

## **HYDROTHERMAL TREATMENT OF Zr, Ti, Sn AND Ge HYDROGENPHOSPHATES**

### **Characterization of the derived compounds by thermal methods**

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The Zr, Ti, Sn and Ge hydrogenphosphates, generally prepared in a crystalline form by the refluxing method, have been submitted to hydrothermal treatment at 180° and 300°C in order to observe if the preparation time can be shortened maintaining their chemical composition and their  $\alpha$ -structure. Simultaneous TG and DTA together with XRD revealed to be very suitable techniques for the characterization of the obtained products.

Zr phosphate is the most stable and gives in all conditions the  $\alpha$ -monohydrated hydrogenphosphate phase. Similar behaviour for the Ti phosphate at 180°C, while at 300°C the compound transforms into  $\gamma$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O. Sn phosphate, even on maintaining its  $\alpha$ -structure, gives rise to more and more dehydrated phases on the increasing of the temperature of the HT and the concentration of the used phosphoric acid.

Ge hydrogenphosphate resulted the least stable under hydrothermal conditions, since even at 180°C it gives rise to GeOHPO<sub>4</sub>. Because of the easy hydrolyzability of Ge, the hydrothermal method is not a way to prepare the crystalline  $\alpha$ -germanium hydrogenphosphate.

**Keywords:** Zr, Ti, Sn, Ge hydrogenphosphates, hydrothermal treatment

### **Introduction**

The crystalline layered inorganic ion-exchangers with formula  $M^{IV}(HPO_4)_2 \cdot H_2O$ , are not only employed for their properties as ion-exchangers or intercalating compounds, but also as starting materials for the preparation of several catalysts to be employed in acid-catalyzed or oxidation reactions. They are generally obtained by refluxing the amorphous materials in H<sub>3</sub>PO<sub>4</sub>. The method, that usually leads to the compounds with  $\alpha$ -structure [1], gives rise to solids with a rather low degree of crystallinity even after a long refluxing time.

This is specially the case of tin or titanium acid phosphates. Since we have observed that the hydrothermal treatment gives materials with an improved crystallinity in a shorter time, we have undertaken a systematic investigation on the  $\alpha$ -monohydrogenphosphates of tetravalent Zr, Ti, Sn and Ge (abbreviated as ZrP, TiP, SnP and GeP) in order to observe which of them maintain or change either the chemical composition or the crystalline structure as a consequence of the hydrothermal treatment. Such information, besides the chemical methods of analysis, has been obtained with simultaneous TG-DTA together with XR diffraction techniques, which revealed to be of extreme utility for the rapidity and relevance of their performance.

## Experimental

The preparation of the crystalline compounds by the refluxing method is performed by boiling the amorphous material in phosphoric acid 10 or 8 M for 100 h [1–4].

The hydrothermal syntheses were carried out by introducing 5 g of amorphous or even refluxed compound in a glass tube with H<sub>3</sub>PO<sub>4</sub> 5 M or 10 M up to 2/3 of the volume. The sealed tube was heated at 180° or 300°C only for 6 or at a maximum of 24 h.

The thermal behaviour of the different compounds was followed with a Stanton Model 801 simultaneous DTA-TG thermoanalyzer (Pt crucible, Pt-Pt/Rh thermocouples, heating rate 5 deg·min<sup>-1</sup>).

The structural modifications caused in the various materials by thermal treatments were checked by taking the X-ray powder patterns on a Philips diffractometer.

The chemical analysis was performed by spectrophotometric methods in the case of phosphorous [5] and germanium [6]; given the strong interference of the presence of the phosphate ions in the germanium determination a previous elimination of the phosphates by means anionic resins was necessary. Tin was determined by A. A. spectrophotometry on a Varian Techtron 100 D Model. Zirconium and titanium were determined gravimetrically after precipitation with cupferron.

## Results

In Figs 1 and 2 the TG and DTA curves are reported obtained for Zr and Ti phosphates prepared with the hydrothermal method. The TG and DTA curves referring to the corresponding compounds prepared by the refluxing procedure are also given.

