

# Crystallization in the Three-Component Systems $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$ ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) at 298 K

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## ABSTRACT

The crystallization in the three-component systems  $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) is studied by the method of isothermal decrease of supersaturation. It has been established that isostructural double compounds,  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ),  $(\text{SG } P2_1/c(C_{2h}^5))$ , crystallize from the ternary solutions within wide concentration ranges. The infrared spectra are discussed with respect to the normal vibrations of the sulfate ions and water molecules. The unit-cell group theoretical treatment of the double salts is presented. The extent of energetic distortions of  $\text{SO}_4^{2-}$  guest ions (about 2 mol%) matrix-isolated in the respective selenates,  $\text{M}'_2\text{M}''(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ), is commented.

**Keywords:**  $\text{Rb}_2\text{Me}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{Me} = \text{Mg, Co, Ni, Cu, Zn}$ ); Solubility Diagrams; X-Ray Powder Diffraction; Infrared Spectra; Matrix Infrared Spectroscopy

## 1. Introduction

The rubidium double sulfates belong to a large number of isomorphous compounds with a general formula  $\text{M}'_2\text{M}''(\text{XO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+, \text{Cs}$ ;  $\text{M}'' = \text{Mg, Mn, Co, Ni, Cu, Zn}$ ;  $\text{X} = \text{S, Se}$ ) known as Tutton salts. They crystallize in the monoclinic space group  $P2_1/c(C_{2h}^5)$  with two formula units in the unit-cell. The crystal structures are built up from isolated octahedra,  $[\text{M}''(\text{H}_2\text{O})_6]$ , (three crystallographically different water molecules are coordinated to the  $\text{M}''$  ions) and tetrahedra  $\text{XO}_4$ . The polyhedra are linked by hydrogen bonds. All atoms, except the divalent metal ions, which lie at centre of inversion  $C_i$ , are located at general positions  $C_1$ . Recently, the crystal structures of some rubidium Tutton sulfates have been reported in Refs. [1,2]. As an example the crystal structures of  $\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  is presented in Figure 1.

In this paper we present the results on the study of the solubility in the three-component systems  $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) at 298 K. The double Tutton compounds  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  are characterized by means of both the infrared spectroscopy

and the X-ray powder diffraction methods. The vibrational behavior of  $\text{SO}_4^{2-}$  guest ions matrix-isolated in Tutton selenates,  $\text{M}'_2\text{M}''(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ), is analyzed. A practical point of studying is that the Tutton compounds could be considered as proton conductors due to the existence of comparatively strong hydrogen bonds determined by the strong proton acceptor capabilities of the sulfate ions.

## 2. Experimental

$\text{Rb}_2\text{SO}_4$  was prepared by neutralization of  $\text{Rb}_2\text{CO}_3$  with dilute sulfuric acid solutions at 333 - 343 K. Then the solutions were filtered, concentrated at 323 - 333 K, and cooled to room temperature. The crystals were filtered, washed with alcohol and dried in air. The sulfates of divalent metals were commercial products. All reagents used were of reagent grade quality (Merck). The solubility in the three-component systems  $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) at 298 K was studied using the method of isothermal decrease of supersaturation. Solutions containing different amount of the salt compounds corresponding to each point of the solubility diagrams

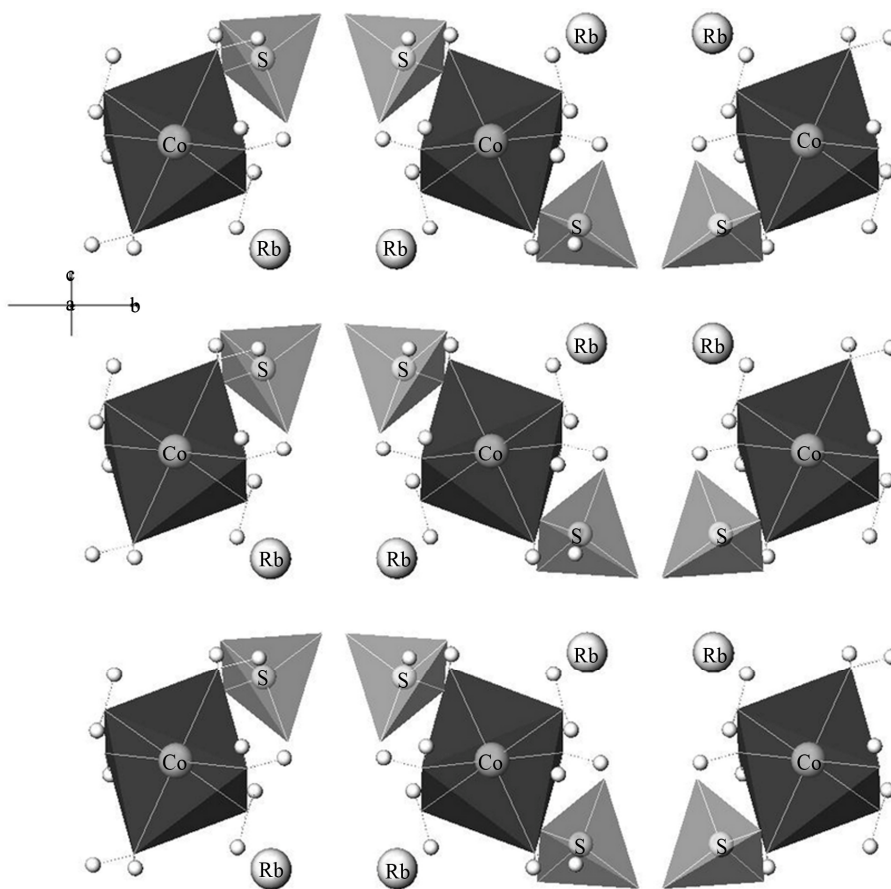


Figure 1. Crystal structure of  $\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (structural data from [1]).

