

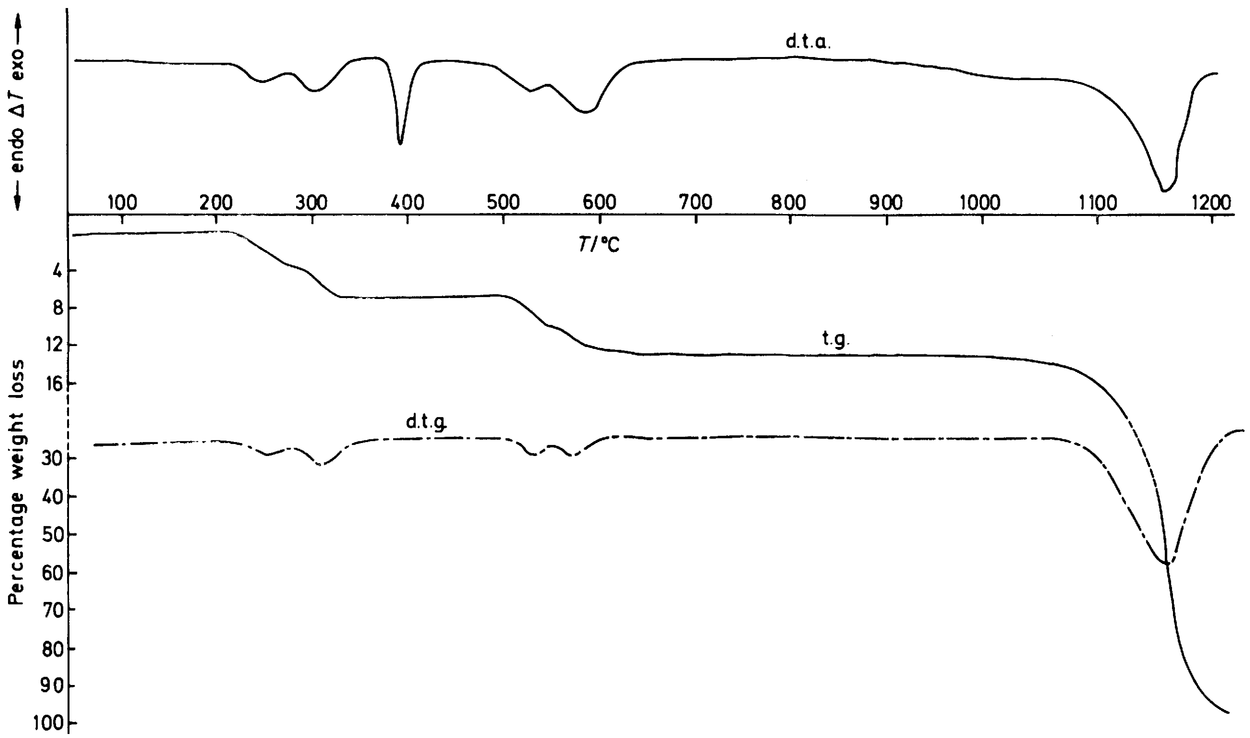


Figure 1. D.t.a., t.g., and d.t.g. curves of $Ge(HPO_4)_2{\cdot}H_2O$

Table 1. X-Ray powder spectra recorded at room temperature (25 °C) after different thermal treatments

$Ge(HPO_4)_2{\cdot}H_2O$ [a]		$Ge(HPO_4)_2$ [b]		Layered GeP_2O_7 [c]		Monoclinic GeP_2O_7 [d]		Cubic GeP_2O_7 [e]		
d/Å	i [f]	d/Å	i [f]	d/Å	i [f]	d/Å	i [f]	d/Å	i [f]	hkl
7.75	vs	7.49	vs	6.10	s	8.75	w	4.38	mw	111
4.08	mw	4.13	w	3.77	m	7.69	w	3.79	s	200
3.89	w	3.83	vw	3.03	w	6.46	w	3.39	m	210
3.40	ms	3.48	mw	2.73	w	5.06	s	3.10	mw	211
3.36	s	3.37	vw	2.40	mw	4.87	s	2.68	w	220
3.13	vw	2.64	vvw			3.95	vw	2.29	mw	113
2.59	ms	2.47	mw			3.69	w			
2.39	m	2.38	w			3.29	w			
2.29	vw					3.02	w			
2.04	w					2.96	w			
1.95	vw					2.91	ms			
1.88	m					2.82	m			
1.87	w					2.43	mw			
						1.96	mw			

[a] Dried over P_4O_{10}. [b] After heating at 300 °C. [c] After heating at 600—800 °C for 3 h. [d] After slow heating at 1 000 °C for 3 h. [e] After rapid heating at 1 100 °C for 3 h. [f] Relative intensity.

