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TG, DTA, DSC and X-ray powder diffraction studies on some nickel selenate hydrates

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Abstract

The thermal dehydration of $NiSeO_4 \cdot 6H_2O$, $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot H_2O$ has been studied by TG, DTA and DSC. The dehydration of $NiSeO_4 \cdot 6H_2O$ depends on both the heating rate and the sample mass. The following intermediate hydrates are produced: $NiSeO_4 \cdot 5H_2O$; $NiSeO_4 \cdot 4H_2O$; $NiSeO_4 \cdot 2H_2O$; $NiSeO_4 \cdot H_2O$ and $NiSeO_4 \cdot 0.5H_2O$. The enthalpies of dehydration of these stages have been determined. The enthalpies of formation of $NiSeO_4 \cdot 6H_2O$; $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot H_2O$ (amorphous and crystalline) as well as the enthalpy of transformation of amorphous $NiSeO_4 \cdot H_2O$ into crystalline $NiSeO_4 \cdot H_2O$ have been calculated from DSC data. The lattice parameters of $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot 2H_2O$ have been calculated. $NiSeO_4 \cdot 4H_2O$ crystallizes in the monoclinic system with lattice parameters: a = 5.959(3) Å; b = 13.771(8) Å; c = 8.023(5) Å; $\beta = 90.66(6)°$; V = 658.3(5) $Å^3$; SG $P2_1/n$. $NiSeO_4 \cdot 2H_2O$ forms orthorhombic crystals with lattice parameters: a = 10.351(4) Å; b = 10.219(4) Å; c = 9.017(5) Å; V = 953.9(6) $Å^3$.

Keywords: Dehydration; DSC; DTA; Heat of dehydration; Heat of formation; Lattice parameters; Nickel selenate hydrates

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1. Introduction

This paper continues our investigations of the thermal dehydration of divalent metal selenate hydrates using TG, DTA and DSC as well as a X-ray powder diffraction at elevated temperatures [1,2,3]. We report results on the thermal dehydration of some nickel selenate hydrates: $NiSeO_4 \cdot 6H_2O$; $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot H_2O$.

Nabar et al. [4], using TG, DTG and DTA, proposed the following mechanism for the thermal dehydration and decomposition of $NiSeO_4 \cdot 6H_2O$:

$$NiSeO_4 \cdot 6H_2O \xrightarrow{300\ C} NiSeO_4 \cdot H_2O \xrightarrow{390\ C}$$

$$NiSeO_4 \xrightarrow{510\ C} NiSeO_3 \xrightarrow{690\ C} NiO$$

According to the above scheme no intermediate hydrates (for example, penta-, tetra- or dihydrates, some of which are known in the literature) were found. In our opinion, the transformation of $NiSeO_4 \cdot 6H_2O$ direct into $NiSeO_4 \cdot H_2O$ is due to the experimental conditions: i.e. the sample mass and heating rate.

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The aim of the present paper is to clarify the literature data on the thermal dehydration of $NiSeO_4 \cdot 6H_2O$, as well as to isolate lower hydrates and study them with TG, DTG and DTA. Based on the results obtained from the DSC measurements both the enthalpies of dehydration for the observed stages and the enthalpies of formation of some nickel selenate hydrates have been calculated.

2. Experimental

Nickel selenate hexahydrate was prepared by neutralization of nickel hydroxide carbonate with a dilute aqueous solution of selenic acid at 60–70°C. The solution was then filtered and concentrated. Crystals of $NiSeO_4 \cdot 6H_2O$ were obtained after cooling the solution at room temperature. These were recrystallized in water and dried in air. The reagents used were p.a. grade (Merck).

According to Snyman et al. [5], $NiSeO_4 \cdot 4H_2O$ could be prepared by heating $NiSeO_4 \cdot 6H_2O$ for 30 min to 100°C (heating rate of $3°C\,min^{-1}$). Our experiments, however, show that this heating time is not sufficient for the preparation of $NiSeO_4 \cdot 4H_2O$. We obtained $NiSeO_4 \cdot 4H_2O$ by heating $NiSeO_4 \cdot 6H_2O$ crystals at about 80°C for several days. The longer time was needed for the crystallization of the initially amorphous salt.