were heated at about 333 - 343 K and cooled to room temperature. Then the saturated solutions were vigorously stirred [3,4]. The equilibrium between the liquid and solid phases was reached in about 20 hours. The analysis of the liquid and the wet solid phases was performed as follows: the  $\text{M}''$  ion contents were determined complexometrically at pH 9.5 - 10 using eriochrome black as indicator (magnesium ions) and at pH 5.5 - 6 using xylenol orange as indicator (cobalt, nickel, copper and zinc ions); the sulfate ions were precipitated as  $\text{BaSO}_4$  with  $\text{Ba}(\text{NO}_3)_2$  solutions and the concentrations of the excess of  $\text{Ba}^{2+}$  ions were determined complexometrically using eriochrome black as indicator; the concentrations of the rubidium sulfate were calculated by difference [5]. The compositions of the solid phases were identified by means of both the X-ray diffraction and the infrared spectroscopy methods. Tutton compounds  $\text{Rb}_2\text{M}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$  were prepared according to the solubility diagrams of the three-component systems  $\text{Rb}_2\text{SeO}_4\text{-MSeO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) [6-8]. The samples,  $\text{M}'_2\text{M}''(\text{SeO}_4)_{1.98}(\text{SO}_4)_{0.02} \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ), were prepared by crystallization from ternary selenate solutions in the presence of  $\text{SO}_4^{2-}$  ions (the data for the potassium and

ammonium selenates are taken from [9]).

The infrared spectra were recorded on a Bruker model IFS 25 Fourier transform interferometer (resolution  $< 2 \text{ cm}^{-1}$ ) at ambient temperature using KBr discs as matrices. Ion exchange or other reactions with KBr have not been observed. In some cases Lorentz band profile for multi peak data was used to determine the correct band positions corresponding to asymmetric stretches of the included  $\text{SO}_4^{2-}$  ions (ORIGIN PRO 6.1). The X-ray powder diffraction spectra were collected within the range from  $5^\circ$  to  $50^\circ 2\theta$  with a step  $0.02^\circ 2\theta$  and counting time 35 s/step on Bruker D8 Advance diffractometer with  $\text{CuK}\alpha$  radiation and LynxEye detector. The lattice parameters of the double salts were calculated using the program ITO and refined with the program LSUCR.

### 3. Results and Discussions

#### 3.1. Solubility Diagrams of the Three-Component Systems $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$ ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) at 298 K

The solubility diagrams of the above systems are presented in Figures 2-6 (the respective experimental data

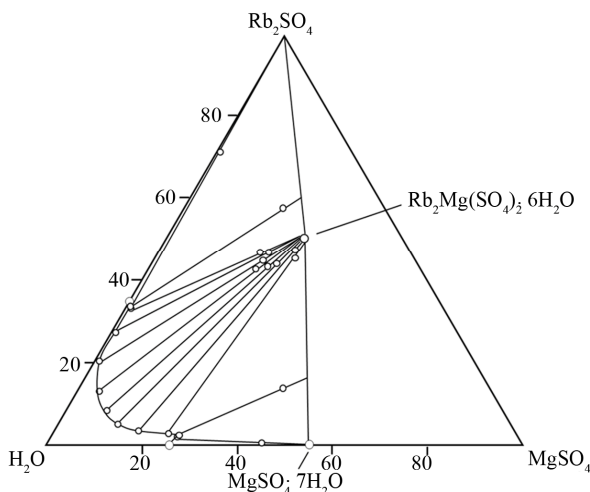


Figure 2. Solubility diagram of the three-component system  $\text{Rb}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  at 298 K.

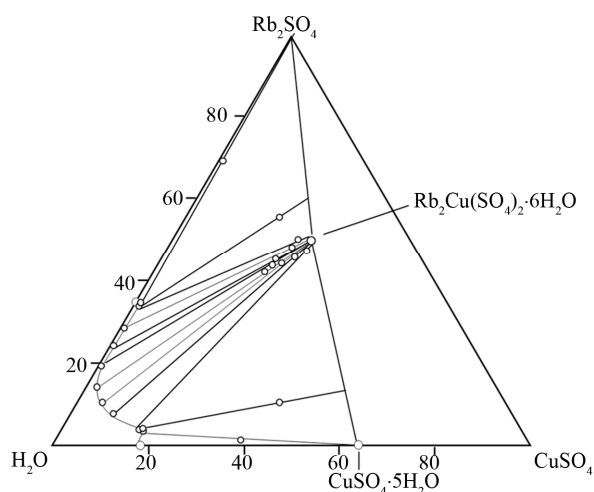


Figure 5. Solubility diagram of the three-component system  $\text{Rb}_2\text{SO}_4\text{-CuSO}_4\text{-H}_2\text{O}$  at 298 K.

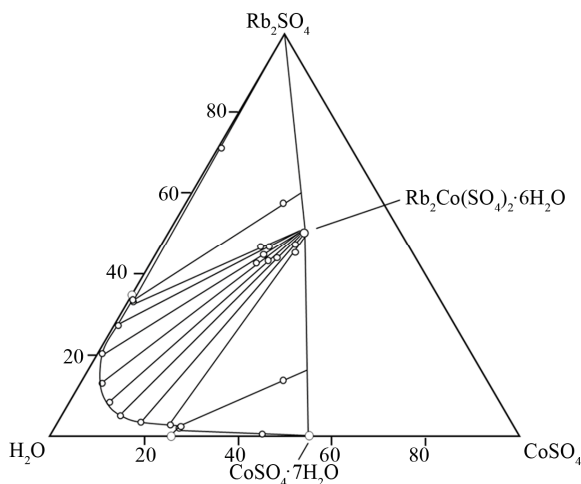


Figure 3. Solubility diagram of the three-component system  $\text{Rb}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  at 298 K.

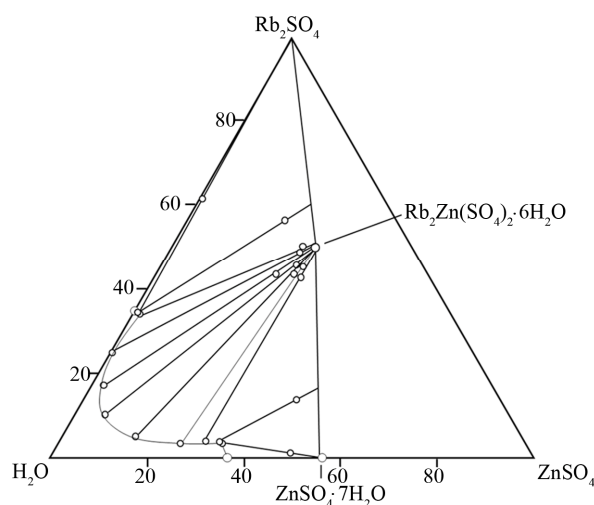


Figure 6. Solubility diagram of the three-component system  $\text{Rb}_2\text{SO}_4\text{-ZnSO}_4\text{-H}_2\text{O}$  at 298 K.

