STRUCTURE MODIFICATION OF K_2SO_4 CRYSTALS BY INSERTING $ZnCl_2$ ADMIXTURE

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X-ray structure and Raman scattering studies of crystals grown from the aqueous solution of K_2SO_4 and $ZnCl_2$ salts have been carried out. The influence of X-ray irradiation on the optical properties of those crystals has been considered.

1. Introduction

Crystals of K_2SO_4 salt belong to the compounds that are isomorphous to K_2SeO_4 and are the reference ones while studying the effects of various kinds in ferroelectric crystals of group A_2BX_4. Chemically pure K_2SO_4 crystals are well studied by spectral methods, in particular, by Raman light spectroscopy [1, 2]. Mixed crystals have also been studied rather carefully. For instance, in work [3], phase transitions (PTs) in mixed $(NH_4)_2SO_4$–K_2SO_4 crystals have been analyzed; in so doing, two kinds of NH_4^+ ions with different dipole moments were supposed to form two sublattices. In mixed crystals, ions with a higher dipole moment are mainly replaced by K^+ ones possessing zero dipole moment. The ion substitution is supposed to result in the variation of the potentials in each sublattice. Proceeding from this idea, the authors of work [4] have examined PTs in the crystalline systems NH_4SO_4–R_2SO_4 (R = K, Rb, and Cs).

In work [5], the methods of Raman and X-ray spectroscopy were used to study the influence of zinc oxide (ZnO) admixture on the properties of polycrystalline $K_2Zn(SO_4)_2$ specimens. In particular, the type of crystals formed on the adding of ZnO into the $K_2S_2O_7$ melt has been determined. Bivalent zinc, Zn(II), was demonstrated to be able to generate anion sulfate complexes and form various compounds, including $K_2Zn(SO_4)_2$. The components ZnO and $K_2S_2O_7$ were mixed in various molar ratios. In the absence of moisture, the mixture was heated up to the temperature of the liquid phase ($T = 500$ °C). It has been found that if the molar content of ZnO in the mixture increases, the intensity of the band with a maximum at 1084 cm^{-1}, which is characteristic of the $S_2O_7^{2-}$ complex, diminishes in the Raman spectra of these melts. Moreover, the intensity of the band at 995 cm^{-1}, which is associated with the $K_2Zn(SO_4)_2$ compound, grows appreciably. After the slow cooling of the melt, there appeared single crystals, which were studied in [5] by X-ray diffraction methods. The structural researches demonstrated that the crystallized $K_2Zn(SO_4)_2$ compound belongs to the spatial group $P\ 2_1/n$ (C_{2h}^5 in the Schönflies notation). A primitive cell contains 4 formular units. Ions K^+ are located between ZnO_5 hexahedra and SO_4 tetrahedra. In works [6, 7], it was also shown that the formation of the $K_2Zn_2(SO_4)_3$ compound is possible from the salts of zinc oxide and pyrosulfates.

Therefore, it follows from literature data that various kinds of crystals can be grown from the mixtures of pyrosulfates and zinc oxide. At the same time, it is known that, in the case of crystals of the A_2BX_4 type, the insertion of an admixture of metal chlorides, where a metal belongs to the iron group ($ZnCl_2$, $MnCl_2$, $NiCl_2$, and others), gives rise to the formation of solid solutions [5]. The aim of this work was to study crystals which can be obtained from the solutions of the K_2SO_4 and $ZnCl_2$ salt mixtures. The grown crystals were studied by X-ray diffraction and Raman scattering methods.

2. Experimental Technique

The crystals concerned were grown up by the method of slow evaporation at room temperature from the aqueous solution of the mixture of K_2SO_4 and $ZnCl_2$ salts. The substances were taken in a 1:1 molar ratio. A single crystal intended for Raman studying was selected taking its optical homogeneity into account. Its dimensions were of about $5 \times 10 \times 15$ mm^3. Specimens $1 \div 2$ mm^3 in volume were used for structural measurements.

