

THERMOANALYTICAL INVESTIGATION OF CRYSTALLIN CERIUM PHOSPHATE

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The crystalline cerium bis-monohydrogen phosphate $\text{Ce}(\text{HPO}_4)_2 \cdot 1.33 \text{H}_2\text{O}$ was synthesized and identified by X-ray and analytical methods.

The thermal decomposition was investigated by simultaneous TG, DTG and DTA measurements. As a result of investigations four endothermic processes with weight loss were found; the first two, nearly equal peaks at 373 and 423 K, the third at 653 K and the last at 1053 K. The material after heating over 1273 K was investigated with the same analytical methods. In connection with these data we supposed that the weight losses may be identified as water and oxygen losses. The thermal analysis was supported by X-ray measurements. Collecting the results of thermal and X-ray analysis crystalline water bound in the molecule in various ways can be quantitatively distinguished. It was found that this phenomena have definite influence on the layer distance.

By the X-ray measurements the change of the crystal structure taking place during the heating process could be followed.

Of the synthetic inorganic ion-exchangers, zirconium phosphate has been investigated in some detail. The thermal analysis of such materials is of current interest. Based on the results obtained for zirconium phosphate [1], the thermal analysis of crystalline cerium phosphate was carried out.

The synthesized sample, which was analyzed, can be identified as the first member of the group $\text{Ce}(\text{OH})_x(\text{PO}_4)_x(\text{HPO}_4)_{x-2x} \cdot y\text{H}_2\text{O}$. The results are reported in this paper.

Experimental

Cerium phosphate was synthesized using the method described by Alberti et al. [2]. The final product was washed with redistilled water to $\text{pH} = 4$ and dried and stored at room temperature over saturated sodium chloride solution ($p/p_0 = 75\%$). Identification of the material was carried out using X-ray diffraction analysis and determination (by analytical methods) of the $\text{PO}_4^{3-}/\text{Ce}$ ratio.

The cerium content of the sample was determined using the colorimetric method described by Sandell [3]. The phosphate content was measured according to Bernhardt [4], using a Unicam photometer.

The X-ray measurements were made using a Dron-1.5 diffractometer with a CuK_α (Ni filter) beam; the high-temperature X-ray measurements were repeated with the same apparatus. The thermoanalytical experiments were carried out with a Paulik–Paulik–Erdey (MOM, Budapest) derivatograph [5], which is able to record TG, DTG, T and DTA curves simultaneously. 256.4 mg of crystalline sample was heated in a medium Pt crucible over the temperature range 298–1273 K at a heating rate of 10 K per min. The measurements were performed in air and alumina ($\alpha\text{-Al}_2\text{O}_3$) was employed as reference material.

Results and discussion

Based on the results of the analytical investigations, the composition $\text{Ce}(\text{HPO}_4)_2 \cdot y\text{H}_2\text{O}$ was calculated for the synthesized sample. Data relating to the identification are collected in Table 1.

Table 1
Data relating to the identification

Alberti $\text{PO}_4^{3-}/\text{Ce}$	Sample synthesized by intensities of the mean peaks, Å		Present authors $\text{PO}_4^{3-}/\text{Ce}$
2.0	15.90 vs 7.89 m 5.43 s 3.95 s 3.41 s	15.86 vs 7.82 m 5.34 s 3.92 s 3.36 s	2.0

vs – very strong, s – strong, m – medium

The results of thermoanalytical investigations are shown in Fig. 1.

The investigations revealed four endothermic processes with weight losses. The first two, nearly equal peaks found at about 373 and 423 respectively are not so high as those at 653 K. The last process begins at about 1053 K, with a similar weight loss as the first one. After being heated over 1273 K, the material was investigated with the same analytical methods as the original sample. Chemical analysis indicated a composition corresponding to a mixture of Ce_2O_3 and P_4O_{10} . In connection with these data we assumed that the weight losses may be identified as water and oxygen losses, as follows: up to 398 K 0.5 mole, to 433 K another 0.5 mole, to 596 K 0.33 mole, and between 586 and 1053 K another one mole water were lost. The endothermic process between 1053 and 1273 K covered the oxygen loss originating from the cerium reduction $\text{Ce(IV)} \rightarrow \text{Ce(III)}$. From the ion-exchange measurements the one mole lost water (between 586 and 1053 K) was identified as structural water, giving exchangeable H^+ ions. In

connection with these data the original material can be described by the formula $Ce(HPO_4)_2 \cdot 1.33H_2O$. The thermal decomposition or changes may be described as follows:

