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On the Double Salt Formation in the Systems Rb_2SeO_4–$ZnSeO_4$–H_2O and Cs_2SeO_4–$ZnSeO_4$–H_2O at 25°C

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Summary. The solubilities in the systems Rb_2SeO_4–$ZnSeO_4$–H_2O and Cs_2SeO_4–$ZnSeO_4$–H_2O at 25°C were studied by the method of isothermal decrease of supersaturation. Comparatively wide crystallization fields of the double salts $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ and $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$ are observed in the solubility diagrams. The double salts form monoclinic crystals which are isostructural with those of the corresponding rubidium and cesium zinc sulfate hexahydrates. TG and TDA measurements indicate that the double salts lose their crystallization water in one step in the temperature intervals of 50–160°C (rubidium salt) and 70–150°C (cesium salt).

Keywords. Rubidium zinc selenate hexahydrate; Cesium zinc selenate hexahydrate; Solubility diagrams; Lattice parameters.

Introduction

The present paper reports on the solubility in three-component systems of the type M_2SeO_4–$MSeO_4$–H_2O in which double salts are expected to be formed. For example, double salts of the type $M_2M(SeO_4)_2 \cdot nH_2O$ ($n = 2$ or 4) are formed in the system Na_2SeO_4–$MSeO_4$–H_2O at 25°C ($M =$ Mn, Co, Cu, Zn, and Cd) [1–3]. Recently, it has been reported that Cs_2SeO_4 forms double salts of the type $Cs_2Ni(Co)(SeO_4)_2 \cdot 6H_2O$ with $NiSeO_4$ and $CoSeO_4$ [4]. Solubility data of the systems Rb_2SeO_4–$ZnSeO_4$–H_2O and Cs_2SeO_4–$ZnSeO_4$–H_2O are lacking in the literature. Whereas the thermal stability and the vibrational spectra of the double salt $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ are known [5], no data are available for $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$.

Results and Discussion

The solubility data for the systems studied are presented in Tables 1 and 2, the corresponding solubility diagrams in Figs. 1 and 2. Comparatively wide crystallization fields of double salts of compositions $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ and

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Table 1. Solubility in the Rb_2SeO_4–$ZnSeO_4$–H_2O system at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		Composition of the solid phase
$ZnSeO_4$	Rb_2SeO_4	$ZnSeO_4$	Rb_2SeO_4	
40.42	–	–	–	$ZnSeO_4 \cdot 6H_2O$
38.75	2.25	63.50	0.20	$ZnSeO_4 \cdot 6H_2O$
38.51	6.61	61.15	0.83	$ZnSeO_4 \cdot 6H_2O$
36.26	8.34	45.99	21.67	$ZnSeO_4 \cdot 6H_2O + Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
36.65	8.75	32.61	41.59	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
28.70	9.01	32.50	45.50	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
23.08	11.23	30.67	37.43	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
12.21	16.98	28.57	43.19	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
5.42	22.25	29.27	45.97	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
0.37	27.68	28.75	46.75	$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$
–	62.02	–	–	Rb_2SeO_4

Table 2. Solubility in the Cs_2SeO_4–$ZnSeO_4$–H_2O system at 25°C

Liquid phase (mass%)		Wet solid phase (mass%)		Composition of the solid phase
$ZnSeO_4$	Cs_2SeO_4	$ZnSeO_4$	Cs_2SeO_4	
40.42	–	–	–	$ZnSeO_4 \cdot 6H_2O$
39.01	4.51	60.03	1.01	$ZnSeO_4 \cdot 6H_2O$
38.50	9.50	61.01	1.52	$ZnSeO_4 \cdot 6H_2O$
37.90	13.36	45.16	34.14	$ZnSeO_4 \cdot 6H_2O + Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
36.18	13.71	28.69	56.41	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
27.96	19.13	29.11	56.04	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
18.58	24.40	27.78	55.05	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
5.50	37.88	27.79	56.01	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
2.11	46.50	26.30	54.50	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
0.20	54.75	26.01	56.50	$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$
–	72.15	–	–	Cs_2SeO_4

$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$ are observed. It can be seen from the data in Tables 1 and 2 that a small amount of Zn^{2+} ions (less than 1%) results from the formation of the double salts.

