Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 469–475

STUDY OF THE CRYSTALLIZATION FIELDS OF COBALT(II) SELENITES IN THE SYSTEM $CoSeO_3$–SeO_2–H_2O

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The solubility of $CoSeO_3$–SeO_2–H_2O system in the temperature region 298–573 K was studied. The phase diagram of cobalt(II)selenites was drawn and the crystallization fields for the different phases were determined. Depending on the conditions for hydrothermal synthesis, $CoSeO_3{\cdot}2H_2O$, α-$CoSeO_3{\cdot}1/3H_2O$, β-$CoSeO_3{\cdot}1/3H_2O$, $CoSeO_3$, $Co(HSeO_3)_2{\cdot}2H_2O$ and $CoSe_2O_5$ were obtained. The different phases were proved and characterized by chemical and X-ray analyses, as well as IR spectroscopy.

Keywords: *cobalt(II)selenites, hydrothermal synthesis, IR spectroscopy, powder X-ray diffraction, solubility diagrams, thermal analysis*

Introduction

Various cobalt(II)selenites have been reported in the literature: $CoSeO_3{\cdot}2H_2O$ [1–12], $CoSeO_3{\cdot}H_2O$ [2, 4, 12–16], $CoSeO_3{\cdot}1/3H_2O$ [12, 14, 15, 17, 18], $CoSeO_3$ [7, 12, 17, 19–22], $Co(HSeO_3)_2{\cdot}2H_2O$ [10, 12, 23, 24], $CoSe_2O_5{\cdot}3H_2O$ [25] and $CoSe_2O_5$ [12, 26]. Only $CoSeO_3{\cdot}2H_2O$ can be found in the natural form of a mineral – cobaltomenite [27, 28]. Under common conditions, $CoSeO_3{\cdot}2H_2O$ crystallizes from aqueous solutions [4, 5, 8, 10, 19]. Its thermal dehydration, however, does not produce lower crystallohydrates as separate phases [14–16]. They can be obtained by hydrothermal treatment at temperatures above 373 K [2, 8, 14, 16] or by employing other special conditions or reagents [19, 21, 25]. The lack of systematic approach in most of the studies cited does not allow to determine clearly the types and number of the different solid phases which are in equilibrium with the liquid phase at various temperatures, as well as the boundaries of the crystallization fields of the known cobalt(II)selenites in the system $CoSeO_3$–SeO_2–H_2O. In this respect, useful information can be obtained from the dissolution isotherms of the system at different temperatures and the values of the parameters characterizing the non-variant (peritonic) points.

The aim of the present work is to study the crystallization fields of cobalt(II)selenites in the system $CoSeO_3$–SeO_2–H_2O in the temperature interval 298–573 K and characterize the phases observed.

Experimental

The initial substance used was $CoSeO_3{\cdot}2H_2O$. It was prepared by precipitating a 0.2 equiv L^{-1} aqueous solution of cobalt(II)nitrate hexahydrate puriss, (Merck) with a 0.2 equiv L^{-1} aqueous solution of sodium selenite pentahydrate puriss (Fluka) at 298 K. The solutions with volumes of 1 L were slowly mixed (5 mL min^{-1}) under continuous stirring with blade mixer. The precipitate obtained was 'aged' in the initial solution at room temperature for a week. The crystalline substance formed was collected on a G4 frit, rinsed vigorously with deionized distilled water and dried in air at ambient temperature for another week. The isolated compound was pink-purple crystalline powder, which was stable in air at laboratory temperature. The results from the chemical and powder X-ray analyses showed the compound had net formula $CoSeO_3{\cdot}2H_2O$. Precipitation at temperatures above 323 K gave a mixture of dihydrate and monohydrate crystalline phases [8]. Thus, the $CoSeO_3{\cdot}2H_2O$ obtained was used as initial substance for the study of the solubility in the $CoSeO_3$–SeO_2–H_2O system at different temperatures. Teflon-lined steel vessels with volume 20 mL^3 were used for the experiment [29]. In these vessels, 1 g $CoSeO_3{\cdot}2H_2O$ and 15 mL aqueous solution of SeO_2 purum (Merck) with concentrations varying from 0 to 65 mass% SeO_2 in 5% steps were placed. The time required for equilibration of the individual samples was from 2 months (at 298 K) to 20 days (at 573 K). The temperatures of the hydrothermal synthesis ranged from 298 to 573 K in 50 K steps. At the end of experiment time, the vessels were cooled and opened and the precipitate was filtered through porous glass filter. Both precipitate and filtrate were analyzed to determine the contents of cobalt(II) and selenium(IV). Selenium(IV) was determined iodometrically by Kotarski method [30]. Cobalt(II) was titrated complexometrically using xylenol orange as an indicator [31]. The Schreinemaker's method was used to study the solubil-

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1388–6150/$20.00

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ity in the $CoSeO_3$–SeO_2–H_2O system. The solubility diagram was drawn according to Gibbs–Roozeboom method. The approach and characterization method for solid phases are similar to these described in [32, 33].