PW1130 diffractometer, using Ni-filtered Cu-K_α radiation. X-Ray diffractograms at high temperature were obtained with an Italstructures model AF3 attachment.

Results and Discussion

Preparation and Composition of Crystalline Germanium Phosphate.—Concentrated phosphoric acid (85% by weight) was added to a solution obtained by diluting $GeCl_4$ in distilled water (10 cm^3 of $GeCl_4$, d = 1.88 g cm^{-3}, in 170 cm^3 of H_2O). H_3PO_4 was added until the molar ratio PO_4 : Ge was 10 : 1.

After refluxing for 9 h, the precipitate was filtered off, washed rapidly with pure ethanol and diethyl ether until PO_4^{3-} and Cl^- were absent, and dried to constant weight over P_4O_{10}. A white crystalline powder was obtained.

The chemical analysis of the compound gave a P : Ge ratio of 2 : 1. The t.g. curve (see below, and Figure 1) shows two weight losses, in the ranges 200—320 and 450—700 °C. Given that the P : Ge ratio remains constant at 800 °C the total weight loss (12.8% in two equal steps of 6.4%) can be related to the elimination of water. From these data, the compound can be represented by the empirical formula $GeO_2{\cdot}P_2O_5{\cdot}2H_2O$ and taking into account the different temperatures at which the two moles of water are lost, the chemical formula is $Ge(HPO_4)_2{\cdot}H_2O$.

The X-ray diffraction pattern of this compound (the corresponding d values are reported in Table 1) is similar to those