Attempts to prepare $NiSeO_4 \cdot 2H_2O$ were unsuccessful since the dihydrate is unstable and transforms in air immediately into $NiSeO_4 \cdot 6H_2O$ or $NiSeO_4 \cdot 4H_2O$, as IR-spectra show. Attempts to prepare $NiSeO_4 \cdot 2H_2O$ at 200°C for 30 min, as Snyman [5] reported, always resulte in the formation of an amorphous nickel selenate monohydrate.

Nickel selenate monohydrate (crystalline) was prepared by heating $NiSeO_4 \cdot 6H_2O$ crystals at 200°C for 20 h.

The salts obtained were analysed chemically (the nickel concentrations were determined complexometrically at pH = 5.5 to 6 using xylenol orange as indicator) and by X-ray powder diffraction with a DRON-3 diffractometer using Cu Kα radiation. The diffraction pattern of $NiSeO_4 \cdot 4H_2O$ was obtained at a scanning speed of $1°C\,min^{-1}$ in the 2θ interval of 5 to 65°. α-SiO_2 was used as a standard. The lattice parameters of $NiSeO_4 \cdot 4H_2O$ were calculated on the basis of 30 reflections using ITO and LSUCR programs. IR spectroscopy was used for the identification of some of the intermediate hydrates.

The thermal dehydrations were studied using a derivatograph Paulik-Paulik-Erdey MOM OD-102 in the temperature range up to 600°C at heating rates of 2.5; 5 and $10°C\,min^{-1}$ using α-alumina as reference. The DSC-measurements were recorded at heating rates of 2.5 or $5°C\,min^{-1}$, using standard Al pans. The temperature and sensitivity were calibrated using indium (purity > 99.9%) as a standard.

3. Results and discussion

TG, DTG and DTA curves of $NiSeO_4 \cdot 6H_2O$, obtained under different experimental conditions, are shown in Fig. 1. The dehydration stages of $NiSeO_4 \cdot 6H_2O$ are seen to depend on the sample mass and the heating rate.

At the lower heating rate ($2.5°C\,min^{-1}$) the DTA and DTG curves are more complicated than those obtained at heating rates of 5 and $10°C\,min^{-1}$ (Figs. 1a,b and c, respectively). $NiSeO_4 \cdot 6H_2O$ is stable up to 80°C and transforms into $NiSeO_4$ in six dehydration stages (Fig. 1a). The first strong endothermic peak with a maximum at 108°C and a shoulder at about 120°C in the DTA and DTG-curves corresponds to the loss of one and two water molecules, respectively, thus producing $NiSeO_4 \cdot 5H_2O$ and $NiSeO_4 \cdot 4H_2O$. The second strong endothermic peak is split into two peaks, with maxima at 156 and 180°C, which correspond to the formation of $NiSeO_4 \cdot 0.2H_2O$ and $NiSeO_4 \cdot H_2O$. Finally, the separation of the last water molecule also occurs stepwise and the TG curve shows that the intermediate $NiSeO_4 \cdot 0.5H_2O$ is formed at about 300°C. At temperatures higher than 380°C, anhydrous nickel selenate is formed.

On the basis of the experimental results, we propose the following mechanism of the thermal dehydration of $NiSeO_4 \cdot 6H_2O$ (Fig. 1a):

