Thermochimica Acta, 20 (1977) 87–92

DTA, ETA, AND TG INVESTIGATIONS OF ZIRCONIUM PHOSPHATES OF DIFFERENT CRYSTALLINITY*

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ABSTRACT

Interpretation of all thermal effects which occur on heating zirconium phosphates is possible when simultaneous DTA, ETA, and TG is applied. A rapid transition of poorly crystalline zirconium phosphate into normal cubic modification at high temperatures is clearly shown by DTA when amorphous zirconium phosphate is used. In contrast, because of the more rigid crystal lattice, this reaction is only visible in ETA when crystalline preparations are heated.

Especially after exchange of protons by cations, some amorphous zirconium phosphates exhibit a second exotherm in DTA. This reaction is believed to depend on growing up of partially crystalline structures.

INTRODUCTION

Inorganic ion exchangers, especially zirconium phosphates, (hereafter called ZrP) are of special interest in the nuclear field because of their high resistance against radiation in comparison to organic exchange resins[1]. Due to variations in production conditions, these substances exist in different degrees of crystallinity, and therefore have different separation characteristics. Since the first description of crystalline ZrPs by Clearfield[2], and Alberti[3], such materials may be prepared in a structure between amorphous and highly crystalline by variation of parameters like concentration, temperature, drying conditions, and so on.

In this work it is shown that such substances can be classified by means of DTA. X-Ray diffraction is not useful in this field, except in the investigation of pure crystalline compounds. Classification of materials is important for predicting ion-exchange properties of a ZrP-material of unknown arrangement of molecule units, because the selectivity of the exchanger is strongly dependent on its degree of crystallinity. Due to storage conditions, there are also possible changes in structure, which can be established by thermal analysis and considered for comparison.

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* Presented at the 2nd Symposium of the German Society for Thermal Analysis held at the University of Konstanz from 5–6 July, 1976.

EXPERIMENTAL

Crystalline ZrP-materials were prepared according to Alberti[3] by decomposing a fluoro complex of zirconium in the presence of phosphoric acid; amorphous samples were prepared by drying a ZrP gel, as described by Clearfield[4], and Treplan[5]. Some materials used were Merck p.a. products. Cited X-ray powder diffraction patterns[4] of substances similar to those investigated here agree well with our results.

The Na forms of the exchanger were prepared by suspending the acid forms in a 0.1 N solution of NaCl and adding the calculated quantity of NaOH[6].

For ETA the samples were labeled by co-precipitation of ZrP and trace amounts of ^{228}Th. The Merck products were impregnated by treatment of the exchanger with a solution of ^{228}Th in diluted HNO_3. Several possibilities for incorporation of radioactive inert gas in solids are given in ref. 7. The specific activity was 3μCi per gram of sample.

For thermal analysis a Netzsch simultaneous thermal analyzer STA, model 429, was used. A special equipment[8] permits simultaneous emanation thermal analysis by counting the alpha activity of radioactive emanation ^{220}Rn released from ^{228}Th labeled samples as a function of temperature.

Experimental conditions for thermal analysis were as follows: sample weight 100 mg; nitrogen medium; carrier gas for emanation was nitrogen with a flow-rate of 5 l h^{-1}; heating rate 10°C min^{-1}; PtRh–Pt thermocouples; Degussit crucibles; Al_2O_3 as a standard.

X-ray analysis was carried out by Dipl. Phys. G. Paul at the Institut für Mineralogie der Technischen Universität München.

RESULTS AND DISCUSSION

Figure 1 gives the results of DTA, ETA, and TG of highly crystalline zirconium phosphate. An investigation of similar materials presented by Horsley and Nowell[9] at the 3rd ICTA, 1971, is also shown.

The structure of crystalline ZrPs is well known[10]. The structure of different treated crystalline ZrPs seems to be the same, because the corresponding X-ray diffraction patterns are identical. Nevertheless, there are little differences in DTA-curves. Furthermore the DTA peaks are not always attributed to the same reactions[9, 11].