Powder X-ray patterns were taken on a wide angle X-ray diffractometer with a goniometer URD-6 (Germany), using cells with a diameter of 12 mm, CoK_α radiation (λ=1.78892 Å) and an iron filter for β-emission. The lattice parameters were derived from 150–165 accurately measured reflections in the range $3\leq 2\theta\leq 60°$. The structures were solved by Patterson or direct methods and refined with the least squares method.

The thermal analyses of the samples was performed on a Paulik–Paulik–Erdey apparatus (MOM, Hungary) by heating to 1073 K at heating rate 5 and 10 K min^{-1} in static air. The samples (50 or 100 mg) were vigorously ground in agate vibration mortar and placed in platinum crucible (7 mm diameter and 14 mm height). The standard used was α-Al_2O_3 heated to 1373 K. The curves were registered with resolutions 1/5 for DTA, 1/15 for DTG and 1 mg for TG.

The IR absorption spectra were taken on a spectrophotometer Specord-75 (Carl Zeiss, Jena, Germany) over the region from 400 to 4000 cm^{-1} (resolution 1 cm^{-1}). The experiments were carried out at room temperature using KBr pellets with concentration of the substance studied 0.3 mass%.

Results and discussion

The results obtained from the experiments carried out showed that the following solid phases formed in the system $CoSeO_3$–SeO_2–H_2O which was in equilibrium with the liquid phase (containing from 0 to 65 mass% SeO_2) within the temperature interval 298–573 K: $CoSeO_3\cdot 2H_2O$ ($CoO\cdot SeO_2\cdot 2H_2O$), $CoSeO_3\cdot 1/3H_2O$ ($CoO\cdot SeO_2\cdot 1/3H_2O$), $CoSeO_3$ ($CoO\cdot SeO_2$), $Co(HSeO_3)_2\cdot 2H_2O$ ($CoO\cdot 2SeO_2\cdot 3H_2O$) and $CoSe_2O_5$ ($CoO\cdot 2SeO_2$). The individual phases were distinguishable by color and crystalline habitus: $CoSeO_3\cdot 2H_2O$ – pink-purple, fine powder; $CoSeO_3\cdot 1/3H_2O$ – light violet, fine crystalline; $CoSeO_3$ – dark violet with metal shine, well crystallized; $Co(HSeO_3)_2\cdot 2H_2O$ – pink, fine crystalline and $CoSe_2O_5$ – pink-violet, fine powder. The samples obtained were identified by the chemical, X-ray diffraction and IR spectroscopy analyses. Figure 1 presents the streak diagrams of the different cobalt(II)selenites.

The interplanar distances and the relative intensities of the peaks are given in Table 1.

According to literary data [6, 10, 12, 36], $CoSeO_3\cdot 2H_2O$ adopted a structure similar to Cu, Mg, Zn, Mn and Ni selenites dihydrates. The structure of $CoSeO_3$ was closely related to that of $CoSeO_3\cdot 1/3H_2O$ [6, 18] and the isotypic compound $NiSeO_3\cdot 1/3H_2O$ [18, 34]. $CoSe_2O_5$ was found to be isomorphous with the M^{2+} analogues $ZnSe_2O_5$ and $MnSe_2O_5$ [25, 26]. Table 2 summarizes the parameters characterizing the crystalline lattices of the selenites studied.

The comparison of the parameters measured was in very good accordance with data obtained from other authors [6, 10, 18, 22, 24, 26, 34]. It should be noted that two separate isomorphous phases (α and β) were observed for both $NiSeO_3\cdot 1/3H_2O$ and $CoSeO_3\cdot 1/3H_2O$ and they had different parameters of the crystalline lattice. Their IR spectra, however, were identical.