$$NiSeO_4 \cdot 6H_2O \xrightarrow{108°C} NiSeO_4 \cdot 5H_2O$$

$$+ H_2O\,(\Delta m_{exp} = 6.9\%;\ \Delta m_{th} = 5.8\%)$$

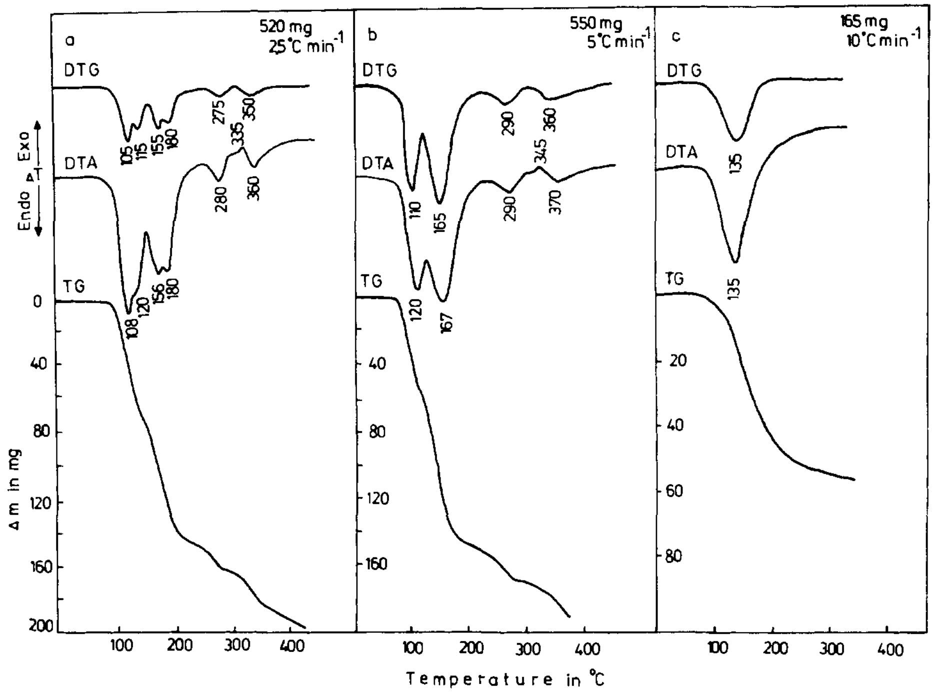

Fig. 1. TG, DTG and DTA curves of $NiSeO_4 \cdot 6H_2O$.

$$NiSeO_4 \cdot 5H_2O \xrightarrow{120^\circ C} NiSeO_4 \cdot 4H_2O$$

$$+ H_2O (\Delta m_{exp} = 12.7\%;\ \Delta m_{th} = 11.6\%)$$

$$NiSeO_4 \cdot 4H_2O \xrightarrow{156^\circ C} NiSeO_4 \cdot 2H_2O$$

$$+ 2H_2O (\Delta m_{exp} = 21.6\%;\ \Delta m_{th} = 23.2\%)$$

$$NiSeO_4 \cdot 2H_2O \xrightarrow{180^\circ C} NiSeO_4 \cdot H_2O + H_2O$$

$$(\Delta m_{exp} = 29.0\%;\ \Delta m_{th} = 29.0\%)$$

$$NiSeO_4 \cdot H_2O \xrightarrow{280^\circ C} NiSeO_4 \cdot 0.5H_2O$$

$$+ 0.5H_2O (\Delta m_{exp} = 31.9\%; \Delta m_{th} = 31.9\%)$$

$$NiSeO_4 \cdot 0.5H_2O \xrightarrow{360^\circ C} NiSeO_4 + 0.5H_2O$$

$$(\Delta m_{exp} = 35.4\%;\ \Delta m_{th} = 34.9\%)$$

For the higher heating rate and the same mass only two strong endothermic peaks with maxima at 120 and 167°C are observed on the DTA curve corresponding to the formation of $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot H_2O$, respectively (Fig. 1b). At the higher heating rate the shoulder at 120°C transforms into a strong endothermic peak (Fig. 1a). The two peaks at 156 and 180°C (Fig. 1a) overlap resulting, in one peak at 167°C. The different heating rate, however, does not influence the latter stages in the temperature interval from 250 to 400°C.

