

Ag(I) SOLID SOLUTIONS IN ZIRCONIUM DIHYDROGEN PHOSPHATE. THERMAL BEHAVIOUR AND PHASE CHANGES*

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The thermal and redox behaviours of some Ag-low-converted zirconium phosphates have been investigated by thermoanalytical and X-ray methods: the conditions for obtaining Ag solid solutions in $\overline{\text{H}\text{H}}$ phases are reported.

The study of zirconium phosphate phases with different ions is increasing due to the potentially useful properties of these materials in several fields, such as ion-exchangers, catalysts or ion-conductors.

They are obtained by ion-exchange. Generally only after a certain ion uptake, which is not the same for the various ions, a new phase is obtained with its characteristic interlayer distance and water content. This is the case with alkali [1], alkaline earth [2], transition metal ions of the first and second series [3, 4] or oxocations [5].

On heating of the partially converted materials, where two or more phases coexist, each phase usually behaves as if it is alone.

In the case of the Ag forms, the behaviour is slightly different: for low-converted materials (<20% Ag conversion), although they also initially contain a small amount of a high-converted phase [6], at 400° they give rise to only one phase [7], similar to the pure $\overline{\text{H}\text{H}}$ form, without the presence of any other higher Ag-converted phase. This suggests that Ag^+ can give solid solutions in $\overline{\text{H}\text{H}}$ phases better than other studied cations do.

With the possibility of their utilization as bifunctional catalysts, combining the strong acidic properties of the predominant $\overline{\text{H}\text{H}}$ form to the activity of Ag^+ or Ag° centers, this investigation aims at a more systematic study of these low-Ag-loaded hydrogen zirconium phosphates, that is:

- (i) the Ag-loading value up to which solid solutions can be obtained in the $\overline{\text{H}\text{H}}$ phase;
- (ii) their thermal stability (temperature ranges and transformations);
- (iii) their stability at room temperature under different conditions;
- (iiii) their redox behaviour.

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Experimental procedure

The materials were prepared by contacting at room temperature 1 g of crystalline $\text{ZrH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ($\overline{\text{HH}} \cdot \text{H}_2\text{O}$ phase) with increasing volumes of 0.01 *N* AgNO_3 solutions, in order to obtain Ag^+ conversions of 6, 13, 20, 26, 35 and 38% of their total exchange capacity.

The thermal behaviour was studied either with a Mettler TA 2000C simultaneous TG-DSC apparatus, or with a Netzsch apparatus, Model 400, for DTA curves and redox behaviour. The sample weight was 10–20 mg.

The solid phases were identified using a Philips diffractometer (Cu $K\alpha$, Ni-filtered radiation) and the high-temperature X-ray diffractograms were obtained with an Italstructure camera, Model 3 F.

Results

From the chemical analysis and TG curves the following compositions of the materials studied resulted:

$\text{ZrH}_2(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	$(\overline{\text{HH}} \cdot \text{H}_2)$
$\text{ZrAg}_{0.12}\text{H}_{1.88}(\text{PO}_4)_2 \cdot 0.95 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.12}\text{H}_{1.88}} \cdot 0.95 \text{H}_2\text{O})$
$\text{ZrAg}_{0.26}\text{H}_{1.74}(\text{PO}_4)_2 \cdot 1.05 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.26}\text{H}_{1.74}} \cdot 1.05 \text{H}_2\text{O})$
$\text{ZrAg}_{0.4}\text{H}_{1.6}(\text{PO}_4)_2 \cdot 0.95 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.4}\text{H}_{1.6}} \cdot 0.95 \text{H}_2\text{O})$
$\text{ZrAg}_{0.52}\text{H}_{1.48}(\text{PO}_4)_2 \cdot 1.08 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.52}\text{H}_{1.48}} \cdot 1.08 \text{H}_2\text{O})$
$\text{ZrAg}_{0.7}\text{H}_{1.3}(\text{PO}_4)_2 \cdot 1.0 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.7}\text{H}_{1.3}} \cdot \text{H}_2\text{O})$
$\text{ZrAg}_{0.76}\text{H}_{1.24}(\text{PO}_4)_2 \cdot 0.98 \text{H}_2\text{O}$	$(\overline{\text{Ag}_{0.76}\text{H}_{1.24}} \cdot 0.98 \text{H}_2\text{O})$

The X-ray diffraction spectra of these hydrated materials are shown in Fig. 1, together with those of the known higher Ag-converted phases [4, 6].