Raman spectra were measured on a modified DFS-52M diffraction spectrophotometer [8]. Modernization of

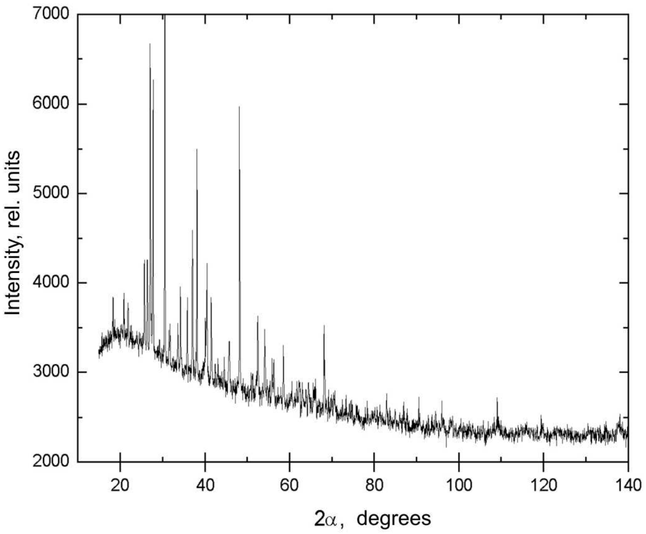

Fig. 1. Crystallogram of the powder K_2SO_4+$ZnCl_2$

the installation made its functional control possible with the help of a personal computer of the IBM type. A number of relevant tasks have been resolved: the control over a stepping motor block which scans the spectrum; regulation – by a serial digital code – of the voltage in a high-voltage power unit intended for the power supply of photomultipliers in the primary and reference channels; fixation of the time interval for calculations of the photon number; input of the numbers of photons from the counter blocks of photomultipliers and their calculation; input and output of additional logic signals (determination of grating parameters, a grating position sensor, filter manipulation, and so on). An LGN-113 helium-neon laser with an emitting power of 15 mW served as an exciting source. Registration was carried out in the photon-counter mode with the frequency resolution $\Delta\nu = 1$ cm^{-1}. The signal has been accumulated for 1 s at every point.

X-ray diffraction studies were carried out on a HZG-4A powder diffractometer. The source of X-rays was a tube with a Fe-anode (emission of radiation with the wavelength $\lambda(\text{Fe } K_\alpha) = 1.93728$ Å). A manganous filter was also used. The parameters were calculated making use of a universal program package CSD (version 4.10) developed for the processing of structural data for single crystals and powders [9, 10].

Specimens were X-irradiated on a RUP-100 installation. The active element was a W-tube which generated radiation at the voltage $U = 100$ keV and the current $I = 13$ mA.

3. Research Results and Their Discussion

Structural researches were carried out using powder specimens which had been prepared from grown single crystals. A recorded crystallogram is exhibited in Fig. 1. The total variation range of angles, at which the measurements were carried out, amounted to 7–73°; the measurement step was 0.05°.

The parameters of the elementary cell at a temperature of 295 K, which were calculated from experimental data, are as follows: $a = 9.0334(5)$ Å, $b = 12.2075(9)$ Å, $c = 6.1523(4)$ Å, $\alpha = 90°$, $\beta = 104.815(4)°$, $\gamma = 90°$, the cell volume $V = 654.3$ Å^3, the total number of elements in the cell is 62, the calculated density $D_x = 2.253(3)$ g/cm^3, the absorption coefficient $\mu = 225.22$ cm^{-1}, $F(000) = 448$ electrons, and the number of free parameters is 64. The element composition and the component content (in percent) of the cell are listed in Table 1. At room temperature, the crystal belongs to the monoclinic spatial group $P\ 2_1/a$ in the international notation (group C^5_{2h} in Schönflies notation). The elementary cell is primitive and contains two formular units.

The computer-assisted analysis of the results obtained showed that crystals with the chemical formula $K_2Zn(SO_4)_2 \cdot 6H_2O$ (potassium hexaaquazinc sulfate, KZSH [11]) are grown from the solution of the salts K_2SO_4 and $ZnCl_2$ taken in a 1:1 ratio. This compound belongs to Tutton's salts described by the general formula $M^I_2M^{II}(SO_4)_2 \cdot 6H_2O$, where M^I is either an alkaline metal (Na, K, Rb, Cs) or NH_4^+, and M^{II} is a bivalent metal (Mg, Fe, Co, Cu, Ni, Zn, and so on). Similar crystals are mainly synthesized from aqueous solutions containing the corresponding quantities of sulfates of metals M^I and M^{II} [12–17].