On the basis of the solubility diagrams of $CoSeO_3$–SeO_2–H_2O system at different temperatures and the compositions at the peritonic points in the Gibbs–Roozeboom diagrams, the polythermal diagram of the system studied was drawn (Fig. 2).

As can be seen from the figure, six different by area crystallization fields and four non-variant points each with three solid phases in equilibrium can be identified. If the composition of the different selenites is described by the general formula $CoO\cdot nSeO_2\cdot mH_2O$, then Fig. 2 shows that phases with small m became stable with the increase of temperature while the phases with small n were more stable with decreased SeO_2 concen-

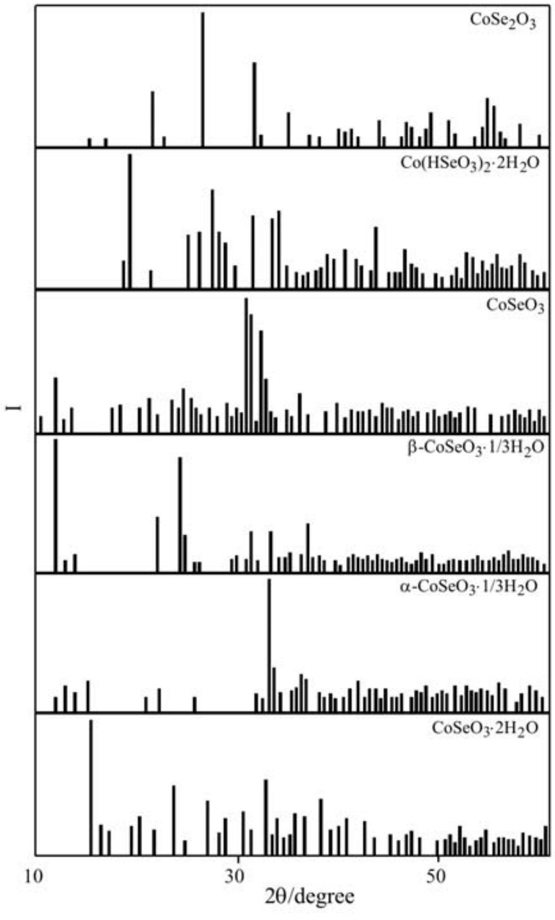


Fig. 1 Streak diagrams of cobalt(II)selenites

Table 1 The interplanar distance (Å) and the relative intensity (%) of the peaks

$CoSeO_3{\cdot}2H_2O$					α-$CoSeO_3{\cdot}1/3H_2O$					β-$CoSeO_3{\cdot}1/3H_2O$					$CoSeO_3$					$Co(HSeO_3)_2{\cdot}2H_2O$					$CoSe_2O_5$				
d/Å	I	h	k	l	d/Å	I	h	k	l	d/Å	I	h	k	l	d/Å	I	h	k	l	d/Å	I	h	k	l	d/Å	I	h	k	l
5.7388	100	0	1	1	6.8127	19	0	0	1	7.3027	100	0	0	1	7.3205	40	2	0	0	4.7461	19	1	1	0	5.6807	4	0	1	1
5.3092	21	1	0	1	5.8463	22	1	–1	1	6.3298	13	1	0	1	6.5521	18	1	1	1	4.6386	100	1	1	–1	4.1493	44	1	1	1
4.5494	20	1	1	1	4.0174	17	2	–1	0	4.0144	32	1	–1	1	4.9736	18	0	2	0	3.5578	34	1	1	1	3.3956	100	0	0	2
4.4125	29	0	2	0	2.7060	100	2	–1	2	3.6705	86	0	2	0	4.1775	26	2	2	–1	3.4251	31	1	1	–2	2.8403	62	0	2	2
4.0619	17	1	1	–1	2.6626	33	2	1	0	3.6165	27	1	–1	–1	3.7518	24	2	2	1	3.2526	73	0	1	2	2.7729	7	2	0	1
3.7770	50	0	0	2	2.5557	14	1	–1	–2	2.8670	30	2	–1	1	3.6602	32	4	0	0	3.1632	23	2	1	–1	2.5730	25	1	2	2
3.2488	39	1	1	2	2.4960	21	1	2	0	2.7090	30	1	–2	1	3.5054	26	0	0	4	3.1420	33	2	0	–2	2.3837	6	1	4	0
3.2209	15	2	0	0	2.4679	22	3	–1	1	2.4873	12	0	3	1	3.4059	13	0	2	3	3.0161	16	1	2	–1	2.2639	12	2	0	2
2.8694	17	0	2	2	2.3221	14	2	2	–2	2.4539	36	3	0	1	3.0987	21	1	3	1	2.8578	54	2	1	–2	2.2497	9	1	3	2
2.7393	55	1	2	2	2.2000	16	3	–3	2	2.3770	11	3	0	2	2.9480	13	4	2	0	2.6495	57	1	2	1	2.2116	13	0	1	3