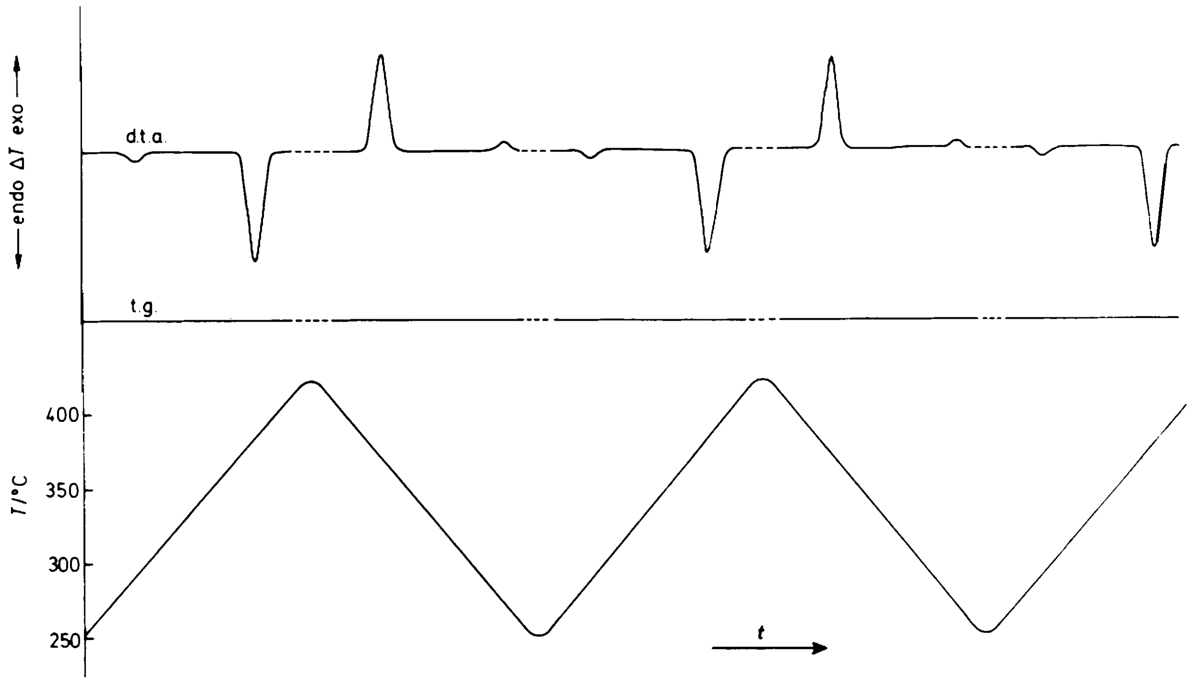


Figure 2. Cyclic thermal curves of germanium bis(monohydrogenphosphate) previously dehydrated at 300 °C

of α-$Ti(HPO_4)_2 \cdot H_2O$ and α-$Zr(HPO_4)_2 \cdot H_2O$, the layered crystalline ion-exchangers obtained either by direct precipitation,[11,12] or by refluxing the amorphous compounds in H_3PO_4 for a very long time (4—20 d).[13,14] In addition, the three materials have their first reflection, which is also the most intense, at low angles and the corresponding *d* values are very close to one another, being 7.75, 7.55, and 7.56 Å for our material, the α-titanium, and α-zirconium acid phosphates, respectively.

These considerations lead us to agree with Winkler and Thilo [6] that $Ge(HPO_4)_2 \cdot H_2O$ is isostructural with α-$Ti(HPO_4)_2 \cdot H_2O$ and α-$Zr(HPO_4)_2 \cdot H_2O$.

Thermal Behaviour.—In Figure 1 are reported the t.g., d.t.g. (derivative t.g.), and d.t.a. curves for crystalline $Ge(HPO_4)_2 \cdot H_2O$.

The dehydration process begins above 200 °C and goes to completion at *ca.* 320 °C. It seems to occur in two steps since two endothermal effects are observed in this range of temperature. The weight loss is 6.4% and corresponds to 1 mole of water per formula weight.

At 370 °C the presence of an endothermic reaction with no corresponding weight loss suggests that a reversible phase transition occurs since an exothermic reaction is observed in the cooling curve of the sample heated up to 420 °C (Figure 2). Cyclic heat-cool experiments between 250 and 420 °C show that the anhydrous phase undergoes two reversible phase transitions, a stronger one occurring at 370—375 °C and a weaker one at 280 °C; during the dehydration process the latter is masked.

Between 450 and 700 °C the anhydrous acid phosphate undergoes a weight loss of 6.4% corresponding to 1 mole of water per formula weight. This weight loss is related to the condensation process of the anhydrous phase to germanium pyrophosphate, GeP_2O_7, a process which is also observed in these temperature ranges for anhydrous Ti or Zr acid phosphates. The process occurs in two steps, this being another similarity already encountered in the above mentioned layered acid phosphates.[15]

Table 2. *X*-Ray powder spectra recorded with a high-temperature camera

$Ge(HPO_4)_2$ at 250 °C		$Ge(HPO_4)_2$ at 320 °C		$Ge(HPO_4)_2$ at 420 °C	
d/Å	*i*	*d*/Å	*i*	*d*/Å	*i*
7.49	vs	7.43	vs	7.34	vs
4.12	vw	4.09	vw	4.11	w
3.36	vw	3.36	w	3.32	mw
2.56	vw	2.56	vw	3.02	vw
2.40	vw	2.41	vw	2.50	vw
				2.41	vw

Above 950 °C a slow weight loss ascribable to a slight decomposition of the germanium pyrophosphate is observed. Given the low weight loss, no definite and clear reactions are recorded in d.t.a. curves in the range 950—1 030 °C.

Between 1 050 and 1 200 °C, together with a marked endothermic reaction, a drastic weight loss takes place which corresponds to more than 60% of the initial weight. Practically the compound is almost completely volatilized.

The *X*-ray powder spectra of samples heated in connection with the different endothermic effects have been recorded either after cooling at room temperature (Table 1) or, when reversible phase transitions occur, with a high-temperature camera (Table 2).