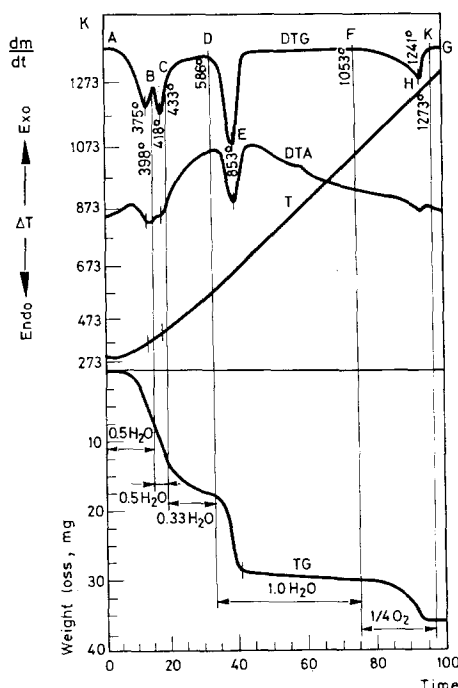
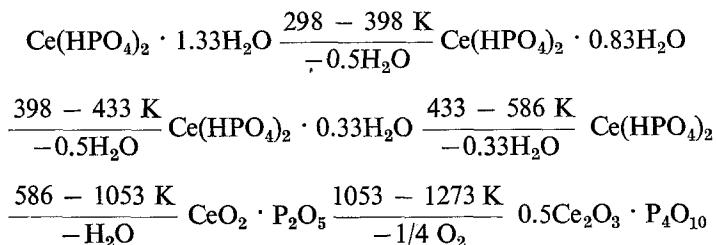


Fig. 1. Thermoanalytical curves of crystalline cerium phosphate

While the water loss between 586 and 1053 K is practically independent of the heating rate, the crystalline water loss is very sensitive to the rate of heating. The above distinguished water quantities showed that part of the crystalline water was adsorbed only on the crystal surface. Further X-ray measurements were carried out to clear up the possible change of the crystal structure during the heating process. The results are given in Figs 2–3. The spectra were obtained at the maximum speed of the goniometer and at the same heating rate as during the thermal analysis. The peak intensity change is continuous in the internal

A - B, and is finished at 398 K. The further water loss is not followed by changing of the X-ray spectra in the temperature interval *B - C - D*. In the region (*D - E - F*) where one mole structural water is lost, an intensive change of the X-ray spectra was found again. Based on these results, we assumed that the first 0.5 mole