It is clear from Fig. 1 that for Zr phosphate the hydrothermal treatments (HT) at 180° or 300°C either with H<sub>3</sub>PO<sub>4</sub> 10 M or 5 M do not give rise to significant

modifications in the curves, except the dehydration kinetics that depend on the degree of crystallinity [7, 8]. For as concerns the chemical composition, it remains  $Zr(HPO_4)_2 \cdot H_2O$ , and the X-ray patterns show that the  $\alpha$ -structure of the material is completely retained.

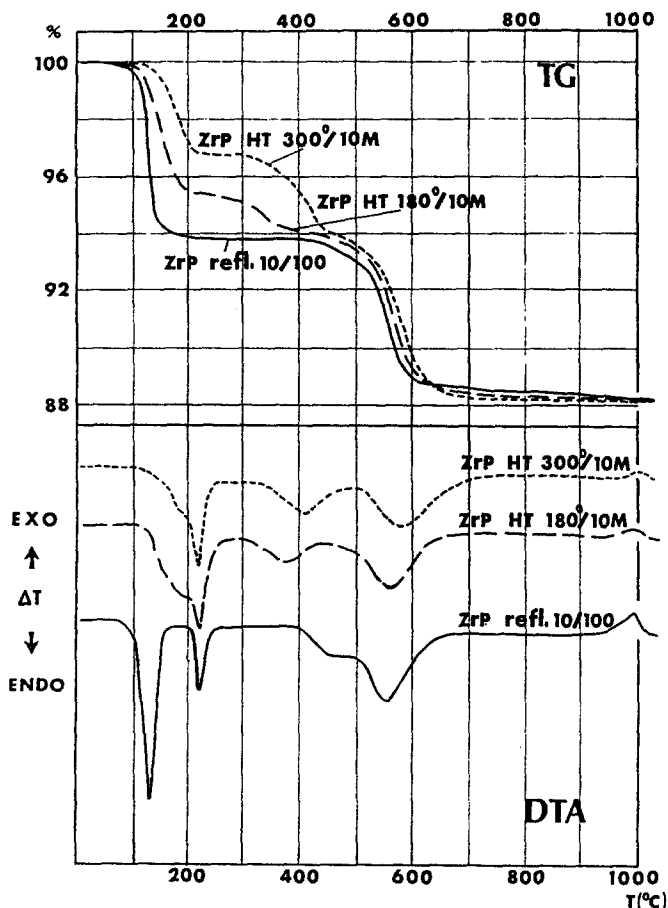


Fig. 1 Simultaneous TG and DTA curves of Zr hydrogenphosphate prepared by refluxing [1] or hydrothermal treatments (HT) at 180° or 300°C in  $H_3PO_4$  5 or 10 M

In the case of Ti phosphate, the HT at 180°C gives, as for Zr phosphate, the monohydrated  $\alpha$ -form  $Ti(HPO_4)_2 \cdot H_2O$ . The slow diminution of the dehydration kinetics suggests an increase of the crystal order or the degree of crystallinity, as it is clearly indicated by the increase of the peaks intensity in the X-ray diffraction patterns of the solid.

When the treatment is performed at 300°C either with  $H_3PO_4$  5 or 10 M a new layered ion-exchanger is obtained having the 'gamma' structure [9], and the

chemical composition corresponds to the formula  $\text{Ti}(\text{HPO}_4)_2 \cdot 2\text{H}_2\text{O}$ . The inter-layer distance of this new phase is 11.6 Å, larger than that of 7.6 Å characteristic of both Zr and Ti monohydrated  $\alpha$ -phases.

The DTA curves can reveal the presence of reversible anhydrous phase transitions: this occurs at 200°C in the case of  $\alpha$ -Zr phosphate phase, at 280°–300°C for  $\alpha$ -Ti phosphate.