An interpretation of the DTA result is possible by combining all thermal analysis methods used. X-ray and IR data confirm the following explanation:

The two endotherms observed at higher temperatures correspond to the two losses in weight, caused by the loss of one mole of water at each temperature. The peak at 321°C is attributed to evaporation of zeolitic water. A significant raise in emanation power and therefore an additional change in structure accompanies the second loss in weight, which is attributed to the condensation of phosphate groups to pyrophosphate, leading to ZrP_2O_7.

A change in structure is also indicated by ETA at 257°C, at the beginning of

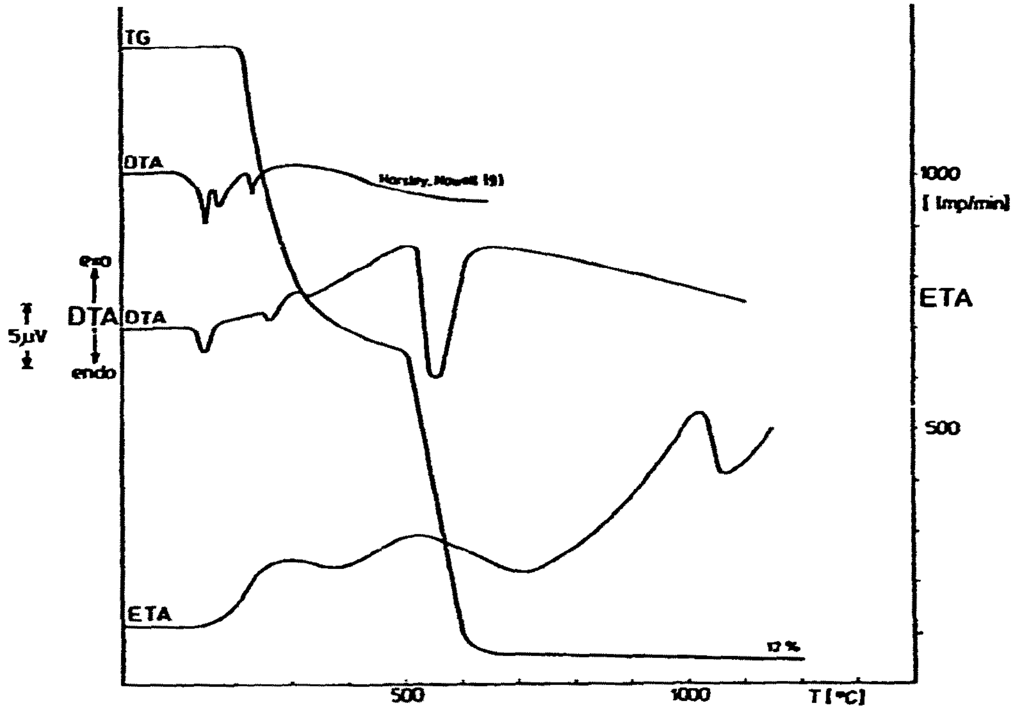

Fig. 1. Thermal analysis of crystalline zirconium phosphate.

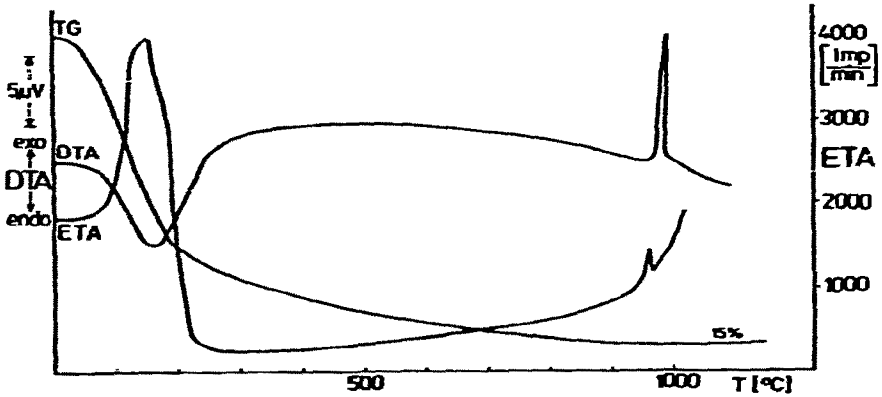

Fig. 2. Thermal analysis of amorphous zirconium phosphate.

the loss in weight. This reaction can be assigned, on the basis of X-ray spectra, to a shortening of the crystallographic c-axis in the ZrP lattice.

