

## Characterization of beryllium selenates by X-ray powder diffraction, DTA and DSC

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BeSeO<sub>4</sub>·2H<sub>2</sub>O and BeSeO<sub>4</sub> have been studied röntgenographically: BeSeO<sub>4</sub>·2H<sub>2</sub>O forms orthorhombic crystals with lattice constants:  $a = 5.843(2) \text{ \AA}$ ;  $b = 9.790(3) \text{ \AA}$ ;  $c = 4.692(1) \text{ \AA}$ ;  $V = 268.4(1) \text{ \AA}^3$ . The crystals of BeSeO<sub>4</sub> are tetragonal:  $a = 4.648(1) \text{ \AA}$ ;  $c = 7.084(3) \text{ \AA}$ ;  $V = 153.1(1) \text{ \AA}^3$ , SG I $\bar{4}$ . The thermal dehydration of BeSeO<sub>4</sub>·4H<sub>2</sub>O has been studied by TG, DTA and DSC methods. The dehydration occurs in four steps and intermediate hydrates BeSeO<sub>4</sub>·2H<sub>2</sub>O, BeSeO<sub>4</sub>·H<sub>2</sub>O and BeSeO<sub>4</sub>·0.5H<sub>2</sub>O are formed. The enthalpies of dehydration of the observed dehydration processes have been determined. The higher value of  $\Delta H_{\text{deh}}$  of BeSeO<sub>4</sub>·4H<sub>2</sub>O as compared to those of other metal selenate tetrahydrates is discussed in terms of the strong Be–H<sub>2</sub>O interaction. The enthalpies of formation of BeSeO<sub>4</sub>·4H<sub>2</sub>O and BeSeO<sub>4</sub>·2H<sub>2</sub>O have been calculated.

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### 1 Introduction

The available literature data on beryllium selenates are scanty. Selivanova et al. reported the X-ray powder diffraction patterns of BeSeO<sub>4</sub>·4H<sub>2</sub>O, BeSeO<sub>4</sub>·2H<sub>2</sub>O and BeSeO<sub>4</sub> (d-values), but the diffraction peaks were not indexed and the lattice parameters were not calculated [1]. It is also known that the heating of BeSeO<sub>4</sub>·4H<sub>2</sub>O produces BeSeO<sub>4</sub>·2H<sub>2</sub>O and BeSeO<sub>4</sub> at 100 and 300°C, respectively [1,2]. The IR spectrum of BeSeO<sub>4</sub>·4H<sub>2</sub>O is given in [3,4] without comments.

In this paper we report crystallographic data of BeSeO<sub>4</sub>·2H<sub>2</sub>O and BeSeO<sub>4</sub> (lattice parameters) and the results of the thermal dehydration of BeSeO<sub>4</sub>·4H<sub>2</sub>O obtained by Thermogravimetry (TG), Differential thermal analysis (DTA) and Differential Scanning Calorimetry (DSC).