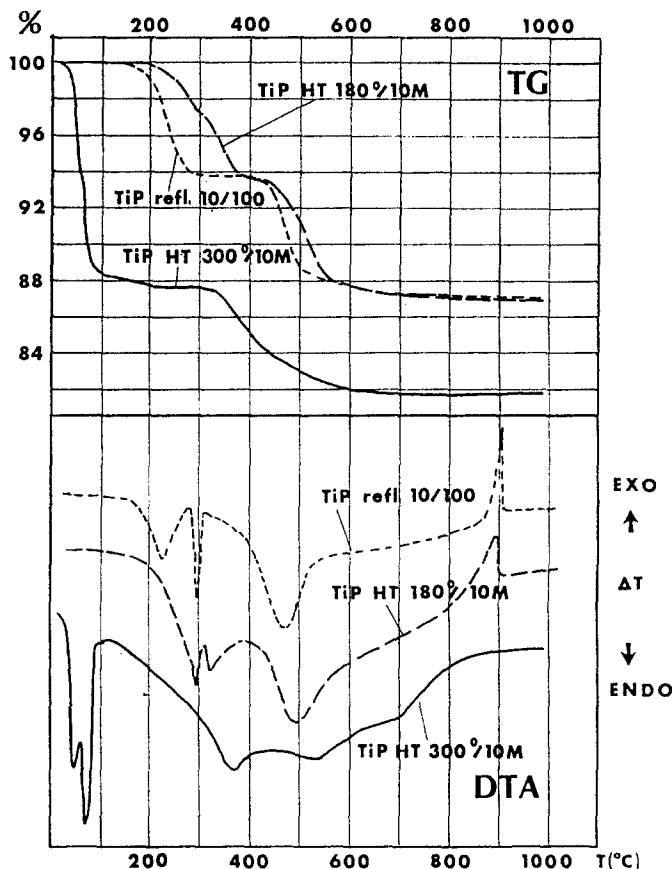


Fig 2 Simultaneous TG and DTA curves of Ti hydrogenphosphate prepared by refluxing [1] or hydrothermal treatments (HT) at 180° or 300°C in  $\text{H}_3\text{PO}_4$  5 or 10 M

Around 850°–900°C the observed exothermic peaks are due to the crystallization of the cubic  $\alpha$ - $\text{TiP}_2\text{O}_7$ . In the case of  $\alpha$ -ZrP the crystallization of  $\alpha$ - $\text{ZrP}_2\text{O}_7$  is delayed at higher temperatures the higher the degree of crystallinity of the products.

Table 1 shows the X-ray diffraction patterns of the phases of Zr and Ti hydrogenphosphates phases obtained by HT at 180° and 300°C. In the Table the XRD of the phases obtained with the classical refluxing procedure are also given.

**Table 1** X-ray diffraction patterns of different zirconium and titanium hydrogenphosphates prepared by refluxing [1] or hydrothermal treatment (HT) at 180°C or 300°C in H<sub>3</sub>PO<sub>4</sub> 5 or 10 M

Zr(HPO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O						Ti(HPO <sub>4</sub> ) <sub>2</sub>					
refl.		180°C		300°C		refl.		H <sub>2</sub> O		2H <sub>2</sub> O	
<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>
7.57	m	7.57	s	7.56	vs	7.56	s	7.56	vs	11.60	vs
										5.75	vvw
										5.56	vvw
4.50	mw	4.49	mw	4.49	mw	4.25	m	4.25	vw	4.29	w
4.44	w	4.45	w	4.45	w	4.05	w	4.03	vvw		
3.57	vs	3.57	s	3.56	s	3.45	vs	3.44	s	3.86	w
3.53	m	3.53	m	3.53	m			3.41	m	3.66	vvw
										3.46	mw
										3.29	
											vvw
2.65	mw	2.64	w	2.64	w	3.15	vw			3.16	vw
						2.61	w	2.60	vw	3.02	w
										2.77	w
										2.55	vw
2.41	w	2.40	vw	2.40	vw	2.49	s	2.49	w	2.44	vvw
								2.37	vw	2.31	w
2.04	w	2.04	vvw	2.04	vvw	2.24	w	2.24	vw		

Figure 3 presents the DTA and TG curves of the different Sn phosphates and Table 2 shows the *d* values and the relative intensities obtained from their X-ray diffraction patterns. Notwithstanding some small differences we believe that the  $\alpha$  structure is retained for all the tin-phosphate HT preparations.

The hydrothermal treatment of Sn phosphate at 180°C gives rise to a material slightly dehydrated and with an increased crystallinity with respect to the refluxed compound. The treatment at 300°C leads to highly crystalline, almost dehydrated tin-monohydrogenphosphates (Fig. 3).

The elimination of the zeolitic water below 200°C for the samples prepared by refluxing or by HT below 200°C, and generally corresponds to 1–1.2 moles of water per formula weight. The process takes place between 200° and 300°C for the samples prepared by HT at 300°C. For this last compounds the amount of zeolitic water is much less, corresponding to 0.15–0.5 moles of water per formula weight according to whether the concentration of H<sub>3</sub>PO<sub>4</sub> is 10 or 5 M respectively.