The following mechanism of dehydration could be proposed:

$$NiSeO_4 \cdot 6H_2O \xrightarrow{120^\circ C} NiSeO_4 \cdot 4H_2O$$

$$+ 2H_2O (\Delta m_{exp} = 10.9\%;\ \Delta m_{th} = 11.6\%)$$

$$NiSeO_4 \cdot 4H_2O \xrightarrow{167^\circ C} NiSeO_4 \cdot H_2O$$

$$+ 3H_2O (\Delta m_{exp} = 29.0\%;\ \Delta m_{th} = 27.6\%)$$

$$NiSeO_4 \cdot H_2O \xrightarrow{290^\circ C} NiSeO_4 \cdot 0.5H_2O$$

$$+ 0.5H_2O\ (\Delta m_{exp} = 31.3\%;\ \Delta m_{th} = 31.9\%)$$

Table 1
X-ray powder diffraction data for $NiSeO_4 \cdot 4H_2O$

d_{calc}/Å	d_{exp}/Å	hkl	I/Io
6.93	6.91	011	20
6.89		020	
5.47	5.48	110	50
4.81	4.82	101	20
4.51	4.51	120	100
4.01	4.01	002	65
3.85	3.85	012	10
3.63	3.64	130	10
3.44	3.44	040	20
3.32	3.32	131	12
3.22	3.22	112	40
3.01	3.00	112	40
2.983	2.985	122	40
2.911	2.909	210	10
2.797	2.796	141	25
2.747	2.748	211	7
2.727	2.724	211	5
2.684	2.688	132	5
2.625	2.623	013	7
2.498	2.497	230	5
2.497		150	
2.386	2.385	142	10
2.384		151	
2.379	2.380	231; 202	< 5
2.345	2.345	212	10
2.310	2.309	123	7
2.293	2.296	123	18
2.292		060	
2.112	2.112	043; 232	20
1.987	1.986	014	15
1.985		143	
1.923	1.922	301;223	15
1.822	1.821	330;153	
1.775	1.775	261	10
1.733		331;312	
1.668	1.669	144;163	20

Table 2
X-ray powder diffraction data for $NiSeO_4 \cdot 2H_2O$

d_{calc}/Å	d_{exp}/Å [5]	hkl 111	I/Io [5]
5.66	5.66	111	56
5.11	5.10	020	30
4.45	4.45	021	67
4.08	4.08	121	26
3.83	3.83	112	26
3.21	3.21	122; 212; 301	100
3.04	3.04	131	96
2.859	2.856	320	11
2.509	2.510	410; 123	26
2.317	2.328	223	15
2.173	2.174	142	11
2.135	2.122	332	11
2.018	2.018	501	19
1.993	1.994	051	7
1.957	1.954	151	7
1.947	1.944	043	11
1.856	1.856	314	7

$$NiSeO_4 \cdot 0.5H_2O \xrightarrow{370^\circ C} NiSeO_4 + 0.5H_2O$$

$$(\Delta m_{exp} = 34.9\%;\ \Delta m_{th} = 34.9\%)$$

For comparison, the DTA curve of the sample (165 mg) heated at 10°C min^{-1} (conditions close to those used by Nabar and Paralkar) is shown in Fig. 1c. Evidently, the heating rate influences the DTA curve shape and only one strong symmetrical endothermic peak appears corresponding to the separation of five water molecules, thus transforming $NiSeO_4 \cdot 6H_2O$ directly into $NiSeO_4 \cdot H_2O$ as Nabar and Paralkar have established.

As it was mentioned, crystalline $NiSeO_4 \cdot 4H_2O$ was prepared by heating $NiSeO_4 \cdot 6H_2O$ crystals at 80°C for 4–5 days. Snyman [5] reported the powder patterns of $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot 2H_2O$, but the diffraction peaks were not indexed and the lattice parameters were not calculated. Our X-ray powder diffraction measurements show that $NiSeO_4 \cdot 4H_2O$ crystallizes in the monoclinic system with lattice parameters: a = 5.959(3) Å; b = 13.771(8) Å; c = 8.023(5) Å; β = 90.66(6)°; V = 658.3(5) Å; SG $P2_1/n$ (Table 1). $NiSeO_4 \cdot 4H_2O$ is proved to be isomorphous with $MgSeO_4 \cdot 4H_2O$ [2], $MgSO_4 \cdot 4H_2O$ [6] and $CoSeO_4 \cdot 4H_2O$ [7].