The results of calculations carried out for the atomic parameters of a KZSH crystal are listed in Table 2.

In Fig. 2, an elementary cell of a $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal is depicted. In contrast to $K_2Zn(SO_4)_2$ crystals, in which Zn is surrounded by a hexahedron of oxygens [5], zinc in KZSH ones is located within an oxygen octahedron. Figure 3 illustrates the spatial geometry of

Table 1. Elements and their content in the elementary cell of the $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

Element	Number of atoms in the cell	Content, at.%	Content, wt.%
H	24	38.71	2.73
K	4	6.45	17.62
Zn	2	3.23	14.73
S	4	6.45	14.45
O	28	45.16	50.47

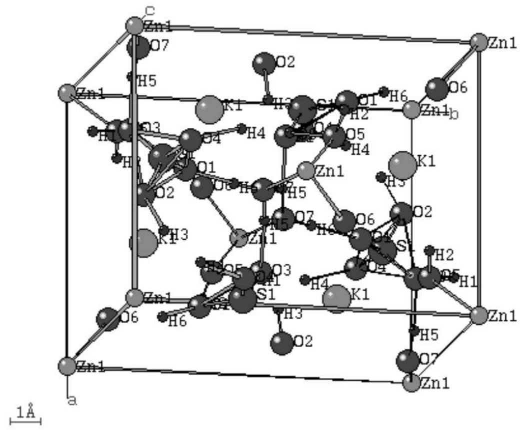

Fig. 2. Elementary cell of the $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

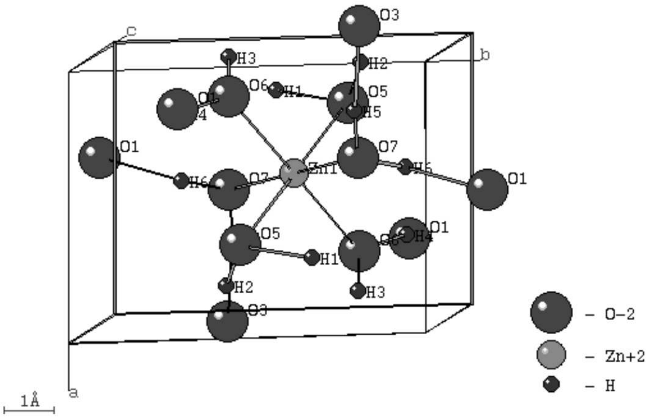

Fig. 3. Geometry of a ZnO_6 octahedron in the structure of $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

the ZnO_6 octahedron. It is evident that all sites are occupied by oxygens (2×O5, 2×O6, 2×O7). In addition, the tetrahedral SO_4 groups located between potassium ions are neatly observed. It should also be noted that the ZnO_6 octahedron is squeezed to some extent along the direction O7–Zn1–aO7. This fact can be explained by the availability of hydrogen bonds which influence the oxygen atoms.

Some basic distances and angles for the crystalline KZSH structure are quoted in Table 3. Comparing those data with the results obtained for $K_2Zn(SO_4)_2$ crystals [5], one can draw conclusion that an insignificant distortion from the perfect tetrahedricity takes place around the sulfur atom, because the valence angles O–S–O are changed from 104.05 to 115.09°.

Table 2. Atomic parameters of the $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

Atom	Coordinates, Å			Equivalent isotropic temperature parameter B(is/eq), Å^2
	x	y	z	
Zn(1)	0	0	0	0.9(3)
S(1)	0.414(2)	0.1342(15)	0.739(3)	1.264
O(1)	0.4086	0.2297	0.5762	1.264
O(2)	0.5553	0.0756	0.7522	1.264
O(3)	0.2848	0.0614	0.6214	1.264
O(4)	0.3948	0.1724	0.9474	1.264
O(5)	0.1720	0.1125	0.1686	1.264
O(6)	−0.1704	0.1144	0.0341	1.264
O(7)	−0.0011	−0.0687	0.3008	1.264
K(1)	0.126(2)	0.3453(13)	347(3)	1.264
H(1)	0.2193	0.0120	0.3210	2.000
H(2)	0.2518	0.1256	0.0920	2.000
H(3)	−0.2700	0.0998	−0.0690	2.000
H(4)	−0.1419	0.1907	−0.0006	2.000
H(5)	−0.1020	−0.0586	0.3373	2.000
H(6)	0.0256	−0.1450	0.3313	2.000

Water molecules and sulfate groups participate in the expansion of hydrogen bonds, which is beneficial for the structural stability of the crystal.