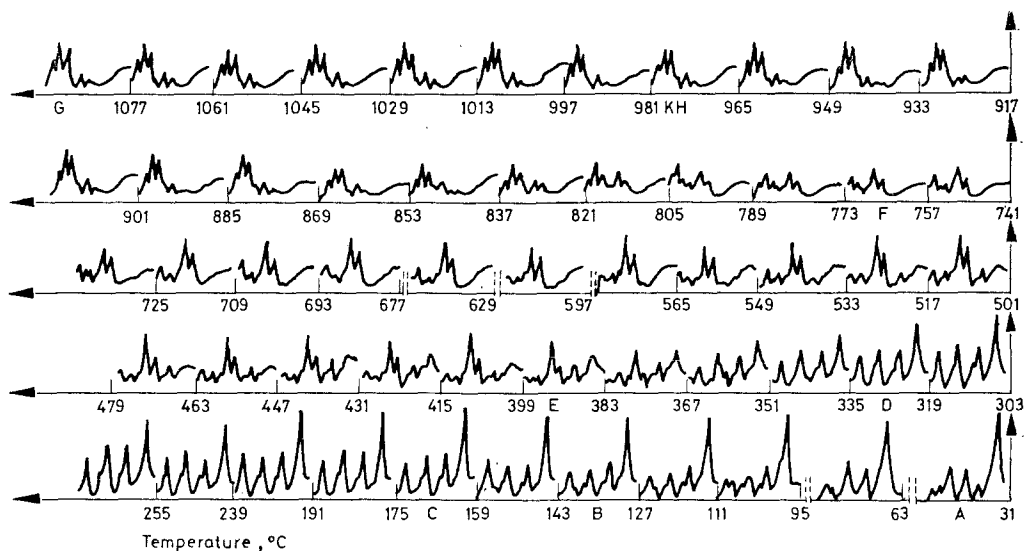


Fig. 2. X-ray diffractograms in the temperature interval 293–1273 K

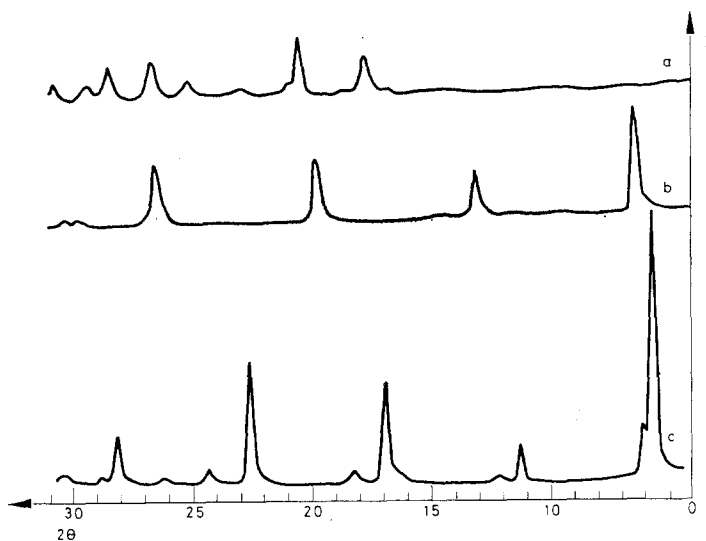


Fig. 3. X-ray diffractograms at various temperatures: curve a — at 973 K; curve b — at 523 K; curve c — at 298 K

crystalline water loss is followed by the change of the structure; the 0.83 mole water loss did not produce a change in the structure of the sample. The loss of structural water caused a considerable change in the structure; after this water loss a new characteristic for the oxides, crystal structure being, but this changed at the moment when the $1/4 O_2$ was lost. These considerations may be confirmed by

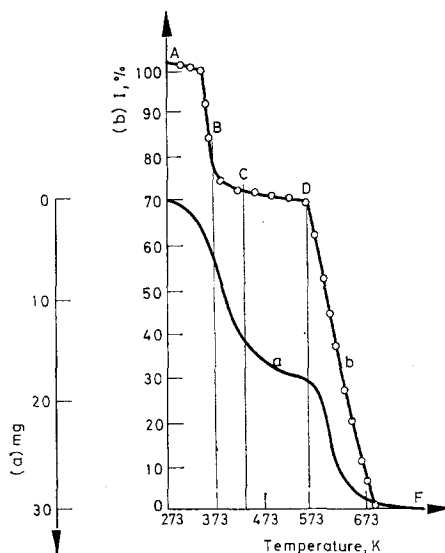


Fig. 4. Comparison of the TG curves with the first peak intensity changes

Table 2

The change of the first interplanar distance and first peak intensity with temperature

T, K	d, Å	I _{rel.} %	T, K	d, Å	I _{rel.} %
303	15.388	100.0	553	13.483	70.0
333	14.717	99.0	563	13.483	69.9
353	14.596	93.5	573	13.483	69.6
373	14.359	78.0	583	13.381	74.5
393	13.586	72.5	593	13.381	57.1
413	13.586	72.3	603	13.381	51.8
433	13.586	72.0	613	13.381	42.0
453	13.483	71.9	633	13.381	32.5
473	13.483	71.2	643	13.381	14.0
493	13.483	70.8	663	13.381	10.0
503	13.483	70.5	673	13.381	7.0
513	13.483	70.3	683	13.381	3.0
523	13.483	70.2	693	13.381	1.0
533	13.483	70.1	703	13.381	0.0

comparing the X-ray spectra in Fig. 3. In curves *b* and *c* similar peaks with various intensities and positions (changes) in the direction of higher 2θ values were found. This means that, in agreement with the water loss for the given temperature interval, only the distance between the layers changed, without any change in the crystal structure. In comparison to these curves, the X-ray spectrum of *a* had a quite different character, corresponding to another crystalline structure. In agreement with the thermal analysis, the material without crystalline water had the composition $\text{Ce}(\text{HPO}_4)_2$.

On the above basis, the interlayer distance depends on the quantity and the form of bonding of the crystalline water.