We have also calculated the lattice parameters of $NiSeO_4 \cdot 2H_2O$, on the basis of the X-ray powder diffraction data reported by Snyman [5]. $NiSeO_4 \cdot 2H_2O$ forms orthorhombic crystals with lattice parameters: a = 10.351(4) Å; b = 10.219(4) Å; c = 9.017(5) Å; V = 953.9(6) Å^3. $NiSeO_4 \cdot 2H_2O$ is proved to be isomorphous with $MgSeO_4 \cdot 2H_2O$ [2] and $MnSeO_4 \cdot 2H_2O$ [8] (Table 2).

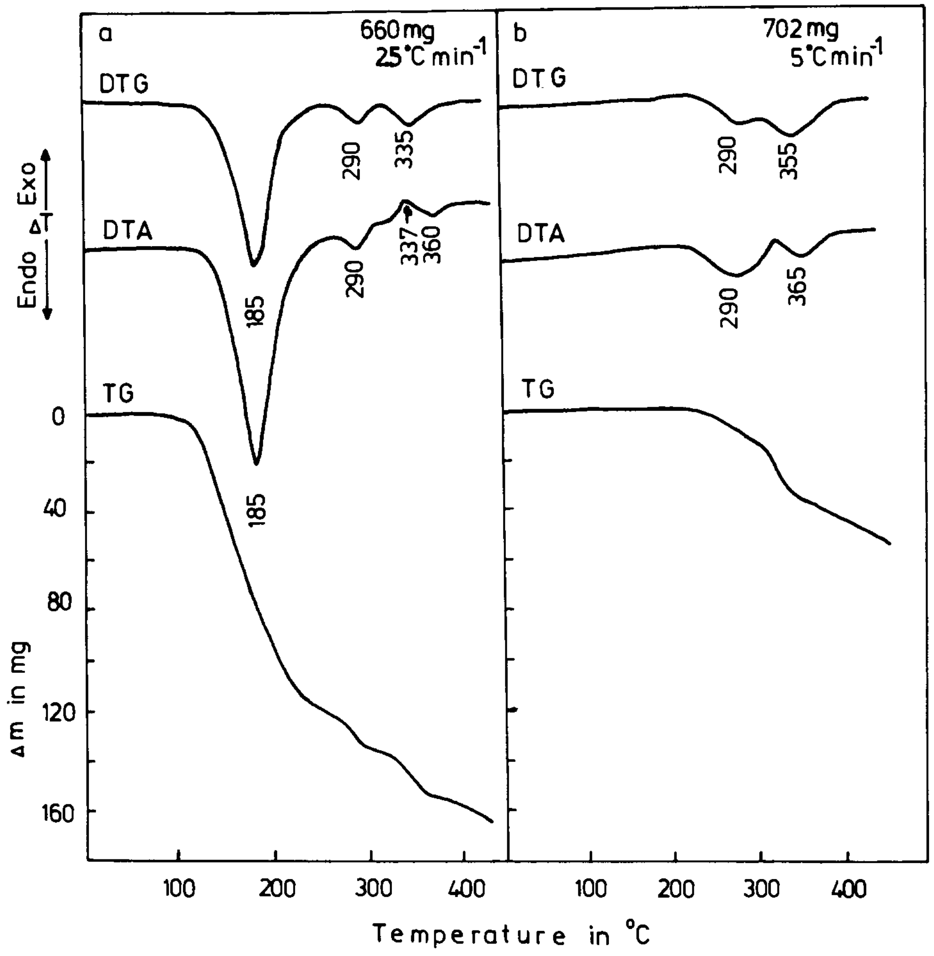

Fig. 2. TG, DTG and DTA curves of $NiSeO_4 \cdot 4H_2O$ (a) and $NiSeO_4 \cdot H_2O$ (b).

The DTA curve of $NiSeO_4 \cdot 4H_2O$ is shown in Fig. 2. The dehydration of the tetrahydrate begins at about 120°C. The strong symmetrical endothermic peak with a maximum at 185°C corresponds to the separation of three water molecules, thus producing $NiSeO_4 \cdot H_2O$. At tempertures higher than 270°C the dehydration of the monohydrate occurs in a similar way to that of the monohydrate obtained as an intermediate in the dehydration of $NiSeO_4 \cdot 6H_2O$ (Fig. 1a,b) and $NiSeO_4 \cdot H_2O$ prepared by heating $NiSeO_4 \cdot 6H_2O$ crystals at 200°C for about 20 h (Fig. 2b).