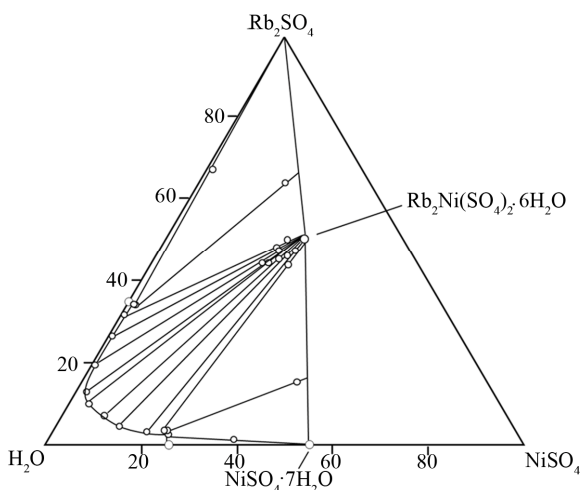


Figure 4. Solubility diagram of the three-component system  $\text{Rb}_2\text{SO}_4\text{-NiSO}_4\text{-H}_2\text{O}$  at 298 K.

are summarized in **Tables 1-5**). It is seen that the simple salts  $\text{Rb}_2\text{SO}_4$ ,  $\text{MgSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{NiSO}_4\cdot 7\text{H}_2\text{O}$ ,  $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$  and  $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$  crystallize within very narrow concentration ranges, whereas the rubidium double sulfates crystallize within wide concentration ranges, thus indicating that strong complex formation processes occur in the ternary solutions.

### 3.2. X-Ray Powder Diffraction Data of Rubidium Tutton Compounds

The X-ray powder diffraction patterns of the rubidium Tutton compounds are shown in **Figure 7**. The double salts form monoclinic crystals (SG  $P2_1/c(C_{2h}^5)$ ).

The calculated unit-cell parameters are presented in **Table 6**. Our results coincide well with those determined from single crystal X-ray diffraction data [1,2].

**Table 1. Solubility in the  $\text{Rb}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  system.**

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
$\text{Rb}_2\text{SO}_4$	$\text{MgSO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{MgSO}_4$	
35.10				$\text{Rb}_2\text{SO}_4$
34.58	1.12	74.41	0.79	-
34.42	2.08	59.17	16.58	$\text{Rb}_2\text{SO}_4 + \text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
34.07	2.03	53.26	21.09	$\text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
29.39	2.48	50.02	19.96	-
25.85	4.13	48.62	20.14	-
21.19	6.11	49.57	21.75	-
17.17	8.66	46.68	21.24	-
13.37	12.96	47.87	23.36	-
9.45	19.25	46.71	23.96	-
6.97	24.01	48.37	24.83	-
7.38	27.54	49.58	25.68	-
7.51	28.51	20.54	37.42	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} + \text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
6.87	28.73	3.19	42.21	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
3.49	27.61	0.64	45.27	-
	27.50			-

**Table 2. Solubility in the  $\text{Rb}_2\text{SO}_4\text{-CoSO}_4\text{-H}_2\text{O}$  system.**

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
$\text{Rb}_2\text{SO}_4$	$\text{CoSO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{CoSO}_4$	
35.10				$\text{Rb}_2\text{SO}_4$
33.54	1.02	71.49	0.76	-
33.28	1.09	57.36	21.37	$\text{Rb}_2\text{SO}_4 + \text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
33.21	1.04	47.24	21.69	$\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
27.43	0.98	47.21	23.56	-
20.68	0.78	45.47	23.38	-
13.32	4.93	42.78	22.84	-
8.48	8.59	43.17	25.31	-
5.44	12.97	44.25	26.83	-
3.79	17.07	47.36	29.14	-
2.83	24.21	45.28	30.07	-
2.40	26.68	14.55	42.73	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O} + \text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
2.19	26.49	0.84	44.93	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$
	26.14			-

**Table 3. Solubility in the  $\text{Rb}_2\text{SO}_4\text{-NiSO}_4\text{-H}_2\text{O}$  system.**

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
$\text{Rb}_2\text{SO}_4$	$\text{NiSO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{NiSO}_4$	
35.10				$\text{Rb}_2\text{SO}_4$
34.72	1.53	67.42	1.17	-
34.68	1.57	63.65	18.67	$\text{Rb}_2\text{SO}_4 + \text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
31.92	0.50	49.96	25.73	$\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
26.44	0.68	48.18	24.58	-
19.85	0.81	47.26	26.22	-
13.00	2.40	43.72	23.19	-
10.52	3.45	44.36	24.65	-
7.59	9.04	45.61	26.29	-
5.08	13.37	46.44	28.07	-
3.97	19.82	47.56	29.45	-
4.02	23.37	43.74	29.67	-
4.06	24.08	15.72	45.67	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O} + \text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
3.85	24.57	1.43	38.79	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$
	26.47			-

**Table 4. Solubility in the  $\text{Rb}_2\text{SO}_4\text{-CuSO}_4\text{-H}_2\text{O}$  system.**

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
$\text{Rb}_2\text{SO}_4$	$\text{CuSO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{CuSO}_4$	
35.10				$\text{Rb}_2\text{SO}_4$
34.81	0.98	69.11	1.02	-
33.72	1.04	55.74	20.14	$\text{Rb}_2\text{SO}_4 + \text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
33.64	1.12	50.47	26.73	$\text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
28.68	1.06	48.26	26.44	-
24.59	0.96	45.49	24.36	-
19.53	0.35	43.72	24.21	-
14.46	2.48	42.64	23.55	-
10.72	4.92	44.26	25.87	-
8.75	9.28	45.82	28.33	-
4.17	16.16	47.48	29.94	-
4.43	16.57	10.45	42.48	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + \text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
3.97	17.01	1.74	38.76	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
	18.30			-