### 2 Experimental

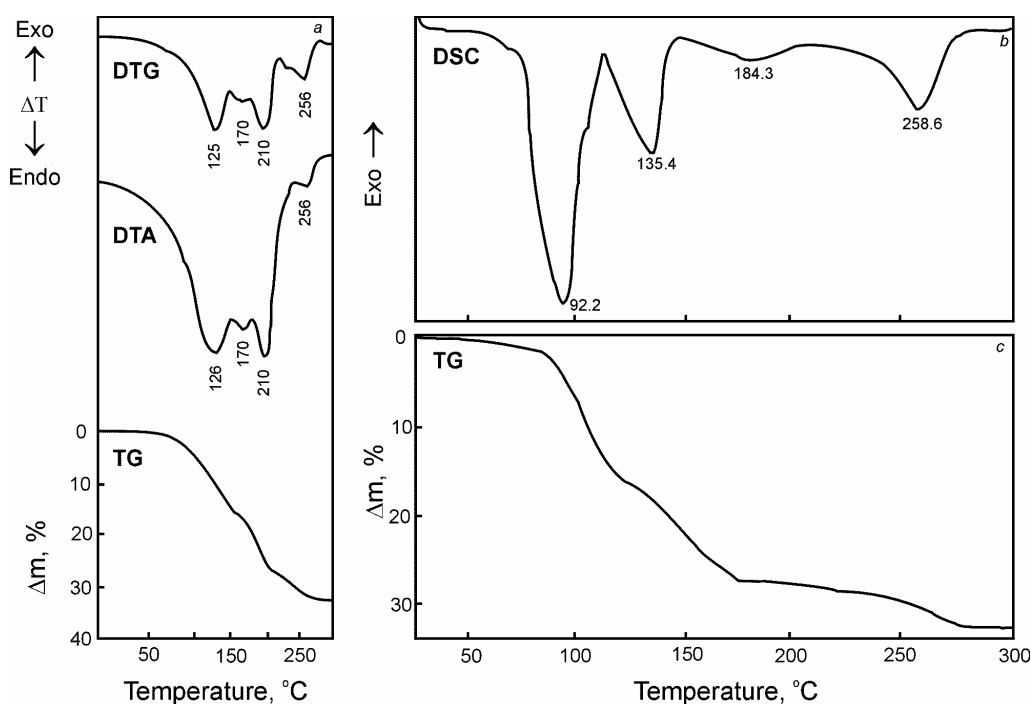
Beryllium selenate tetrahydrate was prepared by dissolving BeO in a slight excess of selenic acid at 50–60°C (the reagents used were “purum” quality – Fluka). The solution was then filtered and concentrated. Crystals of BeSeO<sub>4</sub>·4H<sub>2</sub>O were obtained after cooling the solution to room temperature. They were recrystallized from water and dried in air. BeSeO<sub>4</sub>·2H<sub>2</sub>O was prepared by dehydration of BeSeO<sub>4</sub>·4H<sub>2</sub>O over P<sub>2</sub>O<sub>5</sub> in a desiccator for 15 days. Crystalline anhydrous beryllium selenate was obtained by heating of the tetrahydrate at 300°C for 7–8 hours. The beryllium content in the compounds under study was determined gravimetrically as BeO (heating of the sample at 950°C), while the SeO<sub>4</sub><sup>2-</sup> concentration - as described in [5].

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The X-ray powder diffraction analysis was carried out with a DRON-3 diffractometer using Cu K $\alpha$  radiation at a scanning speed of 1°/min. The lattice parameters were calculated using the programs ITO and LSUCR. The thermal dehydration processes were studied using a derivatograph Paulik-Paulik-Erdey MOM OD-102, a thermogravimetric balance and DSC-822 both of Mettler Toledo Star<sup>c</sup> System. The heating rate was 10°C/min. The experimental error for the enthalpy of dehydration ( $\Delta H_{\text{deh}}$ ) is about 2.5%. The enthalpy values given in the paper are obtained as mean values from three measurements.

### 3 Result and discussion

The simultaneous obtained TG-, DTA- and DTG curves for BeSeO<sub>4</sub>·4H<sub>2</sub>O are given in Fig.1 (a), while a precise TG curve and DSC curve both recorded using Mettler Toledo Star<sup>c</sup> System are shown in Fig. 1 (b) and (c). The measured values of enthalpy of dehydration ( $\Delta H_{\text{deh}}$ ) as well as the mass losses calculated for the each dehydration step according to the TG curve are listed in Table 1.



**Fig. 1** Derivatogram of BeSeO<sub>4</sub>·4H<sub>2</sub>O (a); DSC curve of BeSeO<sub>4</sub>·4H<sub>2</sub>O (b); TG curve of BeSeO<sub>4</sub>·4H<sub>2</sub>O (c).

**Table 1** DSC and TG data for the thermal dehydration of BeSeO<sub>4</sub>·4H<sub>2</sub>O.

Dehydration process	T <sub>onset</sub> /°C	T <sub>end</sub> /°C	$\Delta H_{\text{deh}}$ /kJ/mol	$\Delta m_{\text{exp}}$ /%	$\Delta m_{\text{theor}}$ /%
BeSeO <sub>4</sub> ·4H <sub>2</sub> O → BeSeO <sub>4</sub> ·2H <sub>2</sub> O + 2H <sub>2</sub> O	77.3	103.1	125.9	15.7	16.0
BeSeO <sub>4</sub> ·2H <sub>2</sub> O → BeSeO <sub>4</sub> ·H <sub>2</sub> O + H <sub>2</sub> O	113.6	141.4	47.4	9.1	9.5
BeSeO <sub>4</sub> ·H <sub>2</sub> O → BeSeO <sub>4</sub> ·0.5H <sub>2</sub> O + 0.5H <sub>2</sub> O	157.1				
BeSeO <sub>4</sub> ·0.5H <sub>2</sub> O → BeSeO <sub>4</sub> + 0.5H <sub>2</sub> O	237.1	271.9	60.7	11.0	10.6
BeSeO <sub>4</sub> ·4H <sub>2</sub> O → BeSeO <sub>4</sub> + 4H <sub>2</sub> O			234.0		

