

## THERMOCHEMISTRY OF HYDRATED RARE EARTH ORTHOPHOSPHATES

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The hydrated rare earth orthophosphates  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La–Dy}$ ) contain zeolitic water in the structural channels, which is released reversibly up to  $300^\circ$ . The thermal stabilities of the hydrates depend upon the nature of the Ln atom. The dehydration temperature decreases with decreasing ionic radius  $r$  of  $\text{Ln}^{3+}$ , according to the general equation  $\theta = (r - a)/b$  (where  $\theta$  is the DSC and/or DTG dehydration peak temperature, and  $a$  and  $b$  are empirical constants depending on the experimental conditions).

The contracting-area rate equation was valid for linearization of the isothermal  $\alpha$  vs. time plots in the range  $\alpha \in (0; 0.65)$ . Kinetic values of  $E$ ,  $A$ ,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated and the kinetic stabilities of the hydrates are discussed.

The hydrated rare earth orthophosphates  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La–Lu}$ , Y and Sc) form two structural groups:

(a)  $\text{LnPO}_4$  hydrated ( $\text{Ln} = \text{La–Dy}$ ) crystallizing in hexagonal symmetry [1, 2], which are isostructural with the mineral rhabdophane ( $\text{CePO}_4 \cdot 0.5\text{H}_2\text{O}$ ), in which Mooney [1, 2] found zeolitic water bound in the channels of the structure. Kuznetsov et al. [3, 4] used X-ray diffraction methods and described zeolitic water in  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La, Pr, Nd and Sm}$ ). They concluded that this water does not stabilize the structure of  $\text{LnPO}_4$  up to  $300^\circ$ . Further complementary data on these compounds are given elsewhere [5–9].

(b) The structure of the second group of  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  involves smaller  $\text{Ln}^{3+}$  ( $\text{Ln} = \text{Ho–Lu}$ , Y and Sc). These compounds crystallize in tetragonal symmetry, and the water is arranged differently than in the former group [7].

In this work we have studied the thermochemical properties of the zeolitic water present in  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  of structural group (a), the kinetics of its release and some correlations between the thermal behaviour of the hydrate and the ionic radius of  $\text{Ln}^{3+}$ .

## Experimental

The samples of  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  were prepared by precipitation from 0.2 M solutions of  $\text{Ln}(\text{NO}_3)_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at pH 8–9.

Thermoanalytical measurements were performed with a DuPont 990 Thermoanalyzer, using the TG 951 thermobalance and the DSC cell. 10–20 mg samples were heated isothermally and/or at constant heating rate ( $10 \text{ deg min}^{-1}$ ) in static air or in a  $\text{N}_2$  stream ( $1 \text{ cm}^3 \text{ s}^{-1}$ ), then rehydrated during programmed cooling ( $5 \text{ deg min}^{-1}$ ) in a  $\text{N}_2$  stream saturated with  $\text{H}_2\text{O}$  at room temperature.

Enthalpy changes of dehydration ( $\Delta H_1$ ) or rehydration ( $-\Delta H_2$ ) were evaluated from the DSC curves.

## Results and discussion

In principle, two distinct steps of dehydration occur during heating up to  $300^\circ$  (Figs 1 and 2). The first step indicates the release of physically bound water (hygroscopic water); the escape of zeolitic water occurs at higher temperatures. Whereas the amount of hygroscopic water depends strongly on the conditions of storage, the amount of zeolitic water remains constant for each sample and equilibrium is established very rapidly during rehydration. The reversibility of the dehydration–rehydration processes may be described by the equation:

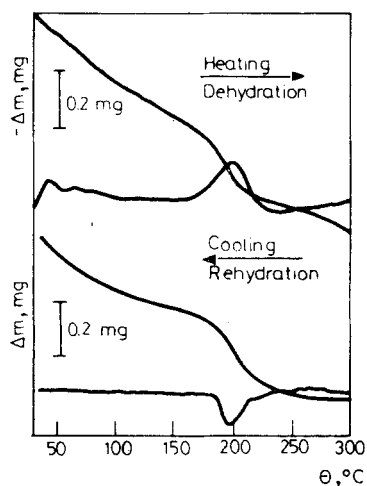
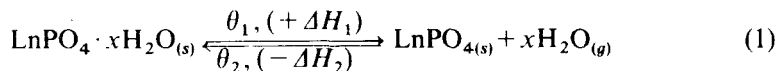


