Dehydration of $GdPO_4 \cdot xH_2O$

[a]I. HORVÁTH, [b]L. P. MEZENTSEVA, and [a]V. FIGUSCH

[a]*Institute of Inorganic Chemistry, Slovak Academy of Sciences, 809 34 Bratislava*

[b]*Institute of Silicate Chemistry, Academy of Sciences of USSR, Leningrad*

Received 25 August 1980

Dehydration and rehydration of hexagonal modification of $GdPO_4$ was studied thermoanalytically by TG and DSC methods. It was found that H_2O molecules are bound in $GdPO_4$ hydrate in two energetically different levels. The first step of dehydration ends at 100°C, the second step takes place between 170 and 230°C. The first step of dehydration corresponds to the release of water molecules bound by weak forces on the surface of crystals and in the pores (hygroscopic water). During the second step the molecules of water bounded in channels of the skeletal structure of $GdPO_4$ are released. The results of TG and DSC analysis have shown the reversibility of the dehydration and the rehydration of $GdPO_4$ in the temperature interval 170—230°C.

The values for enthalpy changes of the first and second step of dehydration of $GdPO_4$ are very close (44.7 and 47.7 kJ mol H_2O^{-1}, respectively) and approximate the values observed for the release of water bound in substances in molecular form.

The amount of water released in the second step of dehydration process can be regarded as a characteristic diagnostic feature of given orthophosphate.

Дегидратация и регидратация гексагональной модификации $GdPO_4$ была изучена термоаналитическими методами ТГ и ДСК. Было обнаружено, что молекулы H_2O в гидрате $GdPO_4$ образуют связь на двух энергетически различных уровнях. Степень I дегидратации заканчивается при температуре 100°C, степень II дегидратации происходит в диапазоне температур 170—230°C. Степени I соответствует выделение молекул воды, связанных с поверхностью кристаллов слабыми силами и порами (гидроскопическая вода), а на степени II улетучиваются молекулы воды, занимающие определенные положения в каналах скелетообразной структуры. Результаты ТГ и ДСК показали, что дегидратация и регидратация $GdPO_4$ в диапазоне 170—230°C являются обратимыми процессами.

Значения изменений энтальпии степеней I и II дегидратации $GdPO_4$ весьма близки (44,7 и 47,7 кДж моль H_2O^{-1} соответственно) и соответствуют значениям, получаемым при освобождении воды, связанной в виде молекул H_2O.

Количество воды, которое освобождается в степени II дегидратации, можно считать характерным диагностическим показателем соответствующего ортофосфата.

The phosphates of lanthanoides (rare-earth elements) belong to substances which are intensively studied with the aim to prepare materials with special properties.

Rare earth orthophosphates can be obtained from aqueous solutions in the form of hexagonal hydrates of the general formula $XPO_4 \cdot 0.5—2.0H_2O$ [1]. They are analogues of the mineral rabdophane ($CePO_4 \cdot 0—0.5H_2O$) and, also of the synthetic bismuthum orthophosphate [2]. Hexagonal gadolinium orthophosphate has unit cell parameters $a = 0.689$ nm and $c = 633$ mm [3]. By heating to 550°C arises monoclinic modification, isostructural with monazite, which is transformed to tetragonal modification at the temperature over 1700°C [4]. The properties of $GdPO_4$ polymorphs are described in [5]. In all three polymorphous modifications the same structural element can be found — a chain of alternating polyhedra [GdO_8] and [PO_4] connected by common edges. Each chain is interconnected with neighbouring four chains by means of perpendicularly oriented Gd—O bonds. In a hexagonal modification the chains are arranged along the symmetry axis. As a consequence of high symmetry of arrangement a loosely packed skeletal structure with channels is formed where molecules of water can be localized [4].

Thermal decomposition of hydrated phases $GdPO_4 \cdot xH_2O$ was studied to this time mostly by the DTA method [4, 6, 7]. In the present work we try to extend the information about this process by means of TG and DSC measurements.

Experimental

Sample preparation

The organophosphate $GdPO_4 \cdot xH_2O$ was prepared by precipitation of $Gd(NO_3)_3$ and $NH_4H_2PO_4$ aqueous solutions (concentration of both approx. 0.2 M) at pH 8—9

$$2Gd(NO_3)_3 + 2NH_4H_2PO_4 = 2GdPO_4 + 2NH_4NO_3 + 4HNO_3$$

The precipitate $GdPO_4 \cdot xH_2O$ was filtered off, rinsed and dried at 120°C in the air. X-Ray diffraction analysis confirmed an almost amorphous character of the substance obtained. Chemical analysis (62.27% Gd_2O_3, 25.05% P_2O_5, loss on heating at 1100°C 12.47%) corresponds to the composition $0.97Gd_2O_3 \cdot P_2O_5 \cdot 2H_2O$.