In Fig. 2 are the corresponding TG and DSC curves. From the reported data it appears that all the materials considered have about the same water content (≈ 1 mole of H_2O) in the starting $\overline{\text{HH}}$ phase, independently of the Ag-loading.

When Ag^+ is present in the materials, a greater tendency to dehydrate is observed at room temperature than is the case for the pure $\overline{\text{HH}}$ form.

The X-ray diffraction patterns indicate that the uptake of Ag ions, together with the formation of a small quantity of a phase with $d_{002} = 0.83$ nm (perhaps $\text{AgAg} \cdot \text{H}_2\text{O}$ phase [6], present in the external part of the ion-exchanger particles) involves the appearance of a doublet at 0.75–0.74 nm (connected perhaps with partial dehydration of the Ag-converted materials at room temperature) and a gradual modification of the spectrum of $\overline{\text{HH}} \cdot \text{H}_2\text{O}$, comprising only slight variations in the d values of its most important reflections, with a gradual atten-

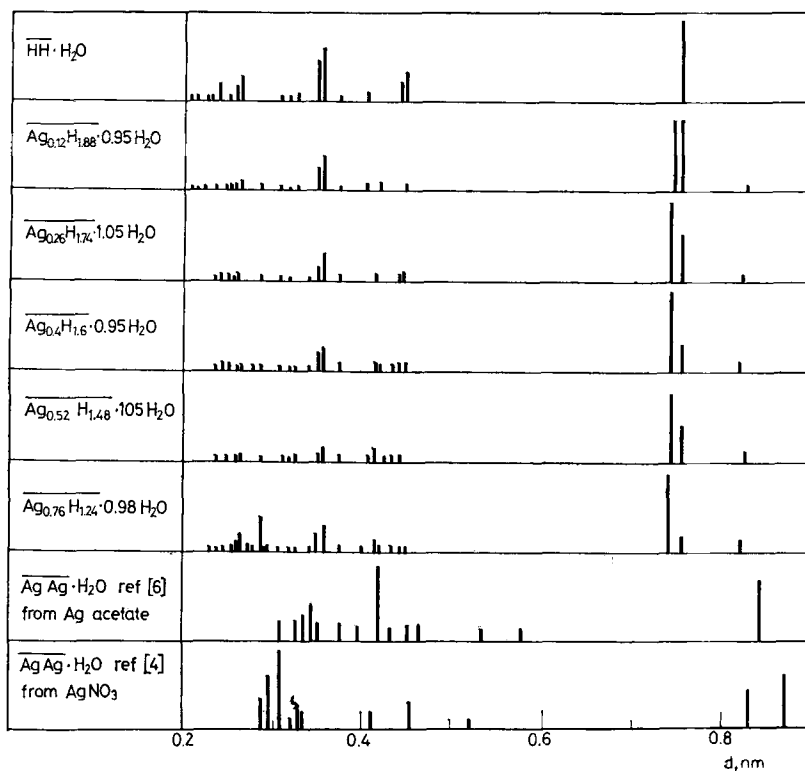


Fig. 1. X-ray diffraction patterns of some Ag-low-converted zirconium phosphates and other known compounds

uation of the intensity of some of them. This suggests that Ag uptake occurs *via* a concomitant formation either of a highly-converted Ag phase in the external part of the exchanger particles, or of a Ag solid solution in the inner parts of the grains.

Up to 20–25% Ag conversion, the reflections of the $\overline{\text{HH}}$ phase, even modified, are still present. At 35% Ag conversion the reflections of the highly-converted Ag phase become predominant.

The thermal behaviour also shows the effect of the presence of Ag^+ . From Fig. 2 we can observe that for the Ag-loaded phases the greater part of the dehydration process is shifted at higher temperatures (250–350°), compared to the $\overline{\text{HH}} \cdot \text{H}_2\text{O}$ phase, which begins to dehydrate at 100–120°.