**Table 5. Solubility in the  $\text{Rb}_2\text{SO}_4\text{-ZnSO}_4\text{-H}_2\text{O}$  system.**

Liquid phase mass%		Wet solid phase mass%		Composition of the solid phases
$\text{Rb}_2\text{SO}_4$	$\text{ZnSO}_4$	$\text{Rb}_2\text{SO}_4$	$\text{ZnSO}_4$	
35.10				$\text{Rb}_2\text{SO}_4$
34.61	1.98	61.48	1.28	-
34.15	1.72	56.57	20.46	$\text{Rb}_2\text{SO}_4 + \text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
33.85	1.34	50.26	27.19	$\text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
25.02	0.50	48.43	27.54	-
17.72	2.63	43.67	25.71	-
10.44	6.36	45.72	28.44	-
4.87	15.06	43.85	29.16	-
3.77	25.45	45.05	30.11	-
4.01	30.86	42.67	30.85	-
3.96	33.75	13.74	44.26	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O} + \text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$
3.79	34.05	1.28	29.04	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
	36.43			-

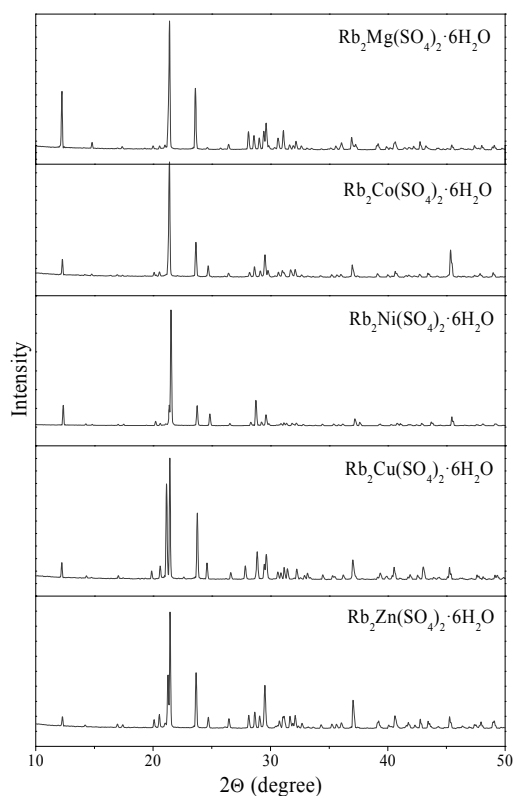
**Table 6. Lattice parameters of the Tutton compounds.**

Tutton salts	$a$ (Å)	$b$ (Å)	$c$ (Å)	$\beta$ (°)	$V$ (Å <sup>3</sup> )
Mg	9.235(2)	12.493(2)	6.227(1)	105.95(2)	690.8(2)
Co	9.198(3)	12.483(5)	6.245(1)	106.12(2)	688.9(2)
Ni	9.147(4)	12.418(4)	6.223(3)	106.06(2)	679.3(3)
Cu	9.269(4)	12.365(4)	6.229(2)	105.38(2)	688.4(3)
Zn	9.198(2)	12.461(4)	6.248(2)	105.9(2)	688.5(1)

### 3.3. Infrared Spectra of Neat Rubidium Tutton Sulfates

The free tetrahedral ions ( $\text{XO}_4^{n-}$ ) under perfect  $T_d$  symmetry exhibit four internal vibrations:  $\nu_1(\text{A}_1)$ , the symmetric X-O stretching modes,  $\nu_2(\text{E})$ , the symmetric  $\text{XO}_4$  bending modes,  $\nu_3(\text{F}_2)$  and  $\nu_4(\text{F}_2)$ , the asymmetric stretching and bending modes, respectively. The normal vibrations of the free sulfate ions in aqueous solutions are reported to appear as follows:  $\nu_1 = 983 \text{ cm}^{-1}$ ,  $\nu_2 = 450 \text{ cm}^{-1}$ ,  $\nu_3 = 1105 \text{ cm}^{-1}$ ,  $\nu_4 = 611 \text{ cm}^{-1}$  [10]. On going into solid state, the normal modes of the ( $\text{XO}_4^{n-}$ ) ions are expected to shift to higher or lower frequencies.

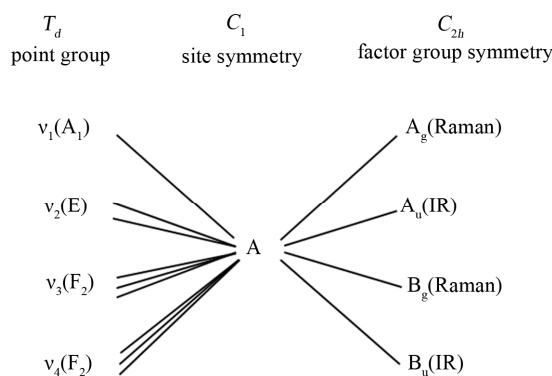
The static field (related to the symmetry of the site on which the  $\text{XO}_4^{n-}$  ions are situated) will cause a removal of the degeneracy of both the doubly degenerate  $\nu_2$  modes and the triply degenerate  $\nu_3$  and  $\nu_4$  modes. Since the tetrahedral ions in the structures of Tutton compounds occupy site symmetry  $C_1$ , two bands for  $\nu_2$  (2A)