The peculiarity of all the SnP samples prepared by HT at 300°C is the presence of a reversible phase transition occurring at 360°C, never observed before in crystalline tin phosphates prepared with the refluxing method. It must be mentioned that all the other crystalline  $\alpha$ -Me(IV) hydrogen-phosphates, isostructural with  $\alpha$ -tin phosphate, show an analogous reversible phase transition

in the range 200°–380°C, the higher the temperature is the greater is the electro-negativity of the tetravalent element ( $Zr < Ti < Ge = Sn$  [10]).

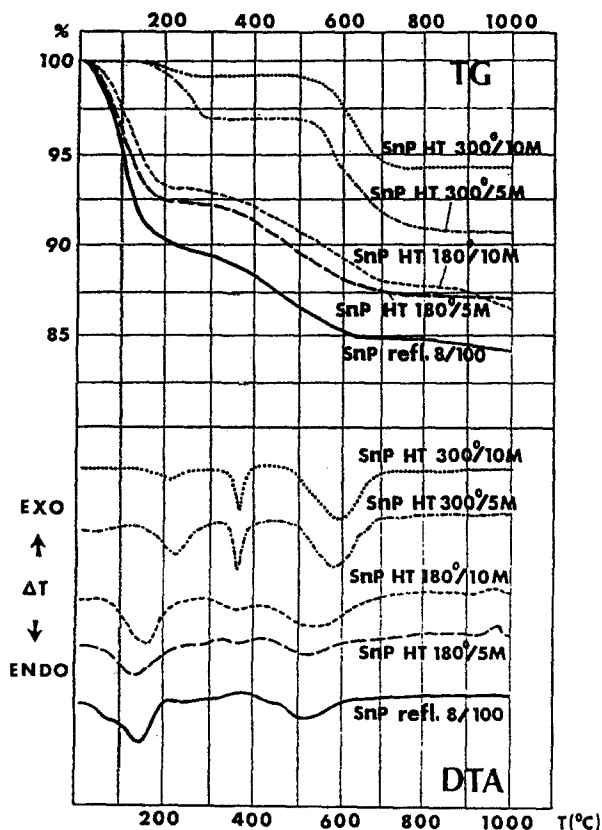


Fig. 3 Simultaneous TG and DTA curves of differently prepared tin monohydrogenphosphates

The condensation process to layered tin-pyrophosphate phases begins at 250°–350°C in the case of the refluxed or HT 180°C samples, the lower the temperature is the smaller the degree of crystallinity of the materials. This process, which begins at temperatures lower than those of the other Me(IV) phosphates, is very slow and proceeds up to 700°–800°C. This indicates that the elimination of the condensation water in the case of tin phosphates finds some hindrance in leaving the solid, probably in connection with the narrowing of the interlayer distance, consequent to the loss of the condensation water.

For the more crystalline samples prepared by HT at 300°C, the condensation process occurs between 500° and 700°C, and corresponds to a weight loss of 1 mole of water per formula weight.

**Table 2** X-ray diffraction patterns of different tin hydrogenphosphates prepared by refluxing [1] or hydrothermal treatment (HT) at 180°C or 300°C in H<sub>3</sub>PO<sub>4</sub> 5 or 10 M

SnP [1]		SnP (HT)		SnP (HT)		SnP (HT)	
8/100		180 ° / 5 M or /10 M		300° / 5 M		300° / 10 M	
<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>
7.82	mw	7.78	m	7.75	ms		
				7.58	m	7.52	vs
4.22	m	4.22	mw	4.22	m	4.27	vw
3.46	s	3.46	s	3.46	s	3.78	vvw
				3.43	ms	3.58	vw
3.16	vw	3.16	vw	3.15	vw		
2.64	vw	2.64	w	2.64	vw		
2.47	mw	2.47	mw	2.47	mw	2.48	w
		2.42	w	2.41	vw		
		2.36	vw	2.36	vw	2.12	vw

**Table 3** X-ray diffraction patterns of different germanium hydrogenphosphates prepared by refluxing (refl.) or hydrothermal treatment (HT) at 180°C in H<sub>3</sub>PO<sub>4</sub> 5 or 10 M