Furthermore at 400° the weight loss of the low-converted Ag phases, as deduced from the TG curves (2°/min heating rate) corresponds to 1 H_2O per mole of exchanger, whilst the pure $\overline{\text{HH}}$ phase gives at the same temperature a weight loss corresponding to 0.7–0.8 H_2O , and for its complete dehydration higher energies

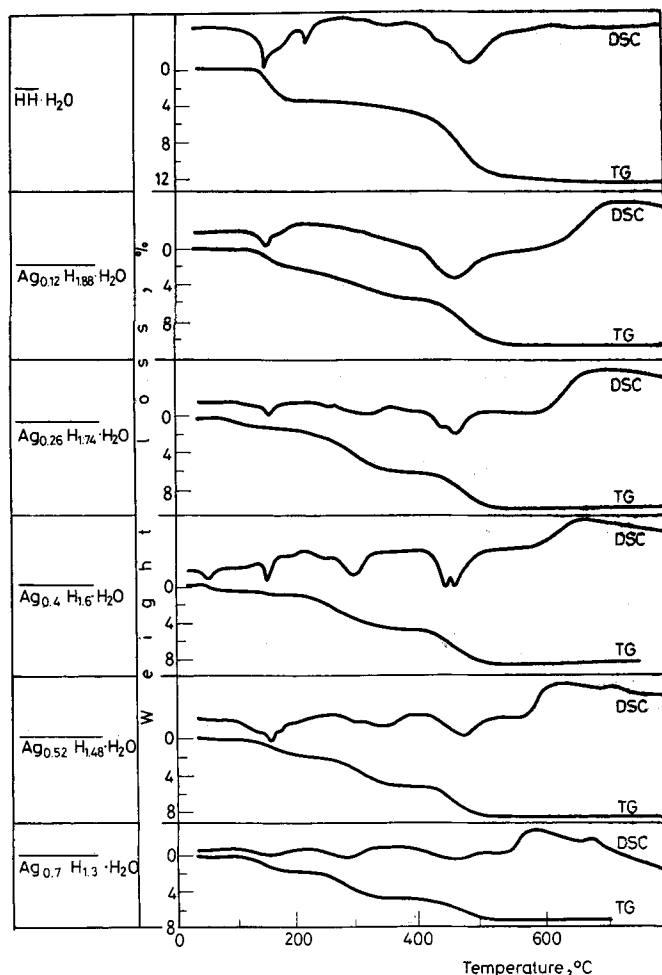


Fig. 2. TG and DSC curves of some Ag-converted zirconium phosphates

are required. It has already been pointed out [8] that the phase transition at 200–250° with a decreasing of d_{002} from 0.74 to 0.68 nm is the cause of such a water retention till 500° and above.

Other differences in the thermal behaviours of the hydrogen and low-Ag-loaded forms are:

(i) all the Ag-converted materials show a small weight loss below 100°, already observed to be characteristic of the highly-converted Ag phases [7] assumed to be present in the external shell of the particles;

(ii) the stopping of the weight loss in the range 100–250° permits observation of the phase transition at 140–150° characteristic of the $\overline{HH} \cdot H_2O$ phase, involv-

ing the decrease of d_{002} from 0.76 to 0.74 nm, no longer covered (as for the pure $\overline{\text{HH}} \cdot \text{H}_2\text{O}$ phase) by the dehydration process;

(iii) the low-converted materials do not show the endothermic reversible phase transition at 200–250° (d_{002} 0.74 \rightleftharpoons 0.68 nm) [8] evident for pure $\overline{\text{HH}}$ anhydrous phase: at 250° the 0.74 nm phase is still present; their DTA curves show only a double endothermic reaction between 250 and 350°, corresponding to water loss.

(iv) for the Ag-low converted materials the loss of cavity water is complete at 400°, whilst for the pure $\overline{\text{HH}}$ phase the last water fraction is eliminated around 500° overlapping with the condensation water loss.

When we examine the X-ray powder patterns of Ag-low-converted materials calcined at 400°, cooled under anhydrous conditions at room temperature and immediately recorded (Fig. 3), it can be seen that, at least up to 20% Ag-converted forms, the main reflections are similar in the d values to those of the α'' $\overline{\text{HH}}$ phase [8] ($d_{002} = 0.68$ nm), known to be stable only in the T range 200–450°, and which again gives an anhydrous phase, with $d_{002} = 0.74$ nm, when cooled to room temperature. Therefore, the heating of these anhydrous Ag-low-converted materials does not maintain the presence of a separate Ag-converted phase (as is observed with higher Ag conversion [6]), but gives rise to solid solutions evidently connected with homogeneous Ag^+ diffusion into the $\overline{\text{HH}}$ phase, and singularly, the presence of Ag^+ involves the persistence at room temperature of a phase with $d_{002} = 0.68$ nm, to date observed only for the pure $\overline{\text{HH}}$ phase and at $T > 200^\circ$. Similar results have been obtained also after 4 days, provided maintained the materials in a dessiccator under anhydrous conditions.