A sample of the crystalline hexagonal modification of $GdPO_4 \cdot xH_2O$ for thermoanalytical study was obtained by heating of the dried precipitate at 400°C for 10 days and by subsequent air humidity hydration at room temperature.

Thermal analysis

The amount of absorbed water was determined by TG 951 thermobalance module of the DuPont 990 thermoanalyzer, the enthalpy changes of the dehydration process using DSC module.

The measurements were made at the following conditions: mass of samples 10—20 mg; temperature interval 20—400°C; rate of heating 10 K min^{-1}; flowing nitrogen atmosphere 1 cm^3 s^{-1}.

After finishing of the dehydration, the process of resorption of H_2O was studied by the TG and DSC method in flowing N_2 saturated with water vapour at 25°C ($p_{H2O} = 2.7$ kPa).

Results and discussion

Thermogravimetric dehydration curve of the hexagonal $GdPO_4 \cdot xH_2O$ is shown in Fig. 1 (curve *a*). A discontinuity on this curve between 100 and 200°C testifies

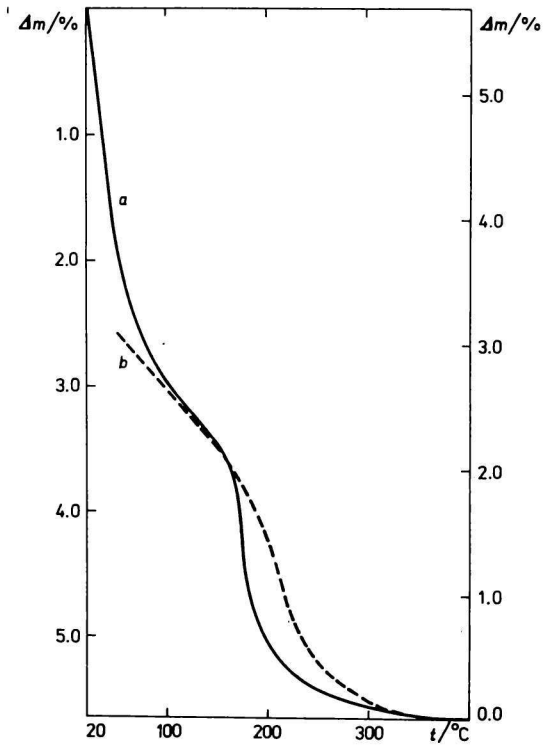

Fig. 1. TG curve of dehydration and rehydration (curve *b*) of $GdPO_4 \cdot xH_2O$. The scale on the right is respective for the curve *b*.

to dehydration in two steps. From the TG curve it was possible to determine the amounts of water released in single steps (Table 1). Curve *b* represents the course of H_2O (g) resorption, as was registered during cooling in thermobalance module.

DSC curves, recorded during heating and cooling of the sample (resorption) are presented in Fig. 2. A stepwise character of the dehydration process was confirmed by two distinct endothermic effects on DSC curve in temperature interval 30—100 and 170—230°C, respectively.

The enthalpy changes were calculated according to the relation

$$\Delta H = k \frac{A}{m}$$

where k is the temperature-dependent calibration factor evaluated from the known phase transformation enthalpies of standard materials (In, Zn, Sn), A is the peak area, and m is the mass of analyzed sample. The obtained ΔH values are presented in Table 1 (negative value $-\Delta H$ represents the heat evolution during resorption of H_2O by dehydrated sample in the course of cooling).

Table 1

Results of thermoanalytical measurements

	Dehydration	
	First step 20—100°C	Second step 170—230°C
Weight loss, %	3.24	2.43
ΔH/kJ mol H_2O^{-1}	44.7	47.7
$-\Delta H$/kJ mol H_2O^{-1}		48.9

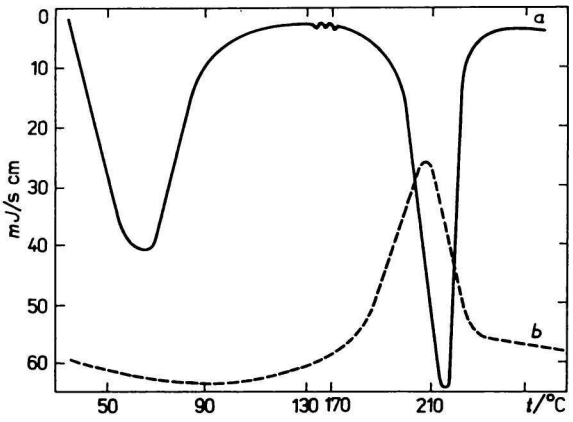

Fig. 2. DSC curves of dehydration and rehydration (curve *b*) of 10.25 mg sample of $GdPO_4 \cdot xH_2O$.