GeP refl.		GeP (HT)							
8/100		180°C/5M		180°C/10M		300°C/5M		300°C/10M	
<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>	<i>d</i>	<i>i</i>
7.78	vs			7.49	vvs				
		4.59	m	4.59	vw	4.59	m		
4.08	mw								
3.89	w								
		3.49	mw	3.49	vw	3.49	mw		
3.39	s								
3.36	s								
		3.17	vs	3.17	m	3.17	vs		
3.07	vw								
		3.04	ms	3.04	vw	3.04	ms		
2.59	ms								
				2.47	mw				
2.39	ms								
		2.31	vw	2.31	vvw	2.31	w		
2.29	vw								
		2.20	w	2.20	vvw	2.20	mw		
		2.17	w	2.17	vvw	2.17	mw		
		1.95	mw	1.95	w	1.95	mw		

Above 900°C the presence of exothermic peaks are indicative of the crystallization of the cubic tin phosphate, or  $\alpha$ - $\text{SnP}_2\text{O}_7$ . This transformation generally occurs very slowly.

For some samples, as for the refluxed or HT 180°C Sn phosphates, the TG curves show a slight weight loss between 900° and 1000°C, which, as we verified, is due to traces of  $\text{H}_3\text{PO}_4$  remained strongly adsorbed on these precipitates during their preparation even after repeated washings [11]. This behaviour is only observed for the tin phosphates compounds and consequently, for some of them the stoichiometric ratio P/Sn is greater than the expected value of 2. The samples obtained by HT at 300°C, which possess a P/Sn = 2, do not show any appreciable weight loss above 800°C [11].

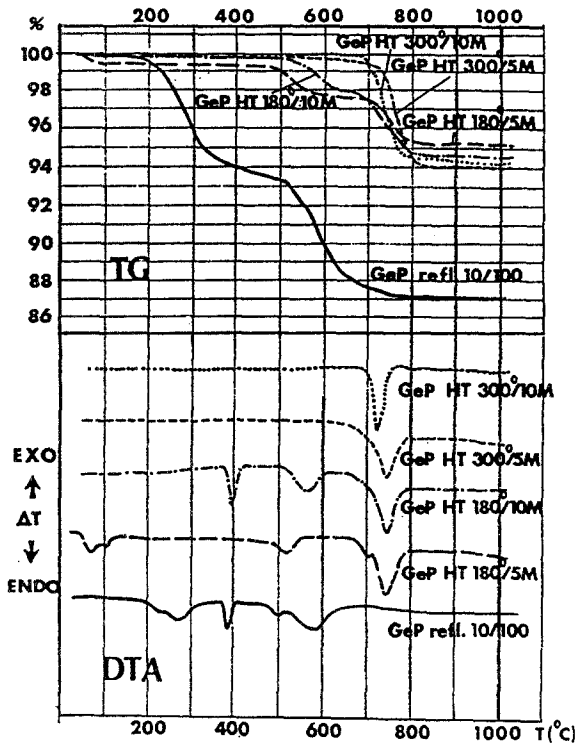


Fig. 4 Simultaneous TG and DTA curves of germanium phosphates prepared by refluxing [1] or by HT at 180° or 300°C in  $\text{H}_3\text{PO}_4$  5 or 10 M

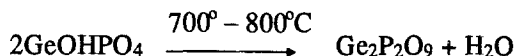
In Fig. 4 the simultaneous TG-DTA curves of Ge hydrogenphosphate prepared by the refluxing method and HT with  $\text{H}_3\text{PO}_4$  5 and 10 M are reported. In Table 3 the X-ray diffraction patterns of the corresponding materials are given.

It is evident from Fig. 4 that the TG-DTA curves of  $\text{Ge}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$  prepared by refluxing [4] are different from those of the materials obtained by HT at 180°C (a partial change), and at 300°C (a drastic change).



The X-ray patterns reported in Table 3 reveal the formation of a new compound: the hydrolyzed phase  $\text{GeOHPO}_4$ . This phase is the only one present after HT at  $300^\circ\text{C}$ , or at  $180^\circ\text{C}$  when  $\text{H}_3\text{PO}_4$  5 M is used. It is in mixture with partially dehydrated Ge monohydrogenphosphate, when treated at  $180^\circ\text{C}$  with  $\text{H}_3\text{PO}_4$  10 M. In the last case the presence of the Ge hydrogenphosphate phase is revealed in the DTA curve by the presence of the anhydrous phase transition at  $370^\circ\text{C}$  as in the case of the compound prepared by refluxing (Fig. 3).

