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Ge-Zr PHOSPHATE SYSTEM: THE ADVANTAGES OF THERMAL METHODS IN THE INVESTIGATION OF PHASE MIXTURES OR SOLID SOLUTIONS

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ABSTRACT

Several Ge and Zr phosphates, coprecipitated with different methods have been characterized by TG-DTA and X-ray techniques; from the data obtained it has been possible to evidentiate when solid solutions or mixed phases are formed. A possible mechanism of their formation is put forward.

INTRODUCTION

In several fields the investigation on mixed compounds is of increasing interest because the specific properties of the single components may be improved by adding other, suitably chosen, elements.

In the case of the layered ion-exchangers of the class of α-acid phosphates of tetravalent metals (Zr,Ti,Ge,Sn), all isostructural, it has been found that properties such as the resistence towards hydrolysis in solution (1), or the acidic strength in catalysis (2,3) can be graduate or improved by preparing mixed Ti-Zr or Ge-Zr phosphates.

However some differences are observed in their properties when solid solutions or mixtures of two phases are obtained.

In the view of a systematic study of the catalytic behaviour of mixed systems of these ion-exchangers, we report the first results of characterization of phases obtained by coprecipitation of Ge and Zr phosphates, performed mainly with thermoanalytical and X-ray techniques.

EXPERIMENTAL

All the materials were prepared by adding an excess of H_3PO_4 to solutions containing Ge and Zr chlorides in the desired ratio, and the precipitate refluxed in mother liquor in order to obtain cry-

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stalline products.

The materials were washed firstly with diluted H_3PO_4 and then with H_2O. After drying over P_2O_5 they were chemically analyzed and examined with X-ray techniques and simultaneous TG - DTA apparatus (Stanton model STA 781, heating rate 1-5°/min, in air, Pt crucibles).

The Ge/Zr values in the bi-phasic compounds could be deduced from the dehydration steps in the TG curves, in this case performed at 1°/min heating rate, and were found to be very close to those of their chemical analyses.

Both TG and chemical analyses supported the general formula α-$Ge_xZr_{1-x}(HPO_4)_2 \cdot H_2O$.

RESULTS AND DISCUSSION

The X-ray powder spectra show that the mixed compounds are poorly crystalline but isostructural with the pure Zr and Ge phosphates (in brief ZrP and GeP). Their interlayer distances (d_{002}) are intermediate between 7.56 Å (pure ZrP) and 7.75 Å (pure GeP), the values ranging in the interval 7.62 - 7.69 Å.

From the weak secondary lines we may suppose that in all the materials having a Ge/Zr ratio $\leq$ 20/80, only one phase is present, very similar to ZrP, even if less crystalline, whilst in the materials with Ge/Zr $\geq$ 35/65, two phases are present.

Therefore we infer that low concentration of Ge is particularly suitable to give solid solutions of Ge in Zr phosphate matrix.

Thermal analyses showed to be very helpful in distinguishing mono-phasic from bi-phasic systems and in better clarifying the dubious X-ray data. Besides they give other important information.

In fig. 1 are given TG and DTA curves of materials with different Ge/Zr ratio, together with those of pure Ge and Zr phosphates.

The TG and DTA curves of fig. 1, a) and b) show a general trend similar to that of the poorly crystalline ZrP (4): the dehydration occurs in only one step below 200 °C, there is only one phase transition at 200 °C, identical to that of ZrP phase, and after the condensation process at 450-600 °C a layered Ge-ZrP_2O_7 is formed, giving at 1000 °C only a single cubic phase, quite similar to α-ZrP_2O_7. This behaviour is given only when the materials are single phases, i.e. in our case, only if Ge is solubilized in a Zr phosphate matrix.

On the contrary, TG and DTA of fig. 1, c),d),e), clearly refer to

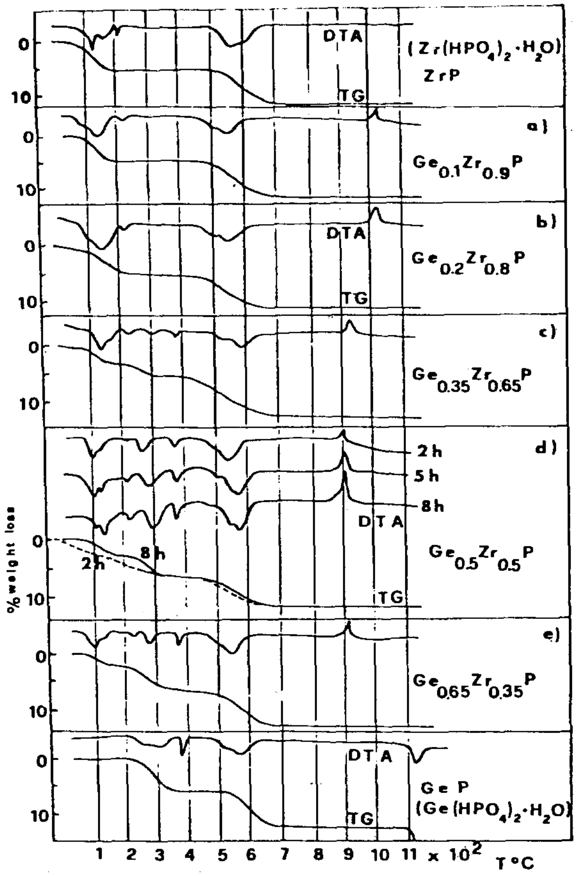

Fig. 1 - Simultaneous TG and DTA curves of Ge-Zr mixed phosphates.

materials (which are) mixtures of two phases, each behaving indipendently from the other: the dehydration process below 200 °C refers to ZrP type phases and that between 220 and 350 °C to those rich in GeP. The amounts of single components can be deduced from the height of the corresponding dehydration steps.

Furthermore, the phase transition observed at ≃ 200 and 370 °C occur in the same T ranges as observed for pure ZrP and GeP phases respectively (4,5).

A further confirmation is given by the non-layered pyrophosphate phases formed after the exothermic peak at ≃ 900 °C: for Ge/Zr ratios ≥ 35/65 both α-ZrP_2O_7 and cubic or monoclinic GeP_2O_7 are present.

The DTA curves provide information on the kinetics of crystallization of the single phases. Thus, as the reflux time increases from 2 to 8 or 16 h, the endothermic peaks at 130 and 200 °C (related to the ZrP-type phases) slowly increases, whilst the peak at 370 °C, due to GeP, is clearly evident, even after only 2 h of reflux. This means that GeP crystallizes more rapidly than does ZrP.

CONCLUSIONS

These first results, besides indicating the possibility for the GeP-ZrP system of giving solid solutions for low loading of Ge or Zr respectively, show how from DTA and TG curves it is possible to differentiate the solid solutions from the mixture of phases, in the latter case making possible a semiquantitative estimation of the single components.

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