**Figure 7. X-ray powder diffraction patterns of  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ).**

and three bands for  $\nu_3$  and  $\nu_4$  (3A), respectively, are expected to appear in the vibrational spectra as predicted from the site group analysis (the nondegenerate  $\nu_1$  mode is activated). Additionally, the factor group analysis ( $C_{2h}$  factor group symmetry) predicts a splitting of each species of A symmetry into  $\text{A}_g + \text{A}_u + \text{B}_g + \text{B}_u$  (related to interactions of identical oscillators, correlation field effects). Consequently, 18 infrared bands ( $9\text{A}_u + 9\text{B}_u$ ) and 18 Raman bands ( $9\text{A}_g + 9\text{B}_g$ ) correspond to the normal vibrations of the tetrahedral ions. The correlation diagram between the  $T_d$  point symmetry,  $C_1$  site symmetry of the sulfate ions and  $C_{2h}$  factor group symmetry is presented in **Figure 8**. Unit-cell theoretical treatment for the translational lattice modes ( $\text{Rb}$ ,  $\text{M}''$ ,  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$ ) and librational lattice modes ( $\text{SO}_4^{2-}$  and  $\text{H}_2\text{O}$ ) yields: 69 modes of  $\text{A}_g$ ,  $\text{A}_u$ ,  $\text{B}_g$  and  $\text{B}_u$  symmetry and 48 modes of  $\text{A}_g$ ,  $\text{A}_u$ ,  $\text{B}_g$  and  $\text{B}_u$  symmetry for the translational and librational modes respectively [11].

Infrared spectroscopic investigations of the potassium Tutton sulfates and selenates are widely discussed in the literature [9,12-17] and those of the rubidium selenates are commented in [8,13,18].

Infrared spectra of  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) in the region of  $4000 - 400 \text{ cm}^{-1}$  are shown in **Figures 9** and **10**. Some structural and spectroscopic data are summarized in **Table 7** (for comparison the

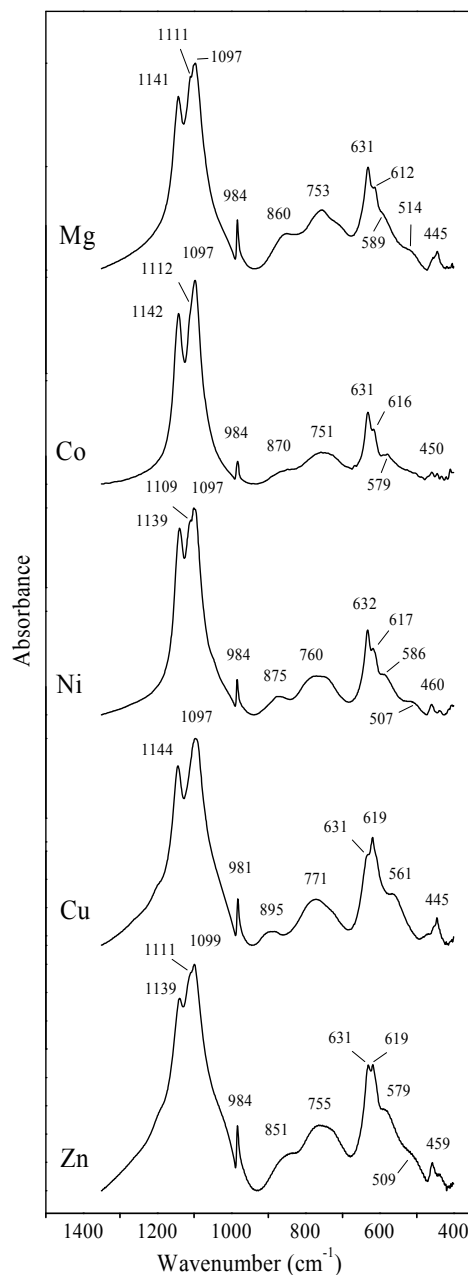


**Figure 8.** Correlation diagram between  $T_d$  point symmetry,  $C_1$  site symmetry and  $C_{2h}$  factor group symmetry ( $\text{SO}_4^{2-}$  ions).

structural and spectroscopic data for the respective potassium and ammonium sulfates are presented; the data are taken from [9]). It is readily seen that the shape of the spectra and the band positions are similar owing to the isostructurality of the double salts. The six infrared bands expected according to the factor group analysis for the asymmetric stretching modes of the sulfate ions coalesce into three bands:  $\text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1141, 1111,  $1097\text{ cm}^{-1}$ );  $\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1142, 1112,  $1097\text{ cm}^{-1}$ );  $\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1139, 1109,  $1097\text{ cm}^{-1}$ );  $\text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1139, 1111,  $1099\text{ cm}^{-1}$ ), and into two bands for  $\text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1144,  $1097\text{ cm}^{-1}$ ). The  $\nu_1$  modes appear at  $984\text{ cm}^{-1}$ . The bending modes  $\nu_4$  are detected in the spectral intervals of  $632 - 612\text{ cm}^{-1}$ .  $\nu_2$  appear at about  $450\text{ cm}^{-1}$  (see **Figure 9**).

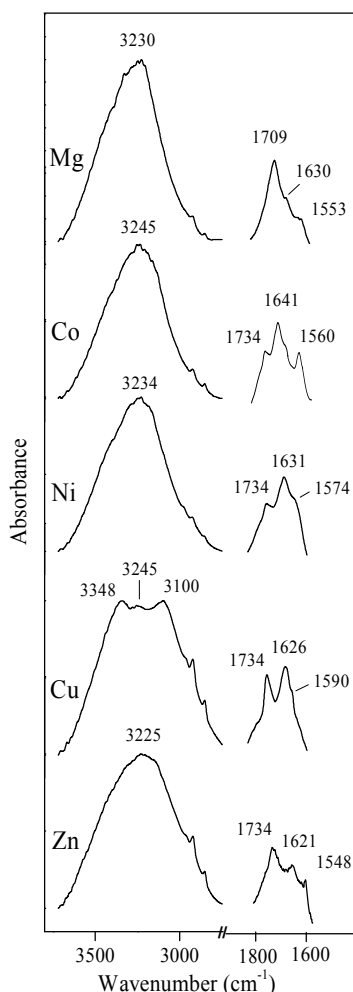
Our infrared spectroscopic findings differ slightly from those reported by Brown and Ross with respect to the number of the bands corresponding to  $\nu_3$  of the sulfate ions. The spectra of the rubidium compounds commented in [13] show more bands for  $\nu_3$  (some of them assigned as shoulders) as compared to our results. We believe that the difference between our spectra and those discussed by Brown and Ross is due probably to the temperatures at which the spectra are recorded. It is mentioned in [13] that some spectra are run at liquid nitrogen temperature. However, there is no indication which spectra are obtained at LNT.