A confirmation of the different behaviours of the pure $\overline{\text{HH}}$ phase and the low-Ag-loaded materials is given by the 6% Ag-converted form, that shows in part the behaviour of the $\overline{\text{HH}}$ phase (see the reflection at $d = 0.74$ nm) in pattern C and in part the behaviour of the 13–20% Ag-converted materials ($d = 0.68$ nm).

In contrast, when these solid solutions are left in the open air, under non-dry conditions, a gradual decrease in the 0.68 peak intensity is observed, together with the rising of two peaks with $d = 0.74$ and 0.81 nm, always corresponding to other already known $\overline{\text{HH}}$ phases, the α and λ , respectively [9], generally considered to be anhydrous or low-hydrated phases. The latter phase has already been observed after reducing Cu phases, and by leaving them under non-dry conditions at room temperature [10].

The relative amount of the two phases is not the same and depends on the % of Ag^+ present, on the time the materials are left in the air, and on the degree of the external humidity. Figure 4 shows the phase evolutions of the various materials, observed via the relative variations of their d_{002} peak intensities as a function of time.

Under non-dry conditions, during the first day a rapid diminution of the 0.68 phase is observed, with a simultaneous increase of the 0.74 and 0.81 phases (the latter seems to change slowly into the 0.74 phase with time).

When they are maintained under dry conditions, the 0.68 phase, predominant for the 13–20% Ag-converted materials, remains quite unaltered even after one