Fig. 1 TG and DTG curves for dehydration and rehydration of  $\text{LnPO}_4$  in  $\text{N}_2$



where  $x$  is the number moles of zeolitic water, and  $\theta_{1,2}$  and  $\Delta H_{1,2}$  are the DTG or DSC peak temperatures and the enthalpy changes of dehydration and rehydration, respectively. The data determined for Eq. (1) are presented in Table 1. They show that the nature of the Ln atom does not influence the amount, but it does lead to variations in the temperature and enthalpy change of the release of zeolitic water. The dehydration peak temperature decreases with decrease of the ionic radius  $r$  of  $\text{Ln}^{3+}$  in the sequence:

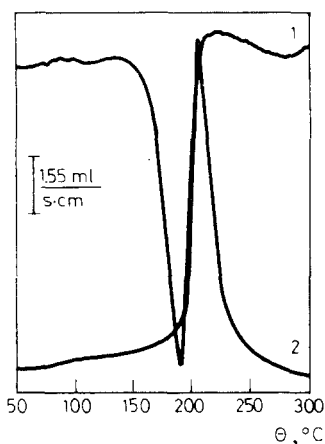


Fig. 2 DSC curves for dehydration (1) and rehydration (2) of  $\text{LnPO}_4$  in  $\text{N}_2$

Table 1 Thermochemical data on dehydration–rehydration reaction of  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$

| Sample            | $\frac{x}{\text{mol H}_2\text{O}}$ | Dehydration                |     |                                   |     |     | Rehydration                                    |     |   |  |
|-------------------|------------------------------------|----------------------------|-----|-----------------------------------|-----|-----|--|-----|---|--|
|                   |                                    | $\theta_1, ^\circ\text{C}$ |     |                                   |     |     | $\Delta H_1$ $\text{N}_2 + \text{H}_2\text{O}$ |     |   |  |
|                   |                                    | $\text{N}_2$               |     | $\text{N}_2 + \text{H}_2\text{O}$ |     | air | $\text{N}_2$                                   |     | $\theta_2, ^\circ\text{C}$ $\Delta H_2$ |  |
|                   |                                    | DSC                        | DTG | DSC                               | DTG | DSC | DSC  | DSC | DSC                                     |  |
| TbPO <sub>4</sub> | 0.46                               | 165                        | 148 | 180                               | 171 | 204 | 59   | 162 | 55                                      |  |
| GdPO <sub>4</sub> | 0.47                               | 175                        | 155 | 196                               | 180 | 208 | 56   | 176 | 49                                      |  |
| EuPO <sub>4</sub> | 0.39                               | 180                        | 162 | 197                               | 191 | 207 | 56   | 177 | 48                                      |  |
| NdPO <sub>4</sub> | 0.53                               | 192                        | 166 | 215                               | 199 | 222 | 45   | 196 | 37                                      |  |
| LaPO <sub>4</sub> | 0.53                               | 200                        | 183 | 230                               | 214 | 243 | 44   | 215 | 32                                      |  |

\* The values of  $\Delta H_1$  and  $\Delta H_2$  are in  $\text{kJ mol}^{-1} \text{H}_2\text{O}$ .

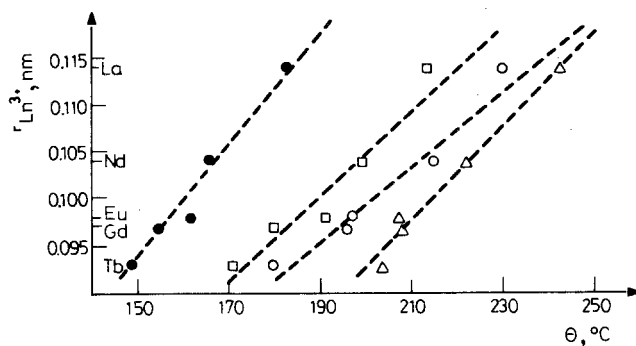


Fig. 3 The relations between DSC and/or DTG peak temperature and the ionic radii of  $\text{Ln}^{3+}$  at various experimental conditions. • DTG ( $\text{N}_2$ ) □ DTG ( $\text{N}_2 + \text{H}_2\text{O}$ ) ○ DSC ( $\text{N}_2 + \text{H}_2\text{O}$ ) △ DSC (sl. air)