2.6546	26	2	0	2	2.0811	17	2	–4	2	2.2659	3	2	3	3	2.8914	100	4	2	–3	2.5160	11	0	2	2	2.1626	6	2	3	1
2.5421	30	2	1	2	2.0414	16	1	–3	4	2.1702	10	1	2	–2	2.8751	87	5	1	–3	2.3464	16	2	1	–3	2.0747	18	2	2	2
2.4740	27	1	0	3	1.9695	9	4	2	1	2.1322	11	1	–3	0	2.8532	8	1	3	2	2.3193	26	2	2	–2	1.9715	17	2	4	0
2.3731	41	2	2	–1	1.8902	17	3	–2	3	2.0904	11	2	1	4	2.8090	77	5	1	0	2.2366	28	3	1	–1	1.9075	6	3	1	1
2.1518	23	3	0	1	1.8327	14	3	–4	3	2.0375	8	1	–1	3	2.7865	31	3	1	3	2.1630	20	1	2	2	1.8934	13	2	4	1
2.0310	14	2	2	–2	1.7475	19	1	4	–3	1.9423	6	3	1	4	2.4868	29	0	4	0	2.0922	45	2	2	1	1.8850	27	1	5	1
1.9936	9	1	2	–3	1.7220	12	2	0	3	1.9022	14	1	4	0	2.1992	16	6	2	–4	1.9899	11	2	1	2	1.8151	20	2	0	3
1.9129	12	0	3	3	1.7032	16	0	0	4	1.8694	11	2	2	–2	2.0570	21	4	4	0	1.9677	28	1	1	3	1.8078	20	1	3	3
1.7794	20	1	3	–3	1.6830	22	3	1	–4	1.8112	7	3	4	1	1.9713	15	1	5	0	1.8335	7	3	1	1	1.7879	9	2	1	3
1.7234	11	3	1	–2	1.6595	19	3	–3	4	1.7882	8	1	–3	2	1.9324	13	6	2	–6	1.7789	14	2	2	2	1.7131	14	2	2	3
1.7023	17	1	5	0	1.6425	17	4	–3	3	1.7216	11	1	2	–3	1.8632	18	1	1	7	1.7443	27	3	1	–4	1.6978	32	0	0	4
1.6466	11	1	4	3	1.5923	19	4	–1	–3	1.7001	8	3	–2	2	1.7863	18	1	5	3	1.7126	20	2	2	–4	1.6920	27	3	3	1
1.5881	12	2	4	–2	1.5862	21	2	–3	–2	1.6257	10	2	5	2	1.7391	19	4	2	–8	1.6628	24	1	4	0	1.6415	4	1	4	3
1.5754	11	1	5	2	1.5700	10	1	1	–5	1.5964	12	3	–1	4	1.6181	16	5	5	–4	1.5820	24	3	3	0	1.6069	17	2	3	3
1.5442	21	4	1	2	1.5598	14	1	–2	–3	1.5462	7	5	1	3	1.5562	18	5	1	6	1.5710	12	4	0	–4	1.5536	6	3	3	2

Table 2 Crystallografic data for cobalt(II)selenites

Parameter	$CoSeO_3 \cdot 2H_2O$	α-$CoSeO_3 \cdot 1/3H_2O$	β-$CoSeO_3 \cdot 1/3H_2O$	$CoSeO_3$	$Co(HSeO_3)_2 \cdot 2H_2O$	$CoSe_2O_5$
Color	pink-purple	light violet	light violet	dark violet	pink	pink-violet
Space group	$P2_1/n$	P-1	P-1	$C2/c$	$P2_1/n$	$Pnab$
a/Å	6.5322	8.1197	7.9874	14.5378	7.1357	6.0753
b/Å	8.8251	8.4383	8.1343	9.9880	6.8758	10.3663
c/Å	7.6455	8.5345	8.4399	14.0460	8.0326	6.7913
α/°	–	123.816	69.297	–	–	–
β/°	80.478	90.538	62.385	107.369	113.193	–
γ/°	–	111.591	67.545	–	–	–
Z	4	2	2	32	2	4
V/Å^{-3}	434.67	434.02	438.49	1946.53	362.26	427.71
d_R/g cm^{-3}	3.392	1.468	1.453	4.525	3.215	4.609