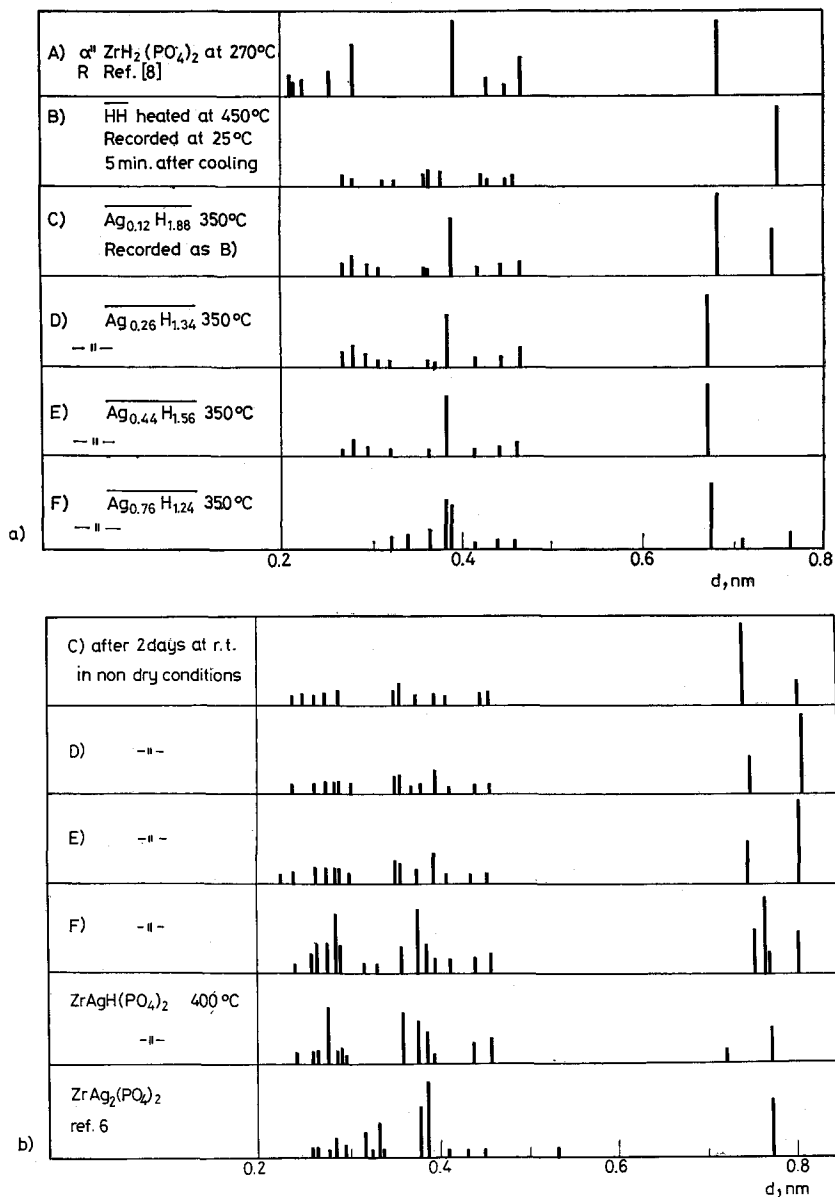


Fig. 3. X-ray diffraction patterns of heated Ag-low-converted zirconium phosphates, recorded at room temperature: comparison between samples maintained under dry conditions and for some days under non-dry conditions

week, and the presence of the other two phases is quite insignificant. In 6% Ag materials, we observed a partial decreasing of the 0.68 phase, giving the 0.74

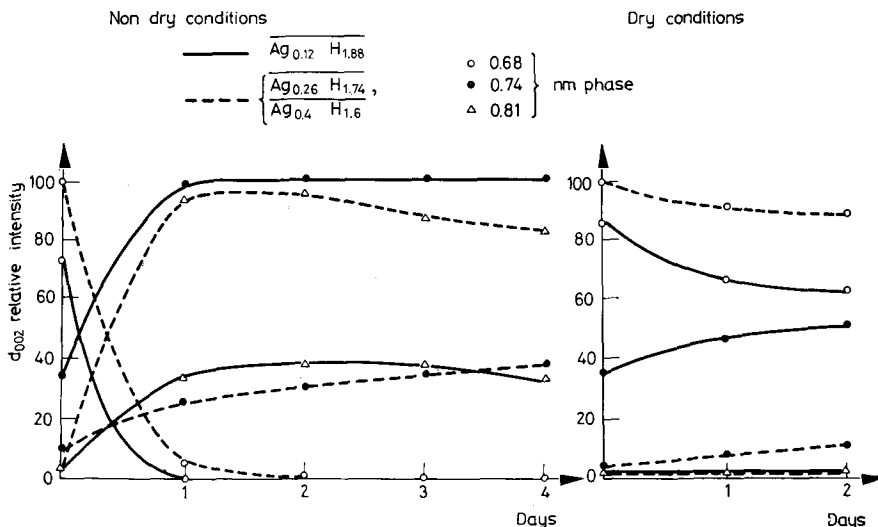


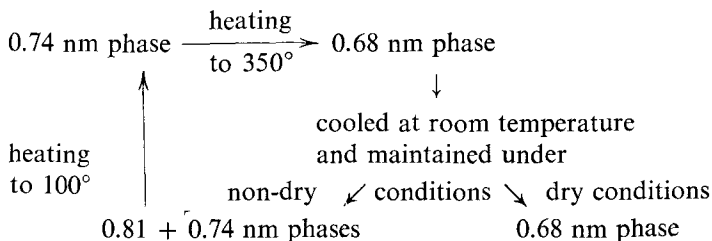
Fig. 4. Phase evolution in heated Ag-low-converted zirconium phosphates, after some days at room temperature

phase, perhaps connected with minor exposure to ambient humidity under the operational conditions recording the X-ray powder spectra.

Evidently the kinetics of the formation the two derived phases is different, the 0.81 phase forming more rapidly, but only in particular conditions of humidity: its stability is lower than that of the 0.74 phase, as shown by its slow transformation into the 0.74 phase.

On heating, the 0.81 phase disappears after the first slight weight loss below 100° (0.15 H₂O), whilst the 0.74 phase is transformed to the 0.68 phase only after further dehydration (≈ 0.25 H₂O) at 250–350°.

The phase transformations of these Ag solid solutions in anhydrous or partially re-hydrated \overline{HH} phases can be summarized as:



The amount of the two existing phases depends on time and on humidity, both favouring the 0.74 phase.