There are no exhaustive data in the literature concerning the Raman studies of $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystals. Therefore, we studied the corresponding single-crystalline specimens by the Raman light scattering method. A $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal contains two formular units and 62 elements per primitive cell. According to the factor-group analysis of the positional symmetry [18], three acoustic and 183 optic vibrations are possible in the crystal concerned. For a KZSH primitive cell which contains four K^+ ions, four $(SO_4)^{2-}$ ions, and two $(Zn \cdot 6H_2O)^{2+}$ octahedral complexes, its

Table 3. Bond lengths (in Å) and interbond angles (in degree) in the $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

		Around Zn1			
Zn1..O5	2,132	O5..Zn1..aO5	179,98	O5..Zn1..O6	89,24
Zn1..aO5	2,132	O5..Zn1..aO6	90,76	O5..Zn1–O7	89,70
Zn1..O6	2,126	O5..Zn1–aO7	90,30	aO5..Zn1..O6	90,76
Zn1..aO6	2,126	aO5..Zn1..aO6	89,24	aO5..Zn1–O7	90,30
Zn1–O7	2,032	aO5..Zn1–aO7	89,70	O6..Zn1..aO6	179,97
Zn1–aO7	2,032	O6..Zn1– O7	90,48	O6..Zn1–aO7	89,52
		aO6..Zn1–O7	89,52	aO6..Zn1–aO7	90,48
		O7–Zn1–aO7	179,99		
		Around S1			
S1–O1	1,528	O1–S1–O2	107,11	O1–S1–O3	104,05
S1–O2	1,444	O1–S1–O4	110,57	O1–S1–aK1	132,05
S1–O3	1,499	O1–S1–bK1	54,41	O1–S1..cK1	121,74
S1–O4	1,415	O2–S1–O3	107,64	O2–S1–O4	115,09
S1–aK1	3,56(2)	O2–S1–aK1	64,88	O2–S1–bK1	55,65
S1–bK1	3,45(2)	O2–S1..cK1	76,07	O3–S1–O4	111,70
S1..cK1	3,75(2)	O3–S1–aK1	46,09	O3–S1–bK1	102,08
		O3–S1..cK1	131,14	O4–S1–aK1	115,34
		O4–S1–bK1	145,90	O4–S1..cK1	39,21
		aK1–S1–bK1	91,2(6)	aK1–S1..cK1	102,8(6)
		bK1–S1..cK1	117,4(6)		

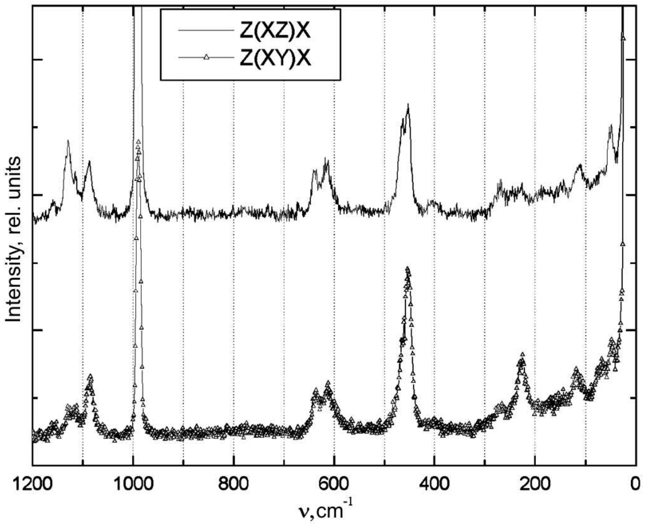

Fig. 4. Raman spectra of the $K_2Zn(SO_4)_2 \cdot 6H_2O$ crystal

optical vibrations can be classified to 57 external (27 translational and 30 orientational) and 126 internal ones. We studied the Raman spectra in the range of 10–1400 cm^{-1}. The bands that correspond to the vibrations of molecular water are located within the frequency range of 2500–3700 cm^{-1}.