The comparison of the data obtained shows that the different methods used give one and the same results. So, the dehydration process of BeSeO<sub>4</sub>·4H<sub>2</sub>O begins at 50°C. Four endothermic peaks, each of them accompanied with a mass loss, are registered both on DTA and DSC curves, indicating that the dehydration of the

tetrahydrate occurs in four steps. Evidently, the maxima of the peaks on the DTA curve (126, 170, 210 and 265°C) are shifted at higher temperatures as compared to those registered on the DSC curve (92.2, 135.4, 184.3 and 258.6°C) due to the larger mass of the sample used in DTA analysis. It is also seen, that the four dehydration stages of  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  occur continuously in the conditions of DTA experiment, while on the DSC curve some of the dehydration processes could be easily distinguished. So, the first strong endothermic peak on the DSC curve according to the mass loss calculated corresponds to the separation of two water molecules, thus forming  $\text{BeSeO}_4 \cdot 2\text{H}_2\text{O}$  (Table 1). The chemical analysis of the sample prepared by an isothermal heating of the tetrahydrate at 75°C for 3 hours confirms the formation of  $\text{BeSeO}_4 \cdot 2\text{H}_2\text{O}$ , but the X-ray pattern of the sample shows that an amorphous product is formed. As it was mentioned, crystalline  $\text{BeSeO}_4 \cdot 2\text{H}_2\text{O}$  was prepared by dehydration of  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$  over  $\text{P}_2\text{O}_5$  for 15 days. It forms orthorhombic crystals with lattice constants:  $a = 5.843(2) \text{ \AA}$ ;  $b = 9.790(3) \text{ \AA}$ ;  $c = 4.692(1) \text{ \AA}$ ;  $V = 268.4(1) \text{ \AA}^3$  (hkl and d-spacings are given in Table 2).

**Table 2** X-ray powder diffraction data of  $\text{BeSeO}_4 \cdot 2\text{H}_2\text{O}$ .

$d_{\text{calc}}/\text{\AA}$	$d_{\text{exp}}/\text{\AA}$	hkl	$I/I_0$	$d_{\text{calc}}/\text{\AA}$	$d_{\text{exp}}/\text{\AA}$	hkl	$I/I_0$
5.02	5.02	110	50	2.212	2.212	221	8
4.89	4.89	020	50	2.125	2.125	112	7
4.23	4.22	011	30	2.033	2.034	141	< 5
3.66	3.65	101	100	1.989	1.989	112	5
3.43	3.43	111	10	1.974	1.073	231	18
3.39	3.38	021	35	1.877	1.877	240	5
2.929	2.929	121	35	1.857	1.857	150	7
2.848	2.847	130	35	1.829	1.829	202	5
2.678	2.678	031	12	1.810	1.809	132; 320	10
2.508	2.509	220	8	1.688	1.688	321	5
2.403	2.403	211	10	1.672	1.672	330	< 5
2.346	2.347	002	8	1.511	1.511	103	< 5

Furthermore, no interval of stability of the dihydrate obtained could be seen on the DSC and TG curves (Fig. 1(b) and (c)). The dehydration process of  $\text{BeSeO}_4 \cdot 2\text{H}_2\text{O}$  continues in three steps registered with three endothermic peaks on the DSC curve and completes at 271.9°C with the formation of an anhydrous beryllium selenate (see Table 1). The endothermic peak at 135.4°C corresponds to the loss of one water molecule, thus producing  $\text{BeSeO}_4 \cdot \text{H}_2\text{O}$ . The transformation of the monohydrate obtained into  $\text{BeSeO}_4$  is registered with two endothermic peaks, i.e. two-stage dehydration. Based on the mass loss calculations a semihydrate,  $\text{BeSeO}_4 \cdot 0.5\text{H}_2\text{O}$  is assumed to be formed as an intermediate product. However, these two dehydration processes are not well distinguished on the DSC curve and for this reason the total value of  $\Delta H_{\text{deh}}$  measured for the transition  $\text{BeSeO}_4 \cdot \text{H}_2\text{O} \rightarrow \text{BeSeO}_4$  is given in Table 1.