The interlayer distance of the monohydrate compound, initially 7.75 Å, goes to 7.43 Å at 320 °C after the complete dehydration and to 7.34 Å after the phase transition at 370—400 °C.

At 400—450 °C a new reflection begins to grow in at 6.10 Å near that at 7.34 Å. On continuing the heating at this temperature, the peak at 6.10 Å increases in intensity with a corresponding decrease of the peak at 7.34 Å.

The slow formation of the new phase with interlayer distance of 6.10 Å is due to the fact that the temperatures of the anhydrous phase transition and of the beginning of the condens-

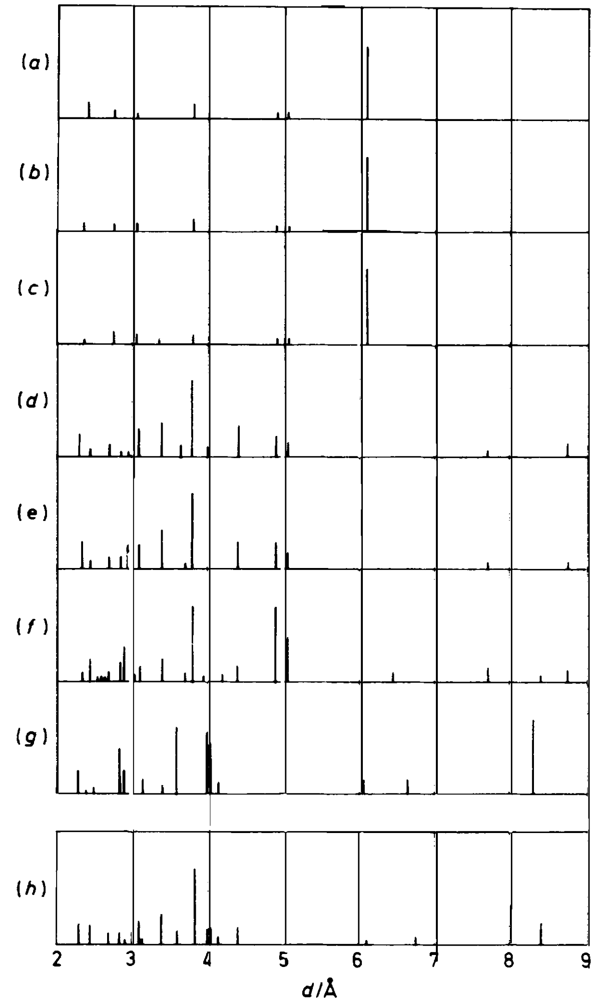


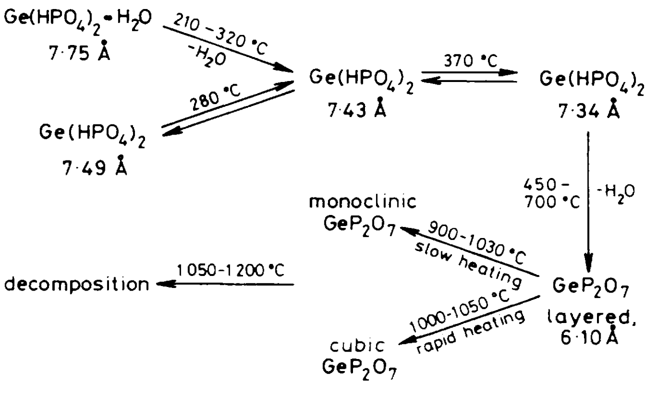
Figure 3. X-Ray powder spectra of GeP_2O_7 phases obtained by gradually heating $Ge(HPO_4)_2$ in different operational conditions: (*a*) 600 °C, 3 h; (*b*) 850 °C, 3 h; (*c*) 950 °C, 2 h; (*d*) 950 °C, 4 h; (*e*) 1 000 °C, 3 h; (*f*) 1 000 °C, 5 h; (*g*) 1 100 °C, 5 h. Spectrum (*h*), obtained by rapidly heating $Ge(HPO_4)_2$ directly (1 100 °C, 5 h), may be taken as a reference spectrum of cubic GeP_2O_7

ation process are very similar, so that it is difficult to separate the two reactions. This also explains the slight but continuous decrease of the intensity of the phase-transition reaction, observed in the cyclic experiments, since less and less of the phase with $d = 7.34$ Å is present.

