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Thermal dehydration of magnesium selenate hydrates

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Abstract

The thermal dehydration of $MgSeO_4 \cdot 6H_2O$, $MgSeO_4 \cdot 4H_2O$ and $MgSeO_4 \cdot 2H_2O$ has been studied by TG, DTA and DSC. The dehydrations occur in steps and the intermediate hydrates $MgSeO_4 \cdot 5H_2O$, $MgSeO_4 \cdot 4H_2O$, $MgSeO_4 \cdot 2H_2O$ and $MgSeO_4 \cdot H_2O$ are produced. The enthalpies of dehydration of the observed stages have been determined. The enthalpies of formation of $MgSeO_4 \cdot 6H_2O$, $MgSeO_4 \cdot 4H_2O$, $MgSeO_4 \cdot 2H_2O$ and $MgSeO_4 \cdot H_2O$ have been calculated from the DSC data.

Keywords: Dehydration; DSC; DTA; Heat of dehydration; Heat of formation; Magnesium selenate hydrates; Selenate

1. Introduction

The thermal dehydration of the magnesium selenate hydrates has not been fully studied. For example, it is known that $MgSeO_4 \cdot 4.5H_2O$, $MgSeO_4 \cdot 2H_2O$ and $MgSeO_4$ are produced by heating of $MgSeO_4 \cdot 6H_2O$ crystals for several hours at ≈ 60, 100 and 340°C, respectively [1]. Selivanova et al. [2] reported the existence of $MgSeO_4 \cdot 4H_2O$, $MgSeO_4 \cdot H_2O$ and $MgSeO_4$ and published their X-ray powder diffraction data. Nabar and Paralkar, using TG, DTG and DTA, proposed the following mechanism for the thermal dehydration of $MgSeO_4 \cdot 6H_2O$ [3]

$$MgSeO_4 \cdot 6H_2O \rightarrow MgSeO_4 \cdot 5H_2O \rightarrow MgSeO_4 \cdot 3H_2O \rightarrow MgSeO_4$$

The purpose of the present paper is to clarify the literature data on the existence of different magnesium selenate hydrates and on their temperature range of stability

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using TG, DTA and DSC, and to determine the ΔH of dehydration ($\Delta_{deh}H$) and ΔH of formation ($\Delta_f H^{\ominus}$) of magnesium selenate hydrates on the basis of DSC data.

2. Experimental

Magnesium selenate hexahydrate was prepared by neutralization of magnesium hydroxide carbonate with an aqueous solution of selenic acid at 60–70°C. The solution was then filtered and concentrated. Crystals of $MgSeO_4 \cdot 6H_2O$ were obtained after cooling the solution to room temperature. These were recrystallized from water and dried in air. The reagents used were p.a. grade (Merck). Magnesium selenate tetrahydrate and dihydrate were obtained by heating $MgSeO_4 \cdot 6H_2O$ crystals in a thermostat at 40°C for 4–5 d and at 80°C for 4 h, respectively. The salts obtained were identified by chemical analysis (magnesium ion concentrations were determined complexometrically) and X-ray diffraction analysis (DRON-3 powder diffractometer, using CuKα radiation). $MgSeO_4 \cdot 2H_2O$ is stable in air at room temperature for only $\approx$3–4 h.

The thermal dehydration processes were studied using a derivatograph (Paulik–Paulik–Erdey MOM OD-102) in the temperature range up to 600°C at a heating rate of 5°C min^{-1} using α-alumina as a reference material (sample mass 200 mg). The DSC measurements were recorded on a Perkin-Elmer DSC-4 instrument up to 400°C at a heating rate of 2 or 5°C min^{-1} using standard Al pans (sample mass 1–2 mg). The temperature and sensitivity were carefully calibrated before the experiments. Indium (purity > 99.9%) was used as a standard substance.

3. Results and discussion

DTA, TG and DSC curves for $MgSeO_4 \cdot 6H_2O$, $MgSeO_4 \cdot 4H_2O$ and $MgSeO_4 \cdot 2H_2O$ are shown in Figs. 1 and 2. The enthalpies of the dehydration stages of the above hydrates are given in Table 1 (the enthalpy values are mean values of three measurements). The experimental error for $\Delta_{deh}H$ is $\approx$2–2.5%.