Based on the DTA, DSC and TG data we propose the following scheme of the thermal dehydration of  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ :



Unfortunately, our attempts to isolate and study the lower hydrates  $\text{BeSeO}_4 \cdot \text{H}_2\text{O}$  and  $\text{BeSeO}_4 \cdot 0.5\text{H}_2\text{O}$  were unsuccessful. It could be mentioned, that the formation of semihydrates during the thermal dehydration of the selenate hydrates has been also reported in the literature [6,7].

The X-ray powder diffraction data of  $\text{BeSeO}_4$  are listed in Table 3. It crystallizes in the tetragonal system with lattice parameters:  $a = 4.648(1) \text{ \AA}$ ;  $c = 7.084(3) \text{ \AA}$ ;  $V = 153.1(1) \text{ \AA}^3$ .  $\text{BeSeO}_4$  is proved to be isomorphous with  $\text{BeSO}_4$  [8] and by analogy to  $\text{BeSO}_4$  we assume that the SG of  $\text{BeSeO}_4$  is  $I\bar{4}$ .

**Table 3** X-ray powder diffraction data of BeSeO<sub>4</sub>.

d <sub>calc</sub> /Å	d <sub>exp</sub> /Å	hkl	I/I <sub>0</sub>	d <sub>calc</sub> /Å	d <sub>exp</sub> /Å	hkl	I/I <sub>0</sub>
3.88	3.88	101	100	1.943	1.943	202	8
3.54	3.54	002	5	1.643	1.643	220	< 5
3.29	3.29	110	20	1.560		213	
2.409	2.407	112	30	1.559	1.559	114	10
2.105	2.105	103	5	1.491	1.491	222	< 5
1.994	1.995	211	13	1.409	1.409	204	< 5

The values of  $\Delta H_{\text{deh}}$  measured are given in Table 1. The value of  $\Delta H_{\text{deh}}$  of BeSeO<sub>4</sub>·4H<sub>2</sub>O (234.0 kJ/mol) has been calculated as a sum of the  $\Delta H_{\text{deh}}$  of the three consecutive processes. In previous papers of one of the authors the values of  $\Delta H_{\text{deh}}$  of MeSeO<sub>4</sub>·4H<sub>2</sub>O (Me = Mg, Co, Ni) to corresponding MeSeO<sub>4</sub> (total dehydration) have been reported: 201.5 kJ/mol for MgSeO<sub>4</sub>·4H<sub>2</sub>O [9]; 222.7 kJ/mol for CoSeO<sub>4</sub>·4H<sub>2</sub>O [10]; 209.4 kJ/mol for NiSeO<sub>4</sub>·4H<sub>2</sub>O [7]. The higher value of  $\Delta H_{\text{deh}}$  of BeSeO<sub>4</sub>·4H<sub>2</sub>O – 234.0 kJ/mol as compared to those of the other metal selenate tetrahydrate is probably due to the very strong Be–H<sub>2</sub>O interactions commented in the literature [11,12].

Using the  $\Delta H_{\text{deh}}$  obtained from DSC measurements (Table 1) as well as the  $\Delta H_f^\circ$  of BeSeO<sub>4</sub> [13], the enthalpies of formation of BeSeO<sub>4</sub>·4H<sub>2</sub>O and BeSeO<sub>4</sub>·2H<sub>2</sub>O have been calculated:

$$\Delta H_f^\circ \text{ of BeSeO}_4 \cdot 4\text{H}_2\text{O} = -2091.7 \text{ kJ/mol } (-2112.9 \text{ kJ/mol})$$

$$\Delta H_f^\circ \text{ of BeSeO}_4 \cdot 2\text{H}_2\text{O} = -1482.1 \text{ kJ/mol } (-1507.5 \text{ kJ/mol})$$

For comparison, the data reported in [13] are given in parentheses. In the literature there are no structural data of beryllium selenate tetrahydrate. Finally, we study BeSeO<sub>4</sub>·4H<sub>2</sub>O by a single crystal X-ray diffraction.

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