At 700 °C only the phase with 6.10 Å as first reflection is observed. We consider it a layered germanium pyrophosphate by analogy with the layered Ti and Zr pyrophosphates obtained by heating crystalline α-Ti and α-Zr acid phosphate at about the same temperature.[15] The *d* values of this phase are listed in Table 1.

By heating at 900—950 °C for a few hours, the phase with $d = 6.10$ Å slowly disappears while there is an increase of non-layered GeP_2O_7 phases: a monoclinic phase, with the major reflections at 5.06 and at 4.87 Å when the sample is gradually heated at 900—1 030 °C, and a cubic one, with the most intense reflection at 3.79 Å, which forms by heating more rapidly at 1 000—1 050 °C. Samples heated at 1 050 °C for 3 h show that the cubic GeP_2O_7 is the prevalent phase obtained.

Generally, the monoclinic and cubic phases are both present in greater or lesser amount depending on the temperature reached, on the heating rate, and the thermal treatment time.



Scheme.

Above 1 050 °C, together with the reflections of cubic and monoclinic GeP_2O_7, other weak reflections are also evident that became stronger while the GeP_2O_7 reflections weaken, as the heating is prolonged.

As mentioned before, at these temperatures GeP_2O_7 begins to slowly decompose with the partial loss of P_2O_5, giving rise to phases with $P_2O_5 : GeO_2 < 1 : 1$ as deduced from the X-ray patterns; these phases have already been reported.[8]

In Figure 3 is reported the evolution of the X-ray powder spectra, taken at room temperature, of the samples heated between 600 and 1 100 °C for different times. It is evident that the layered pyrophosphate phase (6.10 Å) is stable until 850—900 °C, and only by prolonging the heating above 900 °C do the cubic and monoclinic GeP_2O_7 reflections slowly appear.

This slow phase transition explains why the d.t.a. curves do not show the exothermic reactions between 900 and 1 000 °C which are the case for α-TiP_2O_7.[15]

The indexing of the X-ray powder pattern of the phase, which we will call α-GeP_2O_7, confirmed that the cell was cubic with $a = 7.59$ Å. In Table 1 are given the *d* values of cubic α-GeP_2O_7, not reported previously. The sequence of the values is such that the phase is indeed isostructural with α-TiP_2O_7 and α-ZrP_2O_7, thus confirming what Levi and Peyronel [16] had only supposed but not tested for germanium pyrophosphate.

Our results disagree with those of Lelong [5] who mentioned the existence of three GeP_2O_7 phases: the first pseudo-hexagonal, the second monoclinic, obtainable at about 700—1 000 °C, and the third, stable at 1 300 °C. He reported the *d* values only for the first two phases and these markedly differ from those of the phases obtained when $Ge(HPO_4)_2 \cdot H_2O$ is heated at the same temperatures. The spectra given by Lelong are more composite, indicating that probably those materials did not correspond to pure phases.

As concerns the cubic GeP_2O_7 phase mentioned in ref. 5, whose *d* values are not given, we find it very strange that this phase was found to be stable at 1 300 °C, when at 1 200 °C GeP_2O_7 almost completely volatilizes.

Conclusions

$Ge(HPO_4)_2 \cdot H_2O$ can be prepared in crystalline form by refluxing the precipitate obtained from $GeCl_4$ and H_3PO_4 in the appropriate molar ratio 1 : 10. The compound is very hydrolizable in water, but insoluble in ethanol.

The thermal behaviour shows many similarities with the corresponding α-Ti and α-Zr acid phosphates: the dehydration temperature range is higher than for α-Ti and α-Zr phases (200, 170, and 130 °C respectively), as also is the reversible anhydrous phase transition (370 °C for Ge, 260 °C for Ti, 200—220 °C for Zr acid phosphate). This trend may be connected with the decreasing electronegativity on going from Ge to Zr.

The overall thermal behaviour may be summarized as shown in the Scheme.

Acknowledgements

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