In Fig. 4, modes A_g and B_g of the Raman spectra obtained in the $Z(XY)X$ and $Z(XZ)X$, respectively, experimental geometries are depicted. Bands, which are observed in the range 220–280 cm^{-1}, correspond to the vibrations of the ZnO complex. The results obtained correlate well with the Raman spectra measured in work [17].

In addition, new vibration bands active in the $Z(XY)X$ and $Z(XZ)X$ geometries were registered. The most intensive of them and their classification are listed in Table 4. While classifying the obtained bands as the vibrations of certain structural groups, we took advantage of the results of vibrational spectroscopy researches of potassium sulfate crystals [1, 2]. Those bands were not observed in pure potassium sulfate crystals [1, 2].

Table 4. Raman spectrum bands of the $K_2Zn(SO_4)_2 \times$ $\times 6H_2O$ crystal and their classification

A_g, cm^{-1} $Z(XY)X$	B_g, cm^{-1} $Z(XZ)X$	Classification
48	51	t_s
72	–	Multiphonon modes
117	111	t_s
225	–	ν_5^c, t_k
269	269	ν_2^c
453	453	ν_2^s
464	463	ν_2^s
612	614	ν_4^s
637	637	ν_4^s
990	990	ν_1^s
1087	1087	ν_3^s
1114	1114	$\nu_1^s + t_s$
1129	1129	ν_3^s
	1159	ν_3^s

Footnote: Indices s, c, and k designate vibrations of the $(SO_4)_2^-$ anion, $(Zn \cdot 6H_2O)^{2+}$ complex, and K^+ cation, respectively.

While comparing the vibration frequencies in the Raman spectra of crystals obtained from the melt or the aqueous solution, a number of differences were monitored. Their origin is obviously the availability of molecular water $6H_2O$ in the oxygen environment of zinc, and it is this water that causes the distortion of octahedral complexes.

In addition to carrying out the structural researches, we also studied the influence of low exposure doses of X-irradiation on the optical properties of KZSH crystals. The crystals were irradiated for 60 or 90 min. In both cases, the absorption and Raman spectra were recorded right after irradiation. No substantial irradiation-induced variations in the spectra have been revealed: the crystal remained optically transparent within the range of 330–740 nm. Minor changes in the range of multiphonon modes were found in the Raman spectra within the interval of 50–200 cm^{-1}. However, since this interval overlaps with the main laser band, those changes have not been neatly fixed. This means that one may assert that the crystal of potassium hexaaquazinc sulfate is stable with respect to low exposure doses of X-radiation.

4. Conclusions

1. It has been found for the first time that crystals of good optical quality can be grown from the aqueous solution of K_2SO_4 and $ZnCl_2$ salts taken in a 1:1 ratio. Careful X-ray researches and the computer-assisted analysis of the data obtained demonstrated that the crystals, which are grown at room temperature, belong to the C_{2h}^5 symmetry group and have a chemical formula of $K_2Zn(SO_4)_2 \cdot 6H_2O$.
2. New Raman scattering data were obtained for crystals of potassium hexaaquazinc sulfate. The availability of molecular water in the crystal structure was shown to give rise to the squeezing of the ZnO_6 octahedron along the direction O7–Zn1–aO7.
3. The crystal under consideration is stable with respect to low exposure doses of X-radiation and has a wide transparency range. These properties make it

a promising material for the development of radiation-stable electrooptical and acoustooptical modulators.

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МОДИФІКАЦІЯ СТРУКТУРИ КРИСТАЛІВ K_2SO_4 ДОМІШКАМИ $ZnCl_2$

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Резюме

Проведено рентгеноструктурні та КРС-дослідження кристалів, вирощених з водного розчину солей K_2SO_4 та $ZnCl_2$. Розглянуто вплив X-опромінення на оптичні властивості отриманих кристалів.