The normal vibrations of the water molecules appear in the high frequency region of  $3000 - 4500\text{ cm}^{-1}$ . The three crystallographically different water molecules ( $C_1$  site symmetry) in the structures of the Tutton sulfates are expected to display six infrared bands corresponding to the asymmetric and symmetric modes,  $\nu_3$  and  $\nu_1$  respectively. However, due to the strong interactions of identical oscillators O-H the different normal modes overlap and as a result one broad band centered at about  $3230\text{ cm}^{-1}$  is observed in the spectra of the double Tutton salts



**Figure 9.** Infrared spectra of  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $M = \text{Mg, Co, Ni, Cu, Zn}$ ) in the region of  $1400 - 400\text{ cm}^{-1}$  (normal vibrations of the  $\text{SO}_4^{2-}$  ions and water librations).

(with exception of the copper compound) (**Figure 10**). Three bands corresponding to  $\nu_2$  of the three crystallographically different water molecules are observed in the spectra of the compounds under study:  $1709, 1630$  and  $1553\text{ cm}^{-1}$  (magnesium);  $1734, 1641$  and  $1560\text{ cm}^{-1}$  (cobalt);  $1734, 1631$  and  $1574\text{ cm}^{-1}$  (nickel);  $1734, 1626$  and  $1590\text{ cm}^{-1}$  (copper), and  $1734, 1621$  and  $1548\text{ cm}^{-1}$  (zinc). The band positions of the stretching modes indicate that comparatively strong hydrogen bonds are formed in the sulfates and the hydrogen bond strengths



**Figure 10.** Infrared spectra of  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) in the region of the stretching and bending modes of the water molecules.

do not depend on the  $\text{M}''$  chemical nature. The appearance of a band at a lower frequency ( $3100\text{ cm}^{-1}$ ) in the spectrum of the copper compound shows that stronger hydrogen bonds are formed in this salt as compared to other rubidium compounds. This spectroscopic finding is owing to the stronger *synergetic* effect of the  $\text{Cu}^{2+}$  ions, *i.e.* to the strong  $\text{Cu-OH}_2$  interactions (increasing of the acidity of the water molecules) [19,20]. The formation of comparatively strong hydrogen bonds in the rubidium compounds is due to the strong proton acceptor capacity of the sulfate ions [19,20].

The water librations (rocking, twisting and wagging) appear in the region below  $1000\text{ cm}^{-1}$  and a strong overlapping with vibrations of other entities in the structure is expected. Two types of water librations for the Tutton sulfates are discussed briefly in the literature—rocking and wagging, the former observed at higher frequencies [14]. Each type is characterized with two broad bands. The water molecules bonded to the  $\text{M}''$  ions via shorter

$\text{M}''\text{-OH}_2$  bonds display water librations at higher frequencies as compared to those forming longer  $\text{M}''\text{-OH}_2$  bonds (equatorial water molecules). The former  $\text{M}''\text{-OH}_2$  bonds are much more polarized due to the stronger *synergetic* effect of the  $\text{M}''$  ions (stronger metal-water interactions). The mean wavenumbers for the rocking librations are reported to have values of  $855$  and  $740\text{ cm}^{-1}$ , and  $770$  and  $680\text{ cm}^{-1}$  for the potassium and ammonium sulfates, respectively. The respective wagging modes have mean values of  $570$  and  $441\text{ cm}^{-1}$  for the potassium compounds, and  $544$  and  $425\text{ cm}^{-1}$  for the ammonium ones [14]. Thus, the bands in the interval of  $895 - 751\text{ cm}^{-1}$  are attributed to the rocking modes of the water molecules and the bands in the region of  $589 - 507\text{ cm}^{-1}$  to the wagging modes. The close wavenumbers of the water librations confirm the claim that the hydrogen bonds formed in the rubidium Tutton sulfates are of close strength (see Figure 9).

### 3.4. Infrared Spectra of $\text{SO}_4^{2-}$ Ions Matrix Isolated in Tutton Selenates

The method of crystal matrix-spectroscopy provides important information about the local potential at the lattice sites where the guest ions are located as deduced from their extent of distortion and the chemical nature of the ligand environments in the lattice. When the polyatomic ions are doped in host lattices at low concentration (up to 2 - 7 mol%) the correlation field splitting, the dispersion of phonon curves (due to the interactions between identical oscillators) and LO/TO splitting effects (due to the long-range forces of electrostatic origin) are neglected. Thus, the vibrational spectra of the guest ions are determined by the site symmetry, which is assumed to be the same as that of the respective host ions (substitutional mixed crystals). The spectra of matrix-isolated polyatomic ions are an excellent probe of the local potential at called an *energetic* distortion in order to distinguish it from the *geometrical* distortion revealed by structural data [21-23]. Both the site group splitting of the asymmetric modes ( $\Delta\nu_{\text{as}}$ ) and the value of  $\Delta\nu_{\text{max}}$  (the difference between the highest and the lowest wavenumbered components of the stretching and bending modes, respectively) are an adequate measure for the degree of energetic distortion of the polyatomic ions [22,24,25]. Recently, the value of the ratio  $\Delta\nu_{\text{as}}/\nu_{\text{c}}$  (where  $\nu_{\text{c}}$  is the centro-frequency value of the asymmetric modes) has been proposed to calculate the relative splitting of the dopant ions [26].

Numerous papers in the literature are devoted to the vibrational spectroscopic studies of polyatomic ions (for example,  $\text{XO}_3^-$ ,  $\text{XO}_4^{2-}$ ,  $\text{XO}_4^{3-}$ ) doped in various host lattices [21,23-40]. Lutz *et al.* performed solid solution spectroscopic experiments on monoclinic  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ -type and orthorhombic  $\text{Sr}(\text{ClO}_3)_2$ -type



**Table 7.** Some structural and spectroscopic characteristics for the  $\text{SO}_4^{2-}$  ions in the neat Tutton salts ( $V/n$ , unit-cell volumes divided by the numbers of the  $\text{SO}_4^{2-}$  ions; S-O, mean values of the S-O bond lengths;  $\Delta r(\text{SO}_4)$ , the difference between the longest and the shortest S-O bond lengths in the respective tetrahedra;  $\Delta \nu_{\text{max}}$ , the difference between the highest and the lowest wave numbered components of the stretches of the  $\text{SO}_4^{2-}$  ions; the structural data are taken from [1,2,9]).