On the basis of our results it is reasonable to consider the 0.81 nm phase to be a not fully anhydrous phase, as suggested by Clearfield [9], because of the need for moisture in its formation.

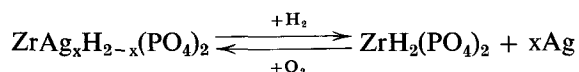
Redox behaviour

The reduction of the 13% and 20% Ag-converted materials with H₂ begins at about 150°. After the exothermic reaction between 150° and 200°, metallic Ag and pure $\overline{\text{H}\overline{\text{H}}}$ 0.74 phase are formed.

From the shape of the Ag reflection at $d = 2.36 \text{ \AA}$ we deduce that the higher the reduction treatment temperature, the better-formed are the metallic Ag crystallites.

On re-oxidative heating Ag can again enter the zirconium phosphate lattice as Ag⁺ as suggested by the disappearance of the metallic Ag reflections in the X-ray powder spectra and by the formation of Ag-zirconium phosphate phases.

The reversible reaction can be summarized as:



and therefore these materials behave similarly to the Ag-highly-converted phases [11] and to Cu-converted materials [10].

This reaction takes place only when the reductive treatment has been carried out under mild conditions ($T = 150 - 250^\circ$), because on reducing at 300–350° a higher segregation of metallic Ag crystallites is obtained, and this, after re-oxidation, makes difficult the homogeneous diffusion of the newly-formed Ag⁺ ions in the whole lattice. As a consequence, the Ag solid solution is no longer formed, and locally Ag-high-converted phases (e.g. the 0.78 nm phase, typical of materials with Ag loadings between 50 and 100% conversion) mixed with $\overline{\text{H}\overline{\text{H}}}$ phase are obtained.

Conclusions

This investigation has shown that when $\overline{\text{H}\overline{\text{H}}} \cdot \text{H}_2\text{O}$ is low-loaded with Ag⁺ by ion-exchange, Ag⁺ can in part give a solid solution phase with $d_{002} = 0.76 - 0.74$ nm, and can to a small extent give rise, on the outside of the particles, to a highly-converted Ag phase ($d_{002} = 0.83$ nm).

On heating, these biphasic materials give a single phase, as shown by the 13–20% Ag-converted samples, evidently due to a diffusion of Ag⁺ the external part of the grains and its homogenization into $\overline{\text{H}\overline{\text{H}}}$ phase,

The interlayer distance of the 0.68 phase formed at 350° is typical of the high temperature $\overline{\text{H}\overline{\text{H}}}$ phase, but the stronger Ag⁺ interaction with the lattice counterions [6] stabilizes this phase even at room temperature.

Its persistence, however, is very short in the presence of moisture, with transformation into phases with, $d_{002} = 0.81$ and 0.74 nm, characteristic of known α and λ $\overline{\text{H}\overline{\text{H}}}$ phases, but evidently in the case of our materials corresponding again to Ag solid solution phases.

However, our data showed that, at least up to around 20%, after a previous thermal treatment, Ag⁺ also remains solubilized at room temperature in phases similar to pure $\overline{\text{H}\overline{\text{H}}}$ phases.

The H₂ reduction followed by re-oxidation processes on these materials gives the same reversible behaviour noticed for the highly-converted Ag forms, but care must be taken in allowing marked segregation of metallic Ag crystallites, because this can hinder the reversibility of the redox processes for these materials.

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RÉSUMÉ — On a étudié le comportement thermique et oxydo-réducteur de quelques phosphates de zirconium faiblement converti par Ag, en se servant des méthodes d'analyse thermique et des rayons X: on communique les conditions permettant d'obtenir des solutions solides d'Ag dans les phases \overline{HH} .

ZUSAMMENFASSUNG — Das thermische und Redoxverhalten einiger Zirkoniumphosphate niedriger Ag-Konversion wurde durch thermoanalytische und Röntgenmethoden studiert; über die Bedingungen zum Erhalten von Ag-Festphasenlösungen in \overline{HH} -Phasen wird berichtet

Резюме — С помощью термоаналитического и рентгенографического методов исследовано термическое и окислительно-восстановительное поведение некоторых Ag-превращенных фосфатов циркония. Приведены условия образования твердых растворов серебра в фазах \overline{HH} .