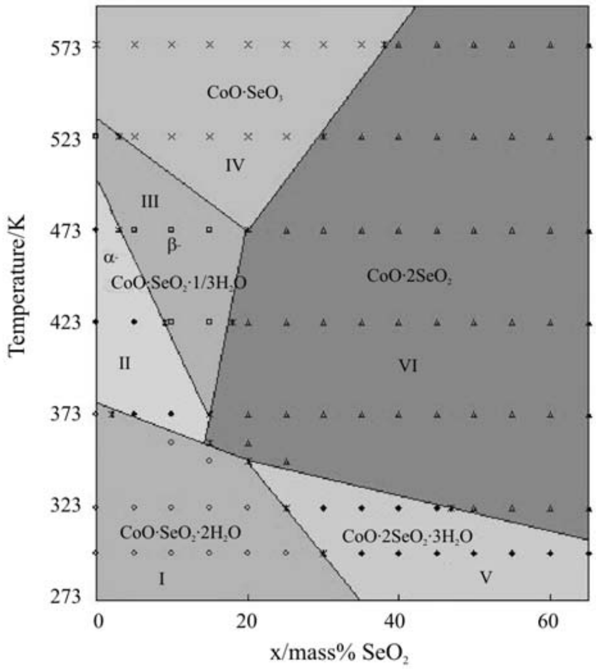


Fig. 2 Crystallization field of selenites in $CoSeO_3$–SeO_2–H_2O system

tration. The boundaries between the crystallization fields with different values of m, however, were not horizontal and those for different n were not vertical. Each boundary had its slope (negative or positive). Similar pattern was observed for the crystallization fields of iron(III)selenites [35]. At relatively low SeO_2 concentrations (<15 mass%), phases with decreasing values of m became more stable: $CoSeO_3 \cdot 2H_2O \rightarrow CoSeO_3 \cdot 1/3H_2O \rightarrow CoSeO_3$. The same tendency was observed for SeO_2 concentrations above 40 mass% with the increase of temperature when the sample passed from $Co(HSeO_3)_2 \cdot 2H_2O$ field into $CoSe_2O_5$ field. Besides, the slope of the boundary between these two fields was negative ($dT/dx<0$). It means that, with the increase of SeO_2 concentration, the equilibrium shifts in the same direction in which it shifts with the increase of temperature, i.e. SeO_2 exerts dehydrating effect and the values of m in the general formula decrease from 2 to 0 (fields I, II, III and IV) and from 3 to 0 (fields V and VI). Similar considerations can be applied to the values of n at T=const and varying SeO_2 concentration. In all the cases studied, the equilibrium shifted to compounds with lower values of n (from 2 to 1, fields V and I and fields VI and IV) with the decrease of SeO_2 concentration in the solution, i.e. hydrolyzation was facilitated. The slopes of the curves separating fields II, III, IV and VI were positive because the increase of temperature and SeO_2 concentration in the solution eased selenites dehydration. The slope of the straight line between fields I and V was negative because both the contents of H_2O and SeO_2 in the solid phase increased simultaneously. The results obtained clearly showed that the hydrothermal treatment of $CoSeO_3 \cdot 2H_2O$ does not give $CoSeO_3 \cdot H_2O$ and $CoSe_2O_5 \cdot 3H_2O$ in the temperature and concentration intervals studied. As it has been reported earlier [8, 14, 15], monohydrate was not observed as intermediate product by the dehydration of the dihydrate and, likewise, $CoSeO_3 \cdot 1/3H_2O$ was not observed by the dehydration of $CoSeO_3 \cdot H_2O$. According to the same authors, the reason for this lack of continuity was the incompatibility of the texture of these crystallohydrates [36]. Figure 3 shows TG, DTA and DTG curves of thermal dehydration and decomposition of $CoSeO_3 \cdot 2H_2O$ at heating rate 10 K min^{-1} and 100 mg sample mass. These conditions are most favorable for the registration of heat effects and mass loss under heating.