The processes in the temperature interval of 250–400°C need some additional comments. $NiSeO_4 \cdot H_2O$ converts into an anhydrous salt in steps with the formation of intermediate $NiSeO_4 \cdot 0.5H_2O$ as the TG, DTG and DTA curves show. An exothermic peak appears on the DTA curve at about 335°C which is probably due to a partial crystallization of the initial amorphous $NiSeO_4 \cdot 0.5H_2O$.

The proposed dehydration shemes are only schematic since the nickel selenate hydrates lose mass continuously with the increase in the temperature, as the TG curves show. No temperature intervals of stability of the intermediate hydrates could be distinguished.

The DSC curves of some nickel selenate hydrates recorded under different experimental conditions

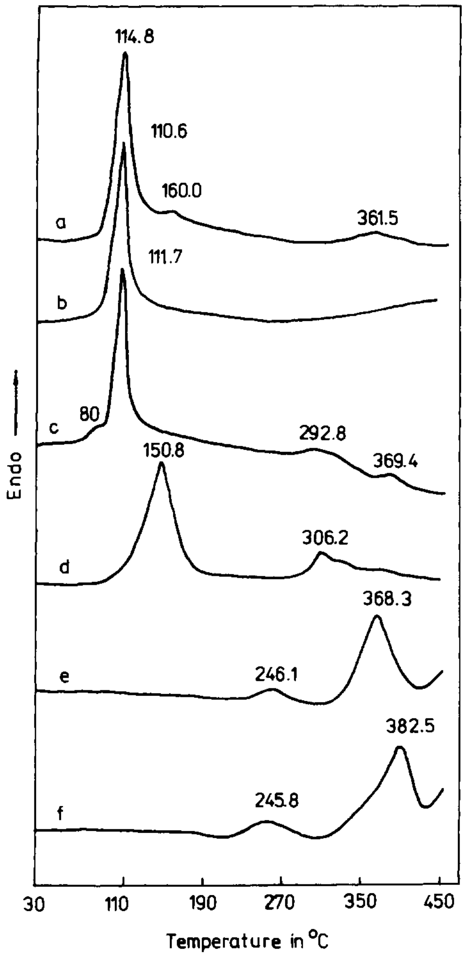

Fig. 3. DSC curves of $NiSeO_4 \cdot 6H_2O$ (a – 8.9 mg, 5°C min^{-1}; b – 9.9 mg, 2.5°C min^{-1}; c – 1.8 mg, 5°C min^{-1}); $NiSeO_4 \cdot 4H_2O$ (d – 8.2 mg, 2.5°C min^{-1}) and $NiSeO_4 \cdot H_2O$ (e – 13.0 mg, 5°C min^{-1}; f – 14.0 mg, 5°C min^{-1})

are shown in Fig. 3. The dehydration of $NiSeO_4 \cdot 6H_2O$ up to 310°C is registered on the DSC curve (Fig. 3a) with a strong unsymmetrical endothermic peak with a maximum at 114°C and a shoulder at about 160°C, resulting from the formation of $NiSeO_4 \cdot 4H_2O$ and $NiSeO_4 \cdot H_2O$, respectively.

A decrease in the heating rate (2.5°C min^{-1}) did not lead to the resolution of the two dehydration steps (Fig. 3b).

For a smaller mass, however, a shoulder at about 80°C appears, which is probably due to the beginning of the separation of the first water molecule. This process, however, overlaps with that of the separation of the next water molecules (Fig. 3c).

The dehydration of $NiSeO_4 \cdot 4H_2O$ begins at 70°C and completes at 270°C producing $NiSeO_4 \cdot H_2O$. No indications of the formation of lower hydrates could be observed on the DSC curve in the temperature interval from 70 to 270°C (Fig. 2d), which coincides with the results obtained from the DTA and DTG measurements (Fig. 2a).