From thermoanalytical measurements and stoichiometry calculations resulted that the studied hexagonal modification of $GdPO_4$ contains 0.84 mole H_2O. The course of thermoanalytical curves has shown, however, that water molecules are bound in two energetically different levels. The first step of dehydration corresponds to the release of the water molecules from the crystal surfaces and the pores (hygroscopic water). The amount of this kind of water depends on conditions of storing of $GdPO_4$ (namely p_{H_2O} of the gas environment, temperature, and time of interaction). Molecules of water released during the second step of dehydration are of other character from the energetical viewpoint. Their amount is constant and the equilibrium is attained after a short time of rehydration. It can be supposed that in this case certain positions in the crystal structure of the substance are occupied by H_2O molecules during hydration. Obviously, the positions in the earlier mentioned channels of skeletal structure are filled, which reminds the water arrangement in zeolites.

The values of enthalpy changes for the release of the both kinds of water bound in hexagonal $GdPO_4$ are very similar (44.7 and 47.7 kJ mol^{-1}) and corresponds to the values observed for the release of water from another hydrates [8]. Higher energy for the release of water positioned in channels of $GdPO_4$ structure testifies to stronger bond of this portion of H_2O in the investigated substance.

Comparison of thermoanalytical measurements of dehydration and rehydration of $GdPO_4$ in the temperature interval 170—230°C has shown that a reversible process takes place. This can be described by the equation

$$GdPO_4 + 0.36H_2O = GdPO_4 \cdot 0.36H_2O$$

Thus, the amount of water is defined, which can be regarded as a characteristic diagnostic feature of given orthophosphate mirroring its structural and physicochemical properties. It can be recommended to distinguish individual kinds of water molecules in the formula of the hydrated phases in the form

$$XPO_4 \cdot n_1H_2O \cdot n_2H_2O$$

where n_1 is the amount of water (in moles) bound on the surface and in the pores of polycrystalline material and n_2 is the amount of water positioned in free spaces in the crystal structure of the hexagonal rare-earth orthophosphate. The material investigated in the present work manifested in this case the composition $GdPO_4 \cdot 0.48H_2O \cdot 0.36H_2O$.

Conclusion

Hexagonal modifications of the rare-earth orthophosphates occur in the form of hydrates. A thermoanalytical study of dehydration and rehydration of

$GdPO_4 \cdot xH_2O$ has shown that the molecules of water are bound in two energetically different levels. In the course of the first step of dehydration hygroscopic water is released between 20—100°C. The amount of this water depends on the conditions of storing. Water molecules, released at higher temperatures, which are supposed to occupy free spaces in the crystal structure remind the water occurring in zeolites. The amount of this kind of water which can be readily resorbed is stable and can be regarded as a characteristic diagnostic feature of a hydrated orthophosphate. The values of the enthalpy changes determined for the first and second dehydration step are both close to the values found for the dehydration process of the hydrates of inorganic salts.

References

1. Petushkova, S. M. and Tananaev, I. V., *Zh. Neorg. Khim. 5,* 1064 (1963).
2. Mooney-Slater, R. C. L., *Z. Kristallogr. B117*, 371 (1962).
3. Kuznetsov, V. G., Petrushkova, S. M., and Tananaev, I. V., *Zh. Strukt. Khim. 5,* 397 (1964).
4. Bondar, I. A., Domanskii, A. I., Mezentseva, L. P., Degen, M. G., and Kalinina, N. E., *Zh. Neorg. Khim. 21*, 2045 (1976).
5. Bondar, I. A. and Tananaev, I. V., in *Uspekhi fiziki i khimii silikatov*, p. 85. Nauka, Leningrad, 1978.
6. Mezel, A. and Ross, S. D., *Spectrochim. Acta 22*, 1949 (1953—1954).
7. Kuznetsov, V. G., Petushkova, S. M., and Tananaev, I. V., *Zh. Neorg. Khim. 14*, 2753 (1969).
8. Hamad, S. El D., *Thermochim. Acta* 17, 85 (1976).

Translated by V. Figusch