As can be seen from the figure, the dehydration of $CoSeO_3 \cdot 2H_2O$ was a one-stage process giving $CoSeO_3$ (mass loss 16.2 mass%) and the product obtained was found to be X-ray amorphous. Intermediate products of the dehydration like $CoSeO_3 \cdot H_2O$ and $CoSeO_3 \cdot 1/3H_2O$ were not registered. The shape of the DTA curve for the dehydration of $CoSeO_3 \cdot 2H_2O$ shows two endothermal effects – the first one 473 K is

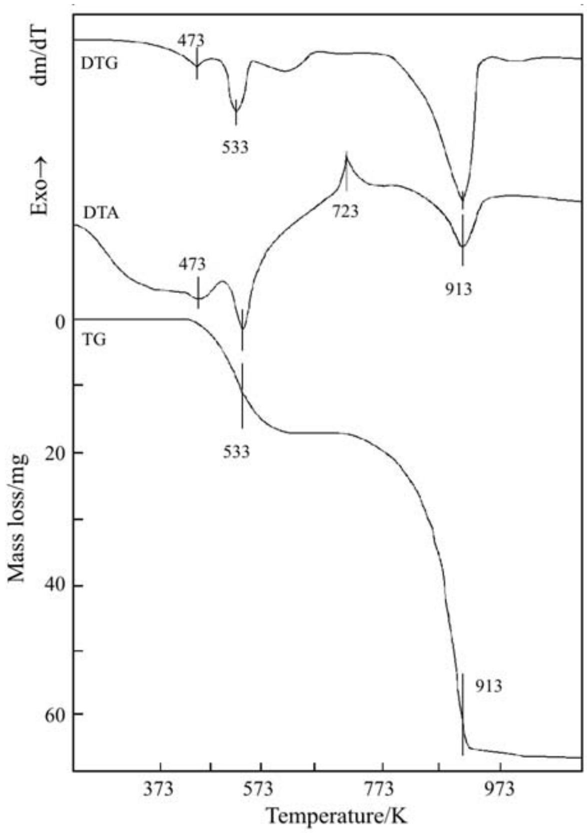


Fig. 3 TG, DTA and DTG curves of thermal dehydration and decomposition of $CoSeO_3{\cdot}2H_2O$

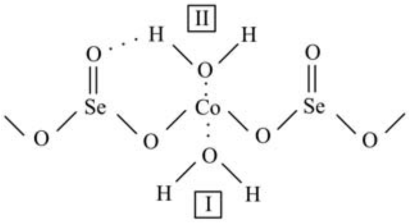
weak and the second one at 533 K is more pronounced. The same effects were registered in the DTG curve. The highest dehydration rate was measured at 533 K. An exo-effect was observed at 723 K and attributed to the crystallization of the amorphous phase [19]. Data from both X-ray and chemical analyses showed that the product corresponds to the formula $CoSeO_3$. At temperatures above 760 K it started to decompose by releasing SeO_2 and formation of CoO. The decomposition was accomplished at about 953 K (mass loss 49.9 mass%) and the highest decomposition rate was observed at 913 K. Based on the method of Coats and Redfern [37] for the kinetics of topochemical reactions under non-isothermal conditions of heating, the values of the activation energies of the processes of dehydration of $CoSeO_3{\cdot}2H_2O$ and decomposition of $CoSeO_3$ were calculated to be 89.43 and 218.66 kJ mol^{-1}, respectively.

The data from IR spectroscopy revealed that the water molecule was in very similar states in $CoSeO_3{\cdot}2H_2O$ and $CoSeO_3{\cdot}1/3H_2O$ while in $CoSeO_3$ $\cdot H_2O$ it was essentially different [8, 14–16].

In the present investigation, a field of $CoSe_2O_5$ $\cdot 3H_2O$ was not registered, probably because Lieder and Gattow [25], obtained it at different conditions and from other reagents. Studying the solubility diagram of the $CoSeO_3$–SeO_2–H_2O system at 298 K, Ebert *et al*. [10] found a field of crystallization of H_2SeO_3 and eutonic point at 69.3 mass% SeO_2. Our experiments did not show such a field since the highest SeO_2 concentration in solutions studied was 65 mass% [37].

The different cobalt(II)selenites obtained were studied by IR spectroscopy and the absorption spectra are presented in Fig. 4. The bands observed were interpreted according to the works of Simon [38–40] and Cody [41, 42] for selenous acid and other authors [8, 10, 12, 15, 16, 23, 43–51] studying IR spectra of different selenites.