As for the endotherm at 143°C, we agree with Horsley and Nowell[9] and consider this (reversible) reaction as a movement of the zeolitic water molecule within its lattice cage.

Besides these four endotherms characteristic of all crystalline ZrPs, ETA indicates an additional change in structure at high temperatures, with no accompanying effect in either DTA nor TG.

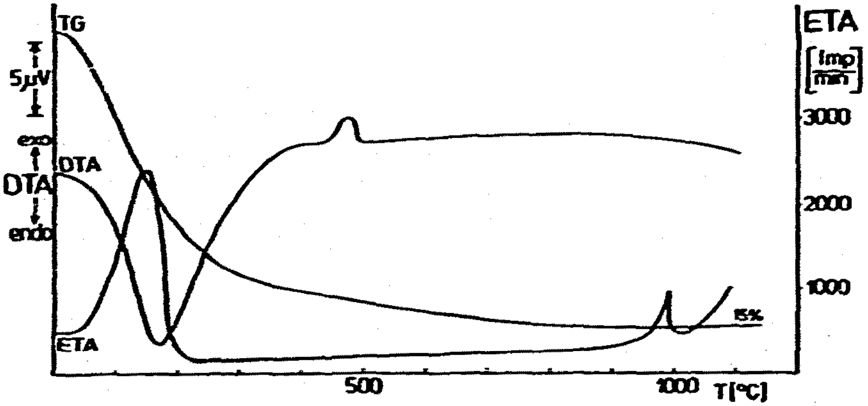

Fig. 3. Thermal analysis of amorphous zirconium phosphate, supplied by E. Merck, Darmstadt.

Thermal analysis results of amorphous ZrP are shown in Fig. 2. In contrast to crystalline ZrP there is only one broadened endotherm corresponding to a marked ETA effect. TG gives a continuous loss in weight. Besides the raise in emanating power at high temperature in this case there is also a sharp exotherm in DTA curve. Such an exotherm was also found during the investigation of ZrP received from Merck, which was called "amorphous ZrP"; but the reaction took place at much lower temperatures (Fig. 3).

Observation of exotherm reactions during investigation of ZrPs at different temperatures, led "casually" to some confusion in the explanation of these effects. It is Clearfield's opinion[2], that excess phosphoric acid shifts the peak to lower temperatures. Szirtes et al.[12] have reported that the greater the crystallinity of the sample, the smaller is the exotherm.

An explanation of all the effects is possible by examining the ETA curves. At high temperature all ZrP samples under investigation here show some change in structure. On the basis of X-ray diffraction this high temperature reaction is a recrystallisation of poorly crystalline zirconium pyrophosphate (ZrP_2O_7) to the normal cubic form, confirming Clearfield's observations[2].

However, the exotherm at lower temperature (Fig. 3) is not accompanied by a significant change in structure, because there is no raise in emanating power. There must be an additional effect to that caused by the real amorphous product, shown in Fig. 2. ETA indicates that recrystallisation is not shifted to lower temperatures; this reaction takes place in the same region as was found for the other samples. Besides, it is evident from TG that condensation of pyrophosphate groups is not complete at 475°C.

The structure of the substance characterized in Fig. 3 is considered to be between those of samples which are highly crystalline and fully amorphous shown in Figs. 1 and 2, respectively. Merck's special production conditions led to a substance containing some ordered regions; these may consist of some chain-like structures, shown in Fig. 4, as described by Baetslé[13].

If such chains are only fragments and are distributed irregularly at first, energy

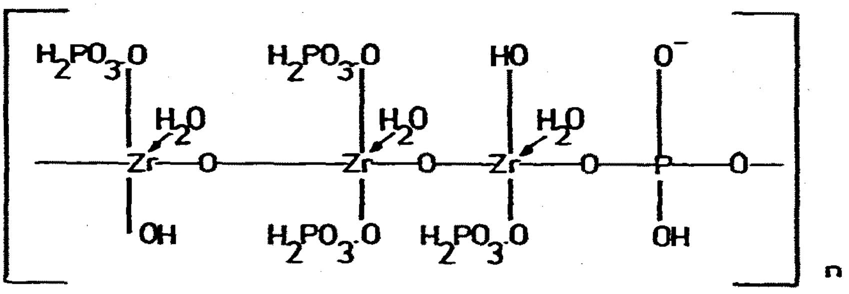

Fig. 4. Possible chain-like structures in amorphous zirconium phosphate (taken from ref. 13).

supply by temperature raising will lead to chain-linking and development of greater regions in a state of higher order. Such a reaction would be exothermic, but does not necessarily need a change in structure to such an extent that it could be recognizable by ETA. This may be an explanation for the observed exotherm in the DTA of Merck's product, without an accompanying ETA effect.