Compounds	$V/n$ ( $\text{\AA}^3$ )	S-O ( $\text{\AA}$ )	$\Delta r(\text{SO}_4)$ ( $\text{\AA}$ )	$\nu_3$ ( $\text{cm}^{-1}$ )	$\bar{\nu}_3$ ( $\text{cm}^{-1}$ )	$\nu_1$ ( $\text{cm}^{-1}$ )	$\Delta \nu_3$ ( $\text{cm}^{-1}$ )	$\Delta \nu_{\text{max}}$ ( $\text{cm}^{-1}$ )
$\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	164	1.474	0.065	1147, 1108, 1098	1115	984	49	163
$\text{Rb}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	172	1.470	0.014	1141, 1111, 1097	1116	984	45	160
$(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	174	1.473	0.021	1147, 1108, 1098	1118	984	49	163
$\text{K}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	165	1.474	0.020	1144, 1100	1122	984	44	160
$\text{Rb}_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	172	1.472	0.015	1142, 1112, 1097	1117	984	45	158
$(\text{NH}_4)_2\text{Co}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	175	1.510	0.065	1146, 1102	1124	982	44	164
$\text{K}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	162	1.473	0.016	1144, 1111, 1101	1119	982	43	164
$\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	169	1.470	0.012	1139, 1109, 1097	1115	984	42	155
$(\text{NH}_4)_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	171	1.476	0.020	1144, 1108, 1100	1117	982	44	164
$\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	164	1.471	0.024	1144, 1102, 1097	1114	984	47	160
$\text{Rb}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	171	1.473	0.024	1144, 1097	1121	981	47	163
$(\text{NH}_4)_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	173	1.473	0.022	1144, 1102, 1095	1114	981	49	163
$\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	164	1.470	0.018	1141, 1108, 1102	1117	982	39	159
$\text{Rb}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	169	1.472	0.013	1139, 1111, 1099	1116	984	40	155
$(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	173	1.474	0.021	1144, 1105	1124	984	39	160

host crystals with incorporated  $\text{ClO}_3^-$ ,  $\text{BrO}_3^-$  and  $\text{IO}_3^-$  ions [21,24,25]. The energetic distortions of tetrahedral ions matrix-isolated in different alkali metal lattices are widely discussed in [26-34]. Recently, infrared spectra of isomorphously included species— $\text{NH}_4^+$  ions isolated in  $\text{KMPO}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Ni}$ ) and  $\text{PO}_4^{3-}$  ions isolated in  $\text{MgNH}_4\text{AsO}_4 \cdot 6\text{H}_2\text{O}$  have been reported [37].

Infrared spectra of mixed crystals

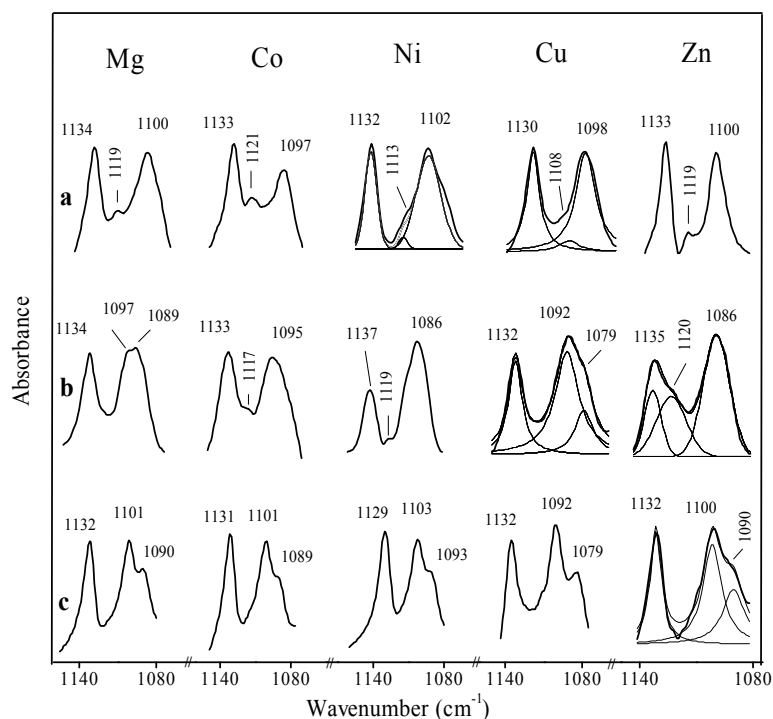
$\text{M}'_2\text{M}''(\text{SeO}_4)_{2-x}(\text{SO}_4)_x \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ;  $x$  is approximately 0.02) are presented in **Figure 11**. The infrared spectroscopic characteristics of the matrix-isolated  $\text{SO}_4^{2-}$  ions are summarized in **Table 8** (the data for potassium and ammonium Tutton salts are taken from [9]).

The matrix-isolated  $\text{SO}_4^{2-}$  ions exhibit three bands corresponding to  $\nu_3$  in agreement with the low site symmetry  $C_1$  of the  $\text{SeO}_4^{2-}$  host ions. Bands of small intensities around  $980 \text{ cm}^{-1}$  appear in the spectra which are assigned to  $\nu_1$  of the guest sulfate ions (the spectra are recorded at higher concentrations of the samples in KBr in order to distinguish the  $\nu_1$  mode; the spectra are not shown; see **Table 8**). When the larger  $\text{SeO}_4^{2-}$  host ions are replaced by the smaller  $\text{SO}_4^{2-}$  guest ions the mean values of the asymmetric stretching modes  $\nu_3$  of the

$\text{SO}_4^{2-}$  guest ions are slightly shifted to lower frequencies as compared to those of the same ions in the neat sulfate compounds due to the smaller repulsion potential of the selenate matrices, *i.e.* to the larger unit-cell volumes of the respective selenates (compare **Tables 7 and 8**).