The most pronounced linear relations  $\theta_1 = f(r)$  are shown in Fig. 3, and may be described by the general equation:

$$\theta_1 = (r - a)/b \quad (2)$$

where  $a$  and  $b$  are constants depending upon the experimental conditions. The best straight-line fit (correlation coefficient = 0.997) was given by DSC measurements in  $\text{N}_2$ . Table 1 also shows some relations between the calorimetric values and the nature of the Ln atom. The enthalpy change of rehydration increases with decreasing  $\text{Ln}^{3+}$  ionic radius in the sequence:

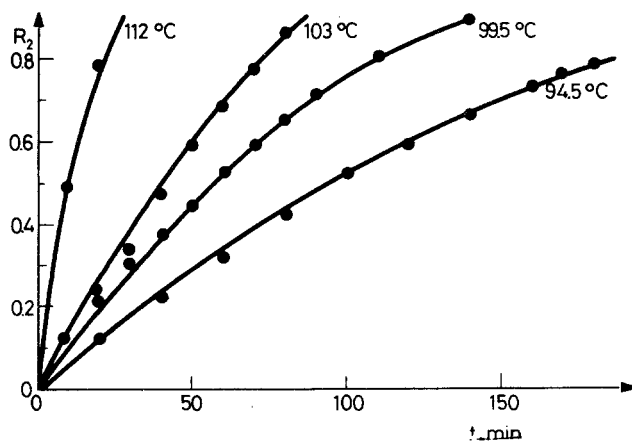


Fig. 4 Isothermal dehydration of  $\text{TbPO}_4 \cdot 0.46 \text{H}_2\text{O}$  in  $\text{N}_2$

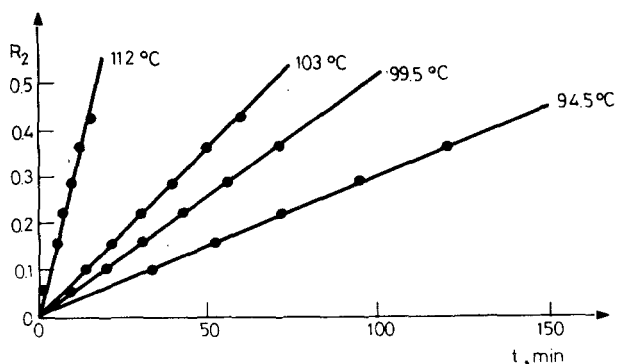


Fig. 5 Dehydration of  $\text{TbPO}_4 \cdot 0.46 \text{H}_2\text{O}$  plotted with the contracting area rate equation

The kinetics of dehydration was studied isothermally. Isothermal  $\alpha$  (fraction dehydrated) vs. time plots (Fig. 4) were correlated with selected kinetic models for the best straight-line fit, and the rate constants were computed. It was found that the dehydration obeyed the rate equation for contracting area (Fig. 5):

$$1 - (1 - \alpha)^{0.5} = kt \quad (3)$$

Finally, the values of energy ( $E$ ), enthalpy ( $\Delta H^\ddagger$ ) and entropy ( $\Delta S^\ddagger$ ) of activation and the preexponential term ( $A$ ) were calculated (Table 2).