Further confirmation of the beginning of crystallisation of this substance is indicated by X-ray diffraction, but this method needs at least 24 h of exposure time.

Now we searched for samples with better crystallinity. It was expected that the better the order of molecules within the substance, the higher would be the temperature of the exotherm caused by chain-linking. This means that the DTA peak may be a good indicator for the crystallinity of the substance under investigation, because chain-linking and ordering in an amorphous material can be easily achieved, but in a more crystalline and rigid substance this reaction needs more energy, that is, higher temperatures.

An investigation of the proceeding crystallisation of ZrPs by means of the shifting of the "chain-linking" peak proved to be impracticable, because the better the crystallinity, the more the exotherm is over-compensated by the strong endotherm condensation reaction. But there is another possibility to observe this reaction as a function of the degree of crystallinity, and to further support the assumption, that exotherms in the DTA of ZrPs may be due to different reactions:

If the protons in ZrP are exchanged by cations, for instance by filling the exchanger to full capacity with Na^+ ions

$$Zr(HPO_4)_2 \cdot xH_2O + 2Na^+ \rightarrow Zr(NaPO_4)_2 \cdot yH_2O + 2H^+$$

then condensation of phosphate groups forming pyrophosphate will be impossible. If the real amorphous material characterized in Fig. 2 is used, the high temperature exotherm should be omitted. But during ion exchange some ordered centres are also introduced into this material, because for electrostatic reasons the Na^+-ions will prefer special sites. Therefore the Na^+-exchanged form should be no longer amorphous, and an exotherm in DTA should be observed at temperatures lower than 900°C. In fact an exotherm at 650°C is recognized during investigation of the fully exchanged amorphous ZrP (Fig. 5); this result indicates a higher state of order compared to Merck's product. At this temperature there is no raising in emanating power

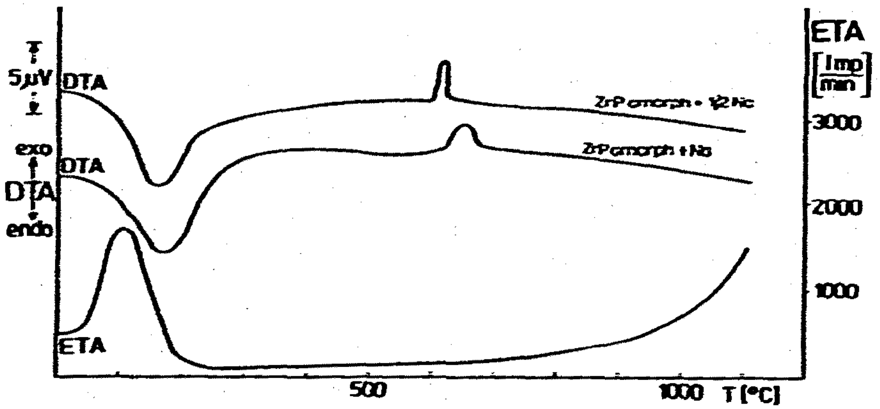

Fig. 5. Thermal analysis of Na^+-exchanged amorphous zirconium phosphate.

and therefore no remarkable change in structure, as was expected. By exchanging only one half of the protons in amorphous ZrP by Na^+-ions, a lower degree of order is reached; in this case the exotherm is observed at 620°C.

Summarizing the results, it could be shown that the "chain-linking" exotherm observed during DTA of ZrPs indicates well the degree of crystallinity of the material. This is emphasized by the fact, that a shifting of this peak on temperature scale is also produced by γ-radiation[14]. DTA also proves to be a suitable method for the investigation of radiation effects in ZrPs, and is further used for this purpose at this laboratory.

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