Figure 4 showed that IR spectra of the selenites studied had some common and some specific bands. For instance, four absorption bands were registered in the high frequency region of $CoSeO_3{\cdot}2H_2O$ spectrum, which were attributed to stretching vibrations of O–H from H_2O molecules. In the interval 1500–1700 cm^{-1} two absorption bands were observed due to the bending vibrations of H_2O molecules. The reason for this is that the two water molecules in the dihydrate are structurally unequal according to the following scheme [46]:



In the environment of the octahedral Co^{2+} cation, one of the water molecules is at a distance equal to the sum of the covalent radii of the metal and oxygen and at almost equal distances from the oxygen atoms of the selenite group. This molecule (denoted as H_2O–I) is loaded almost symmetrically, therefore the difference in the frequencies of its asymmetric ν_{as} and symmetric ν_a vibrations is almost constant with a value of 100–110 cm^{-1} [8, 15]. Hence, the band at 3224 cm^{-1} can be attributed to ν_{as}(O–H)$\cdot H_2O$ and the band at 3129 cm^{-1} – to ν_s(O–H)(H_2O–I). The second water molecule is at higher distance from Co^{2+} ion but at a relatively small distance from Se=O (HOH…OSe<~2.7 Å), forming a strong enough hydrogen bond. The bond of the second hydrogen atom with the oxygen atom in the H_2O molecule remains almost the same as in a free water molecule. Since in such cases of asymmetric loading of the (H_2O–II) molecule the difference between the stretching vibrations could be as much as 500–600 cm^{-1} [8], then the vibrations along both O–H bonds in this molecule can be regarded as independent. Therefore, the band with the highest frequency at 3430 cm^{-1} can be attributed to ν_{free}(OH) of the relatively free OH group in (H_2O–II) while that at 2942 cm^{-1}–ν_{bond}(OH)

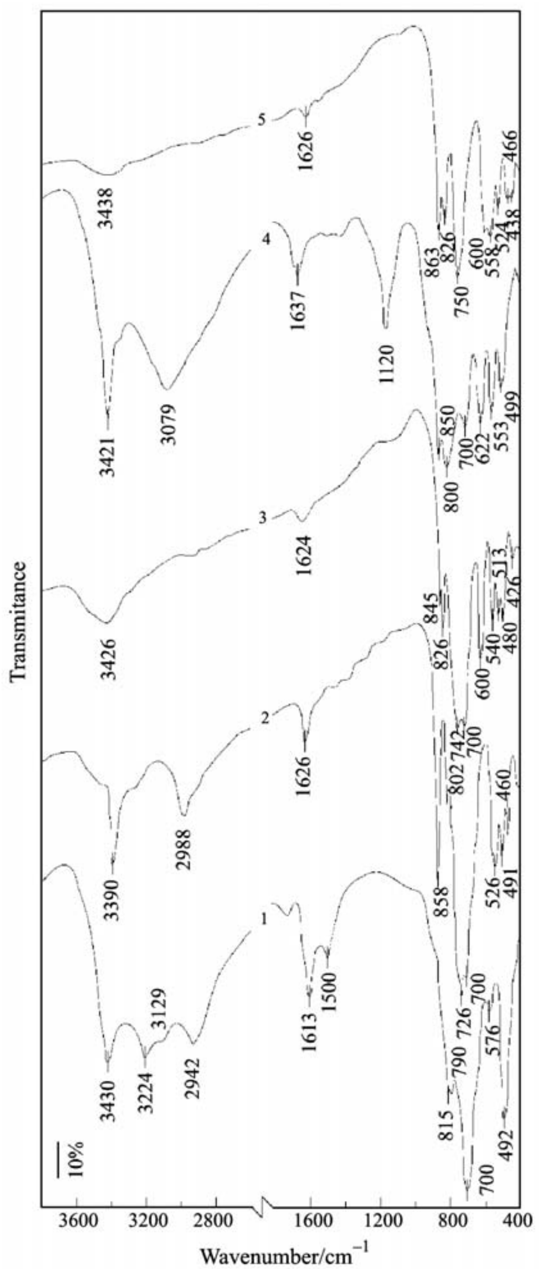


Fig. 4 Infrared absorption spectra of cobalt(II)selenites at 298 K: 1 – $CoSeO_3 \cdot 2H_2O$; 2 – $CoSeO_3 \cdot 1/3H_2O$; 3 – $CoSeO_3$; 4 – $Co(HSeO_3)_2 \cdot 2H_2O$ and 5 – $CoSe_2O_5$

of the OH group bonded by hydrogen bond in the same water molecule. Consequently, the band at 1500 cm^{-1} is probably due to the bending vibrations δ(H_2O–I) and the band at 1613 cm^{-1} – to δ(H_2O–II). The two endothermal effects observed in the DTA curve (Fig. 3) at 473 and 533 K is considered to prove the existence of two substantially different types of water in $CoSeO_3 \cdot 2H_2O$. Similar interpretation was suggested in [46] for other selenites dehydrates.