The double salts were washed with alcohol, dried on air, and identified by chemical analysis, X-ray powder diffraction, differential thermal analysis (DTA), and thermogravimetric analysis (TG).

The chemical analysis shows 49.54 mass% Rb_2SeO_4 and 32.96 mass% $ZnSeO_4$ for $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ (theoretical content: 49.81 mass% Rb_2SeO_4, 33.06 mass% $ZnSeO_4$) and 56.22 mass% Cs_2SeO_4 and 28.51 mass% $ZnSeO_4$ for $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$ (theoretical content: 56.37 mass% Cs_2SeO_4, 28.73 mass% $ZnSeO_4$). On the basis of the derivatograms of the double salts, the following dehydration scheme

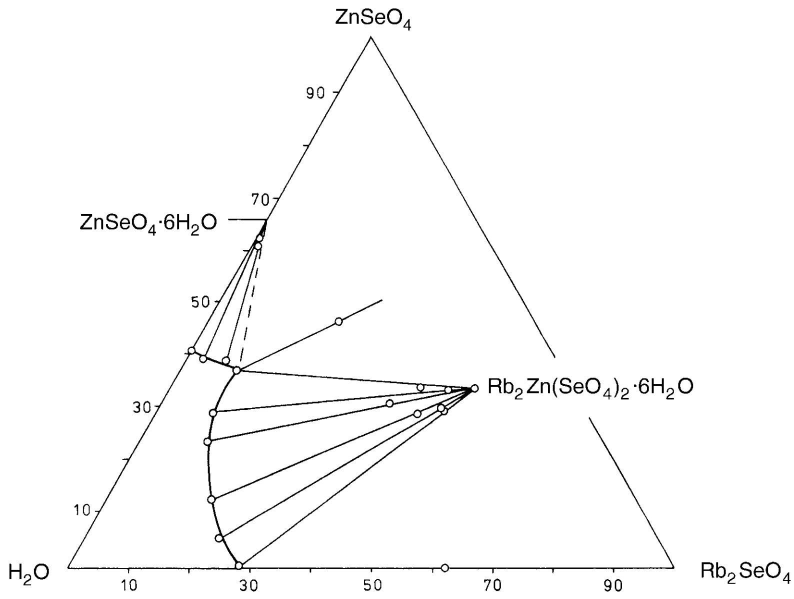

Fig. 1. Solubility in the Rb_2SeO_4–$ZnSeO_4$–H_2O system at 25°C

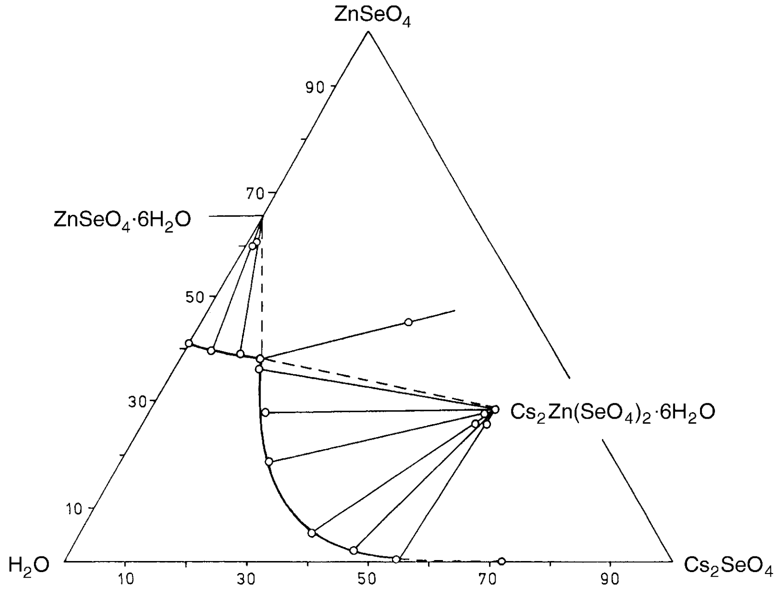

Fig. 2. Solubility in the Cs_2SeO_4–$ZnSeO_4$–H_2O system at 25°C

is proposed (the dehydration processes for both salts occur in one step): $Rb_2(Cs)Zn(SeO_4)_2 \cdot 6H_2O \rightarrow Rb_2(Cs)Zn(SeO_4)_2 (T_{max} = 120°C)$. The *d*-spacings and *khl* indices of the double salts are given in Table 3. The X-ray patterns of $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ and $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$ are identical, thus indicating that the double salts are isostructural. They form monoclinic crystals with the following