The energy of activation and the preexponential term may be used for evaluation of the kinetic stabilities of the hydrates, which may be indicated by the starting temperatures of dehydration, as discussed by Logvinenko [10]. If we assume the highest sensitivity of the DuPont thermobalance to be  $10^{-5} \text{ s}^{-1}$  (expressed as the rate constant), then it is possible to calculate the approximate starting temperatures

Table 2 Kinetic data on dehydration of  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  for  $\alpha \in (0; 0.65)$

| Sample  | $E$ ,<br>$\text{kJ} \cdot \text{mol}^{-1}$ | $A$ ,<br>$\text{s}^{-1}$ | $r$   | $\Delta H^\ddagger$ ,<br>$\text{kJ} \cdot \text{mol}^{-1}$ | $\Delta S^\ddagger$ ,<br>$\text{J} \cdot \text{K}^{-1} \text{mol}^{-1}$ | $\theta_{\text{start.}}$ ,<br>$^\circ\text{C}$ |
|---|--|--------------------------|-------|--|---|--|
| $\text{TbPO}_4 \cdot 0.46 \text{H}_2\text{O}$ | 151  | $10^{17}$                | 0.995 | 148  | 72  | 83.6   |
| $\text{GdPO}_4 \cdot 0.47 \text{H}_2\text{O}$ | 144  | $10^{15}$                | 0.997 | 141  | 45  | 90.3   |
| $\text{EuPO}_4 \cdot 0.39 \text{H}_2\text{O}$ | 127  | $10^{13}$                | 0.996 | 124  | - 3.2   | 91.9   |

$r$  - correlation coefficient of Arrhenius relation (4-5 isothermal measurements);

$\theta$  - the starting temperature of dehydration calculated by means of Arrhenius data and supposed max. sensitivity of thermobalance.

of the release of zeolitic water from  $\text{LnPO}_4$  hydrates via the equation:

$$\ln 10^{-5} = \ln A - \frac{E}{R \cdot \theta_{\text{start}}} \quad (4)$$

where  $A$  and  $E$  are known values from Table 2.

The values of  $\theta_{\text{start}}$  (Table 2) are in good agreement with the sequence determined from the thermal measurements using the DTG or DSC peak temperatures, and confirm the observed correlation between the thermal stabilities of these  $\text{LnPO}_4$  hydrates and the  $\text{Ln}^{3+}$  cation radii.

## References

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**Zusammenfassung** — Die hydratisierten Seltenerdphosphate  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La}$  bis  $\text{Dy}$ ) enthalten in Kanälen ihrer Struktur zeolithisches Wasser, das reversibel bis 300 °C abgegeben wird. Die thermische Stabilität der Hydrate hängt von der Natur des Ln ab. Die Entwässerungstemperatur  $\theta$  sinkt mit abnehmendem Ionenradius  $r$  der  $\text{Ln}^{3+}$ -Ionen gemäss:  $\theta = (r-a)/b$  ( $a$  und  $b$  sind empirische Konstanten, die von den experimentellen Bedingungen abhängen). Die isotherme Entwässerung lässt sich im Umsatzbereich  $0 \leq \alpha \leq 0,65$  mit der Gleichung für kontrahierende Fläche (zweidimensionale Phasengrenzreaktion) beschreiben. Die kinetischen Grössen Aktivierungsenergie  $E$ , -enthalpie  $\Delta H^*$ , und -entropie  $\Delta S^*$  wurden berechnet und die kinetische Stabilität der Hydrate wird diskutiert.

**Резюме** — Ортофосфаты редкоземельных элементов общей формулы  $\text{LnPO}_4 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La} - \text{Dy}$ ) в своих структурных полостях содержат цеолитную воду, выделяющуюся обратимо при температуре до 300°. Термоустойчивость гидратов зависит от природы редкоземельного элемента. Температура дегидратации уменьшается с уменьшением ионного радиуса  $r$  элемента в соответствии с уравнением  $\theta = (r-a)/b$ , где  $\theta$  — ДСК или ДТА температурный пик дегидратации, а  $a$  и  $b$  — эмпирические константы, зависящие от экспериментальных условий. Уравнение скорости реакции типа сжимаемой площади было справедливым для линеаризации графиков изотермическая  $\alpha$  — время в интервале  $\alpha \in \langle 0; 0,65 \rangle$ . Вычислены кинетические величины  $E$ ,  $A$ ,  $\Delta H^*$  и  $\Delta S^*$  и обсуждена кинетическая устойчивость гидратов.