Several factors are expected to influence on the values of  $\Delta \nu_3$  and  $\Delta \nu_3/\nu_c$ : 1) the chemical nature of the metal ions; 2) the repulsion potential of the selenate matrices, and 3) the strength of the hydrogen bonds. The spectroscopic experiments show that the distortion of the  $\text{SO}_4^{2-}$  guest ions as deduced from the values of  $\Delta \nu_3$  and  $\Delta \nu_3/\nu_c$  increase on going from the potassium to the ammonium compounds (see **Table 8**). The formation of hydrogen bonds between the  $\text{SO}_4^{2-}$  guest ions and both the water molecules of the host compounds and the  $\text{NH}_4^+$  host ions obviously facilitate the extent of energetic distortion of the guest ions (for example,  $\Delta \nu_3$  of the sulfate guest ions have values of 30 and  $51 \text{ cm}^{-1}$  in the nickel potassium and ammonium matrices, and 33 and  $49 \text{ cm}^{-1}$  in the zinc potassium and ammonium matrices, respectively). The larger values of  $\Delta \nu_3$  and  $\Delta \nu_3/\nu_c$  of the sulfate guest ions matrix-isolated in rubidium selenate matrices as compared to those of the  $\text{SO}_4^{2-}$  ions included in the potassium matrices are owing probably to the smaller





**Figure 11.** Infrared spectra of  $\text{SO}_4^{2-}$  ions matrix-isolated (about 2 mol%) in  $\text{M}'_2\text{M}''(\text{SeO}_4)_{1.98}(\text{SO}_4)_{0.02} \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4^+$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ) in the region of  $\nu_3$ : potassium selenate matrices (row a); ammonium selenate matrices (row b); rubidium selenate matrices (row c).

**Table 8.** Some spectroscopic characteristics of  $\text{SO}_4^{2-}$  guest ions matrix-isolated in selenate matrices (for the assignments see Table 1; the data for the potassium and ammonium compounds are taken from [9]).

Host compounds	$\text{SO}_4^{2-}$ guest ions (approximately 2 mol%)					
	$\nu_3$ ( $\text{cm}^{-1}$ )	$\bar{\nu}_3$ ( $\text{cm}^{-1}$ )	$\nu_1$ ( $\text{cm}^{-1}$ )	$\Delta \nu_3$ ( $\text{cm}^{-1}$ )	$\Delta \nu_{\text{max}}$ ( $\text{cm}^{-1}$ )	$\Delta \nu_3/c$ (%)
$\text{K}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1134, 1119, 1100	1118	980	34	154	3.04
$\text{Rb}_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1132, 1101, 1090	1108	981	42	151	3.79
$(\text{NH}_4)_2\text{Mg}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1134, 1097, 1089,	1107	980	45	154	4.06
$\text{K}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1133, 1121, 1097	1117	982	36	151	3.22
$\text{Rb}_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1131, 1101, 1089	1107	980	42	151	3.79
$(\text{NH}_4)_2\text{Co}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1133, 1117, 1095	1115	981	38	152	3.40
$\text{K}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1132, 1113, 1102	1116	982	30	150	2.68
$\text{Rb}_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1129, 1103, 1093	1108	982	36	147	3.25
$(\text{NH}_4)_2\text{Ni}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1137, 1119, 1086	1114	979	51	158	4.58
$\text{K}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1130, 1198, 1098	1112	981	32	149	2.88
$\text{Rb}_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1135, 1100, 1084	1106	980	51	155	4.61
$(\text{NH}_4)_2\text{Cu}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1132, 1092, 1079	1101	981	53	151	4.81
$\text{K}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1133, 1119, 1100	1117	982	33	151	2.95
$\text{Rb}_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1132, 1100, 1090	1107	983	42	149	3.79
$(\text{NH}_4)_2\text{Zn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$	1135, 1120, 1086	1114	982	49	153	4.40

local potential at the lattice sites where the sulfate ions are located (*i.e.* to the larger unit-cell volumes of the rubidium selenates) [39].

As far as the influence of the  $\text{M}''$  ion nature on the values of  $\Delta v_3$  and  $\Delta v_3/v_c$  of the sulfate ions is concerned the spectroscopic experiments show that the sulfate ions are stronger distorted in the case of

$(\text{NH}_4)_2\text{M}(\text{SeO}_4)_{1.98}(\text{SO}_4)_{0.02} \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Ni, Cu, Zn}$ ) and  $\text{Rb}_2\text{Cu}(\text{SeO}_4)_{1.98}(\text{SO}_4)_{0.02} \cdot 6\text{H}_2\text{O}$ . These findings are due probably to the formation of stronger hydrogen bonds in these compounds, *i.e.* to the stronger interaction between the water molecules of the host compounds and the sulfate guest tetrahedra (stronger proton donor capacity of the water molecules coordinated to the copper, zinc and nickel cations, *i.e.* to the stronger *synergetic* effect of these ions) [19,20].

#### 4. Conclusions

1) The solubility in the three-component systems  $\text{Rb}_2\text{SO}_4\text{-MSO}_4\text{-H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ) was studied at 298 K.

2) Isostructural compounds,  $\text{Rb}_2\text{M}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $\text{M} = \text{Mg, Co, Ni, Cu, Zn}$ ), crystallize from the ternary solutions within wide concentration ranges due to the strong complex formation processes in the solutions.

3) Comparatively strong hydrogen bonds are formed in the rubidium Tutton sulfates as deduced from both the wavenumbers of the stretching modes of the water molecules and the water librations due to the strong proton acceptor strength of the sulfate ions.

4) The degree of energetic distortion of the  $\text{SO}_4^{2-}$  guest ions in  $\text{M}'_2\text{M}''(\text{SeO}_4)_{1.98}(\text{SO}_4)_{0.02} \cdot 6\text{H}_2\text{O}$  ( $\text{M}' = \text{K, Rb, NH}_4$ ;  $\text{M}'' = \text{Mg, Co, Ni, Cu, Zn}$ ) is analyzed with respect to the values of  $\Delta v_{\text{as}}$  and  $\Delta v_{\text{as}}/v_c$ .

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