The presence of  $\text{GeOHPO}_4$  is indicated by the endothermic reaction occurring between  $700^\circ$  and  $800^\circ\text{C}$  which is due to the weight loss of  $\text{H}_2\text{O}$  following the reaction:



Therefore we can conclude that, as expected, the higher the hydrolyzability of Ge hydrogenphosphate results the lower the  $\text{H}_3\text{PO}_4$  concentration and the higher the temperature of the hydrothermal treatment are.

## Conclusions

The study of the stability of the different hydrogenphosphates of the tetravalent metals (Zr, Ti, Sn, Ge) obtained by hydrothermal treatment up to  $300^\circ\text{C}$ , can be easily and rapidly performed and investigated with simultaneous TG-DTA technique associated with X-ray diffractometry.

The results indicate that only zirconium hydrogenphosphate possesses a high chemical and structural stability, since its  $\alpha$ -structure and its stoichiometry is retained even under hydrothermal treatment at  $300^\circ\text{C}$ .

Titanium and tin phosphates also show high chemical stability in the investigated conditions. As expected, these materials increase their degree of crystallinity and this fact permits to better point out the reversible phase transition of the anhydrous phases, that occurs at around  $300^\circ$  and  $360^\circ\text{C}$  respectively.

In the case of titanium phosphate a drastic structural change from the alpha to the gamma structure takes place under the hydrothermal treatments at  $300^\circ\text{C}$ , thus suggesting a nice and rapid way to prepare this new type of phase.

In the case of tin phosphate a particular weight loss above  $900^\circ\text{C}$  is observed, attributable to  $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5$  that can remain strongly adsorbed on this phosphate on preparation. We presume that the peculiar adsorbing properties of the Sn phosphate phases, that lead to some differences in the total stoichiometry of the compounds, are linked to the chemical characteristics of the tetravalent tin, but also depends on the degree of crystallinity of the Sn hydrogenphosphates formed at the various temperature: at  $300^\circ\text{C}$  the  $\text{H}_3\text{PO}_4/\text{P}_2\text{O}_5$  adsorption is not observed.

Ge phosphate is the less chemically stable among all the investigated compounds, since also at  $180^\circ\text{C}$  it gives rise, in a few hours, to the hydrolysis product  $\text{GeOHPO}_4$ . As expected, the hydrolysis of the  $\alpha$ -form increases with the decrease

of the  $H_3PO_4$  concentration and the increase of the temperature of the hydrothermal treatment.

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**Zusammenfassung** — Die Hydrogenphosphate von Zr, Ti, Sn und Ge wurden mittels der Refluxmethode in kristalliner Form hergestellt und bei 180° und 300°C einer hydrothermischen Behandlung unterzogen, um festzustellen, ob die Herstellungszeit bei gleichbleibender chemischer Zusammensetzung und ihrer  $\alpha$ -Struktur verkürzt werden kann. Simultane TG und DTA zusammen mit Röntgendiffraktion scheinen eine sehr gute Technik darzustellen, um die erhaltenen Produkte zu charakterisieren.

Zr-Phosphate ist am stabilsten und ergibt unter allen Bedingungen eine  $\alpha$ -monohydrate Hydrogenphosphate-Phase. Ein ähnliches Verhalten zeigt das Titanphosphat bei 180°C, während die Verbindung sich bei 300°C in  $\gamma$ -Ti(HPO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O umwandelt. Sn-Phosphat gibt – gerade um seine  $\alpha$ -Struktur zu behalten – durch die steigende Temperatur und steigende Konzentration an Phosphorsäure Anlaß für mehr und mehr dehydratierte Phasen.

Ge-Hydrogenphosphat erwies sich unter hydrothermischen Bedingungen als am instabilsten bereits bei 180°C liefert als GeOHPO<sub>4</sub>. Wegen der leichten Hydrolisierbarkeit von Ge ist die hydrothermische Methode kein Weg, um kristallines  $\alpha$ -Germaniumhydrogenphosphat herzustellen.