To obtain some more information about the separation of the last water molecule, the DSC curves of a crystalline and amorphous monohydrate were recorded (Figs. 3e, f, respectively). In the temperature interval from 205 to 410°C two endothermic peaks could be distinguished on the DSC curve, confirming the results from the DTA and DTG measurements, that the dehydration occurs in two steps: $NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 \cdot 0.5H_2O \rightarrow NiSeO_4$. However, no exothermic peak at about 330°C was observed on the DSC curve, although it was clearly seen on the DTA curves (Figs. 1, 2). Furthermore, the values of the enthalpies of dehydration measured for the two stages are considerably different (see Table 3). The enthalpy of dehydration for the process $NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 \cdot 0.5H_2O$ has values of 2.6 kJ mol^{-1} and 4.0 kJ mol^{-1} for the crystalline and amorphous monohydrate, respectively. This is a negligible part of the total enthalpy of dehydration for the last water molecule. This could be explained if the exothermic peak overlaps with the endothermic peak corresponding to the separation of a "half" water molecule resulting in a smaller overwall enthalpy value.

The DSC data for the stages registered on the DSC curves (the enthalpy values are mean values of three measurements) are listed in Table 3. The experimental error for $\Delta_{deh}H$ is 2 to 2.5%.

The value of $\Delta_{deh}H$ for the dehydration $NiSeO_4 \cdot 6H_2O \rightarrow NiSeO_4 \cdot 4H_2O + 2H_2O$ has been calculated as a difference in the values of $\Delta_{deh}H$ of the hexa- and tetrahydrate, respectively, to anhydrous salts ($\Delta_{deh}H = 158.6$ kJ mol^{-1}).

Using the $\Delta_{deh}H$ data obtained from the DSC measurements, as well as the $\Delta_f H$ of $NiSeO_4$ [10], the enthalpies of formation for some nickel selenate hydrates have been calculated:

Table 3
DSC data for dehydration of nickel selenate hydrates

Dehydration processes	sample mass/ mg	heating rate/ $^{\circ}$C min^{-1}	Tonset/ $^{\circ}$C	ΔH/ kJ mol^{-1}
	8.9	5	102.1	340.9
			322.0	24.1
$NiSeO_4 \cdot 6H_2O \rightarrow NiSeO_4 \cdot H_2O + 5H_2O$	9.9	2.5	96.0	337.0
$NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 + H_2O$			not observed	
	1.8	5	101.0	321.4
			246.7	49.6
$NiSeO_4 \cdot 4H_2O \rightarrow NiSeO_4 \cdot H_2O + 3H_2O$	8.2	2.5	115.4	189.6
$NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 + H_2O$			294.8	19.8
$NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 \cdot 0.5H_2O + 0.5H_2O$ (crystalline)	13.0	5	215.0	2.6
$NiSeO_4 \cdot 0.5H_2O \rightarrow NiSeO_4 + 0.5H_2O$			336.5	21.8
$NiSeO_4 \cdot H_2O \rightarrow NiSeO_4 \cdot 0.5H_2O + 0.5H_2O$ (amorphous)	14.0	5	211.8	4.0
$NiSeO_4 \cdot 0.5H_2O \rightarrow NiSeO_4 + 0.5H_2O$			352.2	17.7

$\Delta_f H$ of $NiSeO_4 \cdot 6H_2O = -2415.1$ kJ mol^{-1} (-2401.6 kJ mol^{-1})

$\Delta_f H$ of $NiSeO_4 \cdot 4H_2O = -1772.9$ kJ mol^{-1}

$\Delta_f H$ of $NiSeO_4 \cdot H_2O$(crystalline) $= -862.4$ kJ mol^{-1}

$\Delta_f H$ of $NiSeO_4 \cdot H_2O$(amorphous) $= -859.7$ kJ mol^{-1}

For comparison the data reported by Selivanova [9] are given in parentheses.

Comparing the values of the enthalpies of formation of the crystalline and amorphous monohydrates, the enthalpy of transformation of the amorphous into crystalline monohydrate has been calculated (-2.7 kJ mol^{-1}).

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