It is seen (Fig. 1(a)) that $MgSeO_4 \cdot 6H_2O$ is stable up to 40°C and anhydrous magnesium selenate is formed in four dehydration stages. The dehydration processes occur in the temperature range 40–380°C and are registered on the DTA curve as four endothermic peaks with maxima at 90 (shoulder), 130, 255 and 330°C, respectively. The mass losses calculated from the TG curves show that the following scheme for the dehydration of magnesium selenate hexahydrate could be proposed

$$MgSeO_4 \cdot 6H_2O(s) \xrightarrow{90°C} MgSeO_4 \cdot 5H_2O(s) + H_2O(g)$$

with $\Delta m_{exp} = 5.8\%$, $\Delta m_{th} = 6.5\%$;

$$MgSeO_4 \cdot 5H_2O(s) \xrightarrow{130°C} MgSeO_4 \cdot 2H_2O(s) + 3H_2O(g)$$

with $\Delta m_{exp} = 26.4\%$, $\Delta m_{th} = 26.3\%$;

$$MgSeO_4 \cdot 2H_2O(s) \xrightarrow{255°C} MgSeO_4 \cdot H_2O(s) + H_2O(g)$$

with $\Delta m_{exp} = 32.7\%$, $\Delta m_{th} = 32.7\%$;

$$MgSeO_4 \cdot H_2O(s) \xrightarrow{330°C} MgSeO_4(s) + H_2O(g)$$

with $\Delta m_{exp} = 38.5\%$, $\Delta m_{th} = 39.2\%$.

Anhydrous magnesium selenate is stable in the temperature range 380–620°C.

The dehydration of $MgSeO_4 \cdot 4H_2O$ (Fig. 1(b)) begins at ≈60°C and occurs in steps. Three endothermic peaks are observed on the DTA curve at 118, 260 and 340°C, corresponding to the formation of $MgSeO_4 \cdot 2H_2O$ ($\Delta m_{exp} = 15.2\%$; $\Delta m_{th} = 15.0\%$); $MgSeO_4 \cdot H_2O$ ($\Delta m_{exp} = 23.6\%$; $\Delta m_{th} = 22.6\%$) and $MgSeO_4$ ($\Delta m_{exp} = 30.5\%$; $\Delta m_{th} = 30.1\%$), respectively.

The different stages of dehydration of the magnesium selenate hydrates could be easily distinguished on the DSC curves (Fig. 2(a), (b) and (c)). According to the DSC data, the dehydration begins at 45 and 80°C for the hexahydrate and the tetrahydrate respectively, and completes at 250°C for both salts. The comparison of the DSC curves shows that the first observed endothermic effect for $MgSeO_4 \cdot 6H_2O$ at $T_{max} = 67.7$°C (Fig. 2(a)) is due to the loss of two water molecules, thus producing $MgSeO_4 \cdot 4H_2O$ (Table 1). At temperatures higher than 80°C the shapes of both DSC curves are identical, indicating the formation of the same intermediate products (Table 1). In the temperature range 80–140°C,

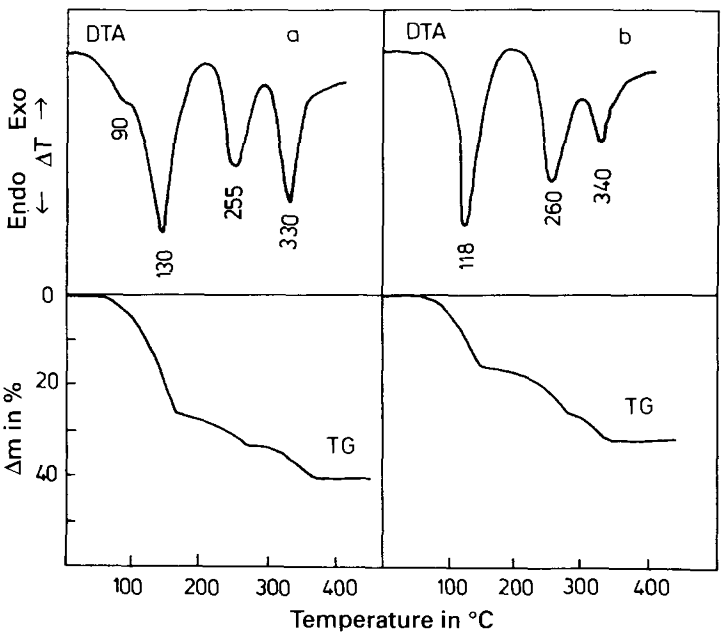

Fig. 1. TG and DTA curves of (a) $MgSeO_4 \cdot 6H_2O$ and (b) $MgSeO_4 \cdot 4H_2O$.