Table 3. X-Ray diffraction data of $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$ and $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$

$Rb_2Zn(SeO_4)_2 \cdot 6H_2O$			$Cs_2Zn(SeO_4)_2 \cdot 6H_2O$		
d_{obs}/Å	*hkl*	I/I_0	d_{obs}/Å	*hkl*	I/I_0
7.17	110	17	7.36	110	6
5.21	−111	18	6.35	020	5
4.43	200	18	6.11	001	10
4.33	021	22	5.51	011	43
4.23	111	38	5.21	120	16
4.20	−121	75	4.53	200	14
3.71	130	11	4.41	021	8
3.32	−131	23	4.24	111	100
3.10	211	100	4.04	−211	10
3.07	040	82	3.82	130	38
2.961	012	7	3.67	121	18
2.900	−231	28	3.48	031	10
2.875	−202	14	3.43	−131	10
2.805	−212	57	3.23	201	10
2.462	−241	15	3.13	211	14
2.394	330	44	3.06	002	40
2.253	321	18	2.969	012	9
2.241	−411	21	2.945	−202	10
2.145	250	31	2.885	221	8
2.136	−341	9	2.840	−122	15
2.042	060	14	2.475	032	14
2.014	142	26			
1.8953	−351	26			

lattice parameters: $Rb_2Zn(SeO_4)_2 \cdot 6H_2O$: $a = 9.173(1)$ Å, $b = 12.257(2)$ Å, $c = 6.302(2)$ Å, $\beta = 105.02(2)°$, $V = 684.4(2)$ Å^3; $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$ $a = 9.445(5)$ Å, $b = 12.686(5)$ Å, $c = 6.365(2)$ Å, $\beta = 106.32(1)°$, $V = 732.1(4)$ Å^3. Furthermore, the X-ray powder diffraction data of the double selenates are similar to those of the corresponding sulfates ($Rb_2Zn(SO_4)_2 \cdot 6H_2O$ and $Cs_2Zn(SeO_4)_2 \cdot 6H_2O$) [7, 8]; therefore all four salts are assumed to be isostructural.

Experimental

$ZnSeO_4 \cdot 6H_2O$ was prepared by neutralization of zinc hydroxide carbonate with an aqueous solution of selenic acid at 50°C. The solution was then filtered and concentrated. The crystals of $ZnSeO_4 \cdot 6H_2O$ obtained by cooling the solution to ambient temperature were recrystallized from water and dried in air. Cs_2SeO_4 and Rb_2SeO_4 were prepared from solutions of the corresponding carbonates and selenic acid. Crystallization of the salts occurs slowly at ambient temperature. The crystals were recrystallized according to Ref. [4]. All reagents used were of *p.a.* quality (Merck). The solubilities in the systems Rb_2SeO_4–$ZnSeO_4$–H_2O and Cs_2SeO_4– $ZnSeO_4$–H_2O at 25°C were studied using the method of isothermal decrease of supersaturation described elsewhere [6]. The equilibrium was reached in about 20 h. The concentration of the Zn^{2+} ions in the liquid and the wet solid phases was determined complexometrically at $pH = 5.5$–6 using xylenol orange as indicator. The concentration of the SeO_4^{2-} ions was determined complexometrically according to Ref. [1]. The concentrations of the Cs^+ and Rb^+ ions were calculated by difference. The X-ray diffraction patterns were obtained with a DRON-3 powder diffractometer using CuK_α radiation at a scanning speed of $1° \cdot min^{-1}$. The measurements were performed in a 2θ diffraction interval of 10–45°; α-SiO_2 was used as a standard. The lattice parameters were calculated using the programs ITO and LSUCR [9]. The thermal dehydration of the double salts was studied using a derivatograph Paulik-Paulik-Erdey MON OD-102 in the temperature range up to 400°C at a heating rate of $10°C \cdot min^{-1}$ using α-alumina as a reference material (sample mass 200 mg).

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