All these considerations were sustained by the fact that only one absorption band at 1626 cm^{-1} was observed for $CoSeO_3 \cdot 1/3H_2O$, representing the bending vibrations of (H_2O–II) molecules, thus confirming that in this case the water molecules were structurally equal. Two clearly distinguishable bands at 3390 and 2988 cm^{-1} were registered in the high frequency region of the same spectrum. Since the difference between them was quite big (~400 cm^{-1}), they can be attributed to stretching vibrations of ν_{free}(OH) from (H_2O–II). For $CoSeO_3$, however, no absorption bands were observed from 1500 to 1300 cm^{-1} except for the low intensity broad bands at 1624 and 3426 cm^{-1} probably due to small quantities of physically adsorbed water on sample surface.

A number of bands were registered in the region 900–400 cm^{-1} and their number increased from $CoSeO_3 \cdot 2H_2O$ to $CoSeO_3$, i.e. as dehydration proceeds, the characteristic bands were more distinctly measured and the IR spectrum had more details. Four types of characteristic bands were found: ν(Se–O) in SeO_3^{2-} anion, ρ(H_2O), ν(Co–O) and δ(O–Se–O). These absorption bands were observed in the IR spectra of the other selenites; they were analyzed by other authors [8, 10, 15, 16].

Beside the characteristic bands for the water ν(O–H) and δ(H_2O) at 3421 and 1637 cm^{-1}, the IR spectrum of $Co(HSeO_3)_2 \cdot 2H_2O$ (Fig. 4, spectrum 4) showed two new intensive absorption bands at 3079 and 1120 cm^{-1}. According to other authors [10, 23], they represent ν(O–H)(Se–OH) and δ(OH)(Se–OH). The significantly lower values of these vibrations were attributed to the formation of strong hydrogen bonds. A number of absorption bands were observed from 850 to 400 cm^{-1} and one of them is at 622 cm^{-1} for ν(Se–O)(Se–OH) [10].

The spectrum of $CoSe_2O_5$ (Fig. 4, spectrum 5) showed two low intensity and wide absorption bands at 3438 and 1626 cm^{-1}. They were due to the stretching and bending vibrations, respectively, of small amounts of physically adsorbed water on sample surface. Taking into account the composition and specific features of the thermal decomposition of the diselenites, $CoSe_2O_5$ can be regarded as a product of attachment – co-ordination bonding of a molecule SeO_2 to $CoSeO_3$. Therefore, the IR spectrum showed both absorption bands for the almost free SeO_2 [48, 51] and SeO_3^{2-} ions [43–51]. The large number of bands present in the interval 850–400 cm^{-1} are usually connected with the vibration structure of the diselenite anion [O_2Se–O–SeO_2]. The spectrum is considered to summarize the vibrations of (SeO_2)-groups and (Se–O–Se) bridges [40, 49–51]. According to the authors who have studied various selenites, the bands in the interval 900–860 cm^{-1} are due to ν_{as}(SeO_2); 840–780 cm^{-1} – ν_s(SeO_2); 600–560 cm^{-1} – ν_{as}(Se–O–Se); 530–475 cm^{-1} – ν_s(Se–O–Se); 410–330 cm^{-1} – δ(SeO_2) and those from 300 to 250 cm^{-1} – to δ(Se–O–Se).

Conclusions

It may be concluded, that the absorption bands observed in the IR spectra of the different selenites studied, together with the results from the powder X-ray diffraction and chemical analyses irrefutably prove the existence of different crystalline forms of cobalt(II)selenites and provide enough data to determine the corresponding crystallization fields of stability in the solubility diagram of the system $CoSeO_3$–SeO_2–H_2O.

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Received: December 20, 2004
In revised form: March 22, 2005

DOI: 10.1007/s10973-005-6812-7