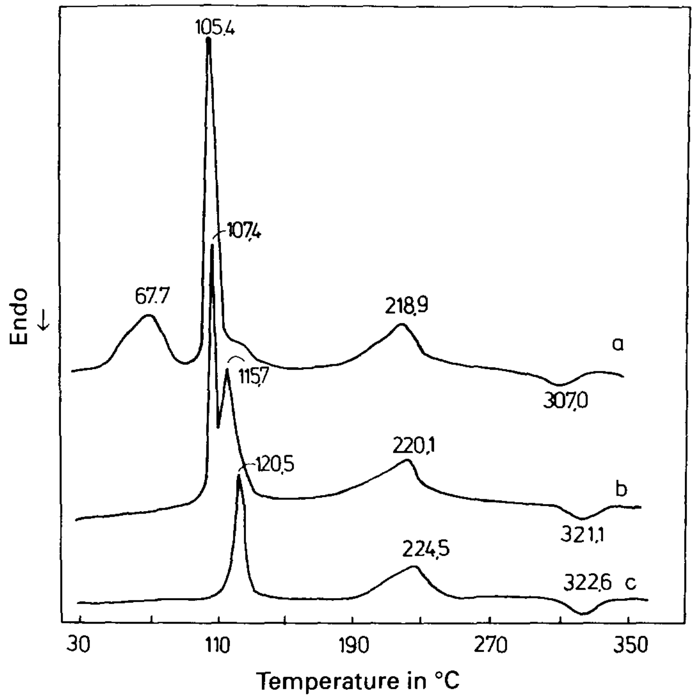

Fig. 2. DSC curves of (a) $MgSeO_4 \cdot 6H_2O$, (b) $MgSeO_4 \cdot 4H_2O$ and (c) $MgSeO_4 \cdot 2H_2O$.

$MgSeO_4 \cdot 4H_2O$ is transformed into $MgSeO_4 \cdot H_2O$, which is stable up to 170°C. At temperatures above 170°C anhydrous magnesium selenate is formed. The peak shapes in both DSC curves corresponding to the stage tetrahydrate → monohydrate (80–140°C) show that this dehydration process occurs in steps. Taking into consideration the DTA data, we assume that $MgSeO_4 \cdot 4H_2O$ is converted through $MgSeO_4 \cdot 2H_2O$ to $MgSeO_4 \cdot H_2O$. Unfortunately, DSC measurements at a lower heating rate of 2°C min^{-1} did not lead to the resolution of the two dehydration steps. In order to isolate $MgSeO_4 \cdot 2H_2O$, the crystals of $MgSeO_4 \cdot 6H_2O$ were heated at 80°C for 4 h. The DSC curve of the dihydrate is shown in Fig. 2(c), and it proves that the stage $MgSeO_4 \cdot 4H_2O \rightarrow MgSeO_4 \cdot 2H_2O$ assumed above did occur.

The observed exothermic effect at $T_{max} = 322.3$, 321.1 and 322.6°C in Fig. 2(a), (b) and (c), respectively, is due either to a polymorphous transition of anhydrous magnesium selenate or to the formation of amorphous $MgSeO_4$ followed by a transformation into crystalline $MgSeO_4$. Our X-ray diffraction study of $MgSeO_4 \cdot 6H_2O$ at elevated temperature shows that amorphous $MgSeO_4$ is formed at ≈250°C and crystallizes at higher temperature [4]. For that reason we assume that the above exothermic effect corresponds to the formation of a crystalline $MgSeO_4$ from the amorphous product initially obtained.