Comparison of the weight loss curves (TG) and the change in intensity of the first peak (X-ray diffractograms) *vs.* temperature (Fig. 4; Table 2) revealed a decrease in the interval *A* – *B*. The intensity is almost constant in the interval *B* – *D*, but decreases quickly to zero in the temperature interval *D* – *F*. It can be seen that all these changes are in good agreement with the weight losses. To summarize the above findings from the results of the thermal and X-ray analysis, crystalline water bound in the molecule in various ways can be quantitatively distinguished. It was found that this phenomenon has a definite influence on the layer distance. Via the X-ray measurements, the changes taking place in the crystal structure during the heating process could be followed.

References

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RÉSUMÉ — Le bis(monohydrogène)phosphate de cérium $[\text{Ce}(\text{HPO}_4)_2 \cdot 1,33 \text{H}_2\text{O}]$ cristallin a été synthétisé et identifié par les méthodes analytiques et par rayons X.

La décomposition thermique a été suivie par TG, TGD et ATD simultanées. Les résultats des essais ont mis en évidence quatre processus endothermiques avec perte de poids: les deux premiers, avec des pics sensiblement égaux à 373 et 423 K, le troisième à 653 K et le dernier à 1053 K. Après chauffage au-dessus de 1273 K le matériau a été étudié à l'aide des mêmes méthodes analytiques. D'après ces données, les pertes de poids peuvent sans doute être attribuées à des pertes d'eau et d'oxygène. L'analyse thermique a été étayée par examen aux rayons X. Le rapprochement des résultats a permis de distinguer de façon quantitative divers modes de liaison de l'eau de cristallisation dans la molécule. On établit que ce phénomène a une influence définie sur la distance des couches.

Les mesures aux rayons X ont permis de suivre le changement de la structure cristalline pendant le chauffage.

ZUSAMMENFASSUNG — Das kristalline Cer-bis-phosphat $[\text{Ce}(\text{HPO}_4)_2 \cdot 1.33 \text{H}_2\text{O}]$ wurde synthetisiert und durch Röntgen- und analytische Methoden identifiziert.

Die thermische Zersetzung wurde durch simultane TG-, DTG- und DTA-Messungen untersucht. Als Ergebnis der Untersuchungen wurden vier endotherme Vorgänge mit Gewichtsverlust gefunden: die ersten zwei annähernd gleichen Peaks bei 373 und 423 K, der Dritte bei 635 K und der Letzte bei 1053 K. Nach Erhitzen über 1273 K wurde die Substanz mit den gleichen analytischen Methoden untersucht. Im Zusammenhang mit diesen Angaben wurde angenommen, dass die Gewichtsverluste der Abgabe von Wasser und Sauerstoff zugeordnet werden können. Die Thermoanalyse wurde durch Röntgenuntersuchungen unterstützt. Durch gemeinsame Auswertung der Ergebnisse der Thermo- und Röntgenanalyse konnte das im Molekül auf verschiedene Arten gebundene Kristallwasser quantitativ unterschieden werden. Es wurde gefunden, dass dieses Phänomen einen ausgeprägten Einfluss auf den Abstand der Schichtenentfernung hat.

Durch Röntgenmessungen konnten die während des Aufheizvorganges stattfindenden Veränderungen der Kristallstruktur verfolgt werden.

Резюме — Кристаллический бис-монозамещенный фосфат церия $[\text{Ce}/\text{HPO}_4/2 \cdot 1.33 \text{H}_2\text{O}]$ был синтезирован и идентифицирован рентгенографическим и аналитическим методами. Термическое разложение было исследовано одновременным измерением ТГ, ДТГ и ДТА. В результате исследования было найдено четыре эндотермических процесса, сопровождающихся потерей веса: первые два, почти равных пика, при температурах 373 и 423 К, третий — при 653 К и последний — при 1053 К. Это соединение после нагревания выше 1273 К было исследовано теми же самыми аналитическими методами. На основе полученных результатов было предположено, что потери веса могут быть идентифицированы как потеря воды и кислорода. Данные термического анализа были подтверждены рентгенографическими измерениями. Полученные результаты термического и рентгенографического анализов позволяют количественно различить кристаллизационную воду, различным образом связанную в молекуле. Было найдено, что это явление оказывает определенное влияние на слоистое расстояние. Продолжаются рентгенографические исследования изменения кристаллической структуры, имеющей место в процессе нагревания.