The $\Delta_{deh}H$ for the dehydration $MgSeO_4 \cdot 4H_2O(s) \rightarrow MgSeO_4 \cdot 2H_2O(s) + 2H_2O(g)$ has been calculated as a difference in $\Delta_{deh}H$ of tetra- and dihydrates, respectively, to anhydrous salts ($\Delta_{deh}H = 65.3$ kJ mol^{-1}).

Using the $\Delta_{deh}H$ data obtained from the DSC measurements, as well as the $\Delta_f H^{\ominus}$ of $MgSeO_4$ [5], we have calculated the enthalpies of formation for the hexa-, tetra-, di- and monohydrates of magnesium selenate.

$\Delta_f H^{\ominus}$ of $MgSeO_4 \cdot 6H_2O = 2721.6$ kJ mol^{-1} (2793.9 kJ mol^{-1})

$\Delta_f H^{\ominus}$ of $MgSeO_4 \cdot 4H_2O = 2152.1$ kJ mol^{-1} (2204.8 kJ mol^{-1})

$\Delta_f H^{\ominus}$ of $MgSeO_4 \cdot 2H_2O = 1603.1$ kJ mol^{-1}

$\Delta_f H^{\ominus}$ of $MgSeO_4 \cdot H_2O = 1280.2$ kJ mol^{-1} (1310.3 kJ mol^{-1})

For comparison the data reported by Selivanova [5] are given in parentheses.

Our attempts to isolate and study $MgSeO_4 \cdot 5H_2O$, the existence of which was registered on the DTA curve, were unsuccessful. However, its temperature range of stability is clearly seen in the X-ray diffraction patterns obtained at elevated temperature. These results, as well as the crystallographic data of all magnesium selenate hydrates, will be published subsequently [4].

Table 1
DSC data for dehydration of magnesium selenate hydrates

Phase transition	T_{onset}/°C	ΔH/(kJ mol^{-1})
$MgSeO_4 \cdot 6H_2O(s) \rightarrow MgSeO_4 \cdot 4H_2O(s) + 2H_2O(g)$	53.2	79.8
$MgSeO_4 \cdot 4H_2O(s) \rightarrow MgSeO_4 \cdot 2H_2O(s) + 2H_2O(g)$	103.2	154.4
$MgSeO_4 \cdot 2H_2O(s) \rightarrow MgSeO_4 \cdot H_2O(s) + H_2O(g)$		
$MgSeO_4 \cdot H_2O(s) \rightarrow MgSeO_4(s) + H_2O(g)$	189.8	66.7
$MgSeO_4(s)$ (amorphous) $\rightarrow MgSeO_4(s)$ (crystalline)	300.5	−12.0
$MgSeO_4 \cdot 6H_2O(s) \rightarrow MgSeO_4(s) + 6H_2O(g)$		288.4
$MgSeO_4 \cdot 4H_2O(s) \rightarrow MgSeO_4 \cdot 2H_2O(s) + 2H_2O(g)$ }	104.8	138.2
$MgSeO_4 \cdot 2H_2O(s) \rightarrow MgSeO_4 \cdot H_2O(s) + H_2O(g)$ }		
$MgSeO_4 \cdot H_2O(s) \rightarrow MgSeO_4(s) + H_2O(g)$	186.1	58.8
$MgSeO_4(s)$ (amorphous) $\rightarrow MgSeO_4(s)$ (crystalline)	305.1	−12.5
$MgSeO_4 \cdot 4H_2O(s) \rightarrow MgSeO_4(s) + 4H_2O(g)$		201.5
$MgSeO_4 \cdot 2H_2O(s) \rightarrow MgSeO_4 \cdot H_2O(s) + H_2O(g)$	117.7	79.5
$MgSeO_4 \cdot H_2O(s) \rightarrow MgSeO_4(s) + H_2O(g)$	194.5	70.2
$MgSeO_4(s)$ (amorphous) $\rightarrow MgSeO_4(s)$ (crystalline)		−12.8
$MgSeO_4 \cdot 2H_2O(s) \rightarrow MgSeO_4(s) + 2H_2O(g)$		136.2
$MgSeO_4 \cdot H_2O(s) \rightarrow MgSeO_4(s) + H_2O(g)$		55.1 [a]

[a] The $\Delta_{deh}H$ value is calculated as a mean value from the DSC data for this phase transition of hexa-, tetra- and dihydrates.

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