THE INFRARED SPECTRA OF TETRAHEDRAL ANIONS IN MIXED CRYSTALS

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Group analysis of the infrared spectra of $KClO_4$–$KMnO_4$, $KClO_4$–KBF_4 and K_2SO_4–K_2XO_4 (where X is Se, Cr, Mn) mixed crystals was carried out. These systems form D_{2h}^{16} orthorhombic substitution mixed crystals; the symmetry of the anion is T_d. Analysis of the infrared spectra of samples with sufficiently diluted studied anion revealed the expected decrease in symmetry to C_s symmetry.

Study of the infrared spectra of mixed crystals permits analysis of the effects of crystal symmetry, expressed by the standard correlation method, proper symmetry $G_V \rightarrow$ $\rightarrow$ site-symmetry $G_S \rightarrow$ factor symmetry G_F. Interaction between vibrations of species in the elementary cell, appearing in the spectra of polycrystalline substances as broad bands, can be eliminated or suppressed by diluting the studied species in a suitably selected mixed crystal. So far, the infrared spectra of mixed crystals with space groups T_d^4 and D_{4h}^{19} have been studied[1-4]. This work was carried out in order to confirm the decrease in the proper symmetry of the tetrahedral anions MnO_4^-, ClO_4^-, BF_4^-, SO_4^{2-}, CrO_4^{2-}, SeO_4^{2-} and MnO_4^{2-} in mixed crystals with orthorhombic space group D_{2h}^{16} on the basis of analysis of the infrared spectra of these substances. The initial pure substances are isostructural, crystallized in space group D_{2h}^{16} and their lattice parameters fulfill conditions for the formation of mixed crystals.

EXPERIMENTAL

A number of samples of mixed crystals were prepared in a wide concentration range. The samples were prepared using *p.a.* $KMnO_4$, $KClO_4$, KBF_4, K_2SO_4, K_2SeO_4 was prepared by neutralization of *p.a.* H_2SeO_4 with a *p.a.* KOH solution. K_2CrO_4 was prepared from *p.a.* $K_2Cr_2O_7$ by reaction with a solution of *p.a.* KOH. K_2MnO_4 was obtained from *p.a.* $KMnO_4$ by the procedure described by Scholder and Waterstradt[7]. Crystalline $KMnO_4$ was gradually added to a KOH solution. The mixture was heated under a reflux condenser. After cooling, crystalline K_2MnO_4 was separated on a frit, washed with 40% KOH, methanol and ether. The crystals were dried in a desiccator containing P_2O_5.

Samples of mixed crystals in the $KClO_4$–$KMnO_4$, $KClO_4$–KBF_4, K_2SO_4–K_2SeO_4 and K_2SO_4–K_2CrO_4 systems were prepared from aqueous solutions. The pure initial substances in the required stoichiometric ratios were dissolved in distilled water and then concentrated until crystallization commenced; the crystals were dried in the air. Samples of the K_2SO_4-K_2MnO_4 system were prepared by dissolving weighed amounts of K_2MnO_4 and K_2SO_4 in a 5 $mol\,l^{-1}$ solution of KOH. The solution was concentrated at 50°C and cooled to 20°C. The crystals separated were collected under vacuum on a frit, washed and dried in a desiccator over P_2O_5. The ratio of the two components in the samples was found colorimetrically using a SPECORD UV VIS instrument (C. Zeiss, Jena, GDR) and a SPECOL instrument from the same manufacturer. The formation of mixed crystals was confirmed by X-ray analysis of powder samples.

The X-ray analysis was carried out on a Geigerflex instrument from Rigaku Denki, Japan. The $KClO_4$-KBF_4 and K_2SO_4-K_2SeO_4 systems were analyzed using a Cu anode, Ni filter; a Cr anode and V filter were used for the $KClO_4$-$KMnO_4$ system. The K_2SO_4-K_2CrO_4 and K_2SO_4-K_2MnO_4 systems were measured using a Mikrometa 2 diffractograph from Chirana, Czechoslovakia, using a Cu anode and Ni filter.

The lattice parameters of the individual mixed crystals were calculated from the diffractograms. The calculations were carried out on a ICL 4—72 computer using the X-RAY 72 program (OVCVŠ, Prague). The infrafed spectra of the pure substances and mixed crystals were measured on a Perkin-Elmer 325 grating spectrophotometer using KBr pellets (diameter 13 mm) in the range 4 000—200 cm^{-1}.

RESULTS AND DISCUSSION

Crystallographic data for the initial substances used, required for structural interpretation of the vibrational spectra, were taken from the literature[5-7]. All the substances crystallized in the D_{2h}^{16} – Pnma space group, $Z = 4$. The proper symmetry of the anion is T_d. X-ray analysis of $KMnO_4$-$KClO_4$ mixed crystals was published by A. L. Greenberg and G. H. Walden[8]. The calculated values of the lattice parameters a, c were directly proportional to the contents of permanganate and perchlorate in the mixed crystals; the dependence of parameter b was not linear. X-ray structural analysis of the $KClO_4$-KBF_4-H_2O system was also carried out[9]. Griffith[10] studied the infrared spectra of oxoanions in the solid phase. He found that the symmetry of the anion is always lower than T_d, most probably C_s ($2A' + A''$ triplet, ν_1 activation). The infrared spectra of $KMnO_4$ in KBr tablets were interpreted[11,12] in terms of site-symmetry. At low concentrations of MnO_4^-, the formation of solid solutions without a decrease in the tetrahedral symmetry of MnO_4^- was confirmed. It was concluded from crystallographic measurements[12] that the ClO_4^- tetrahedra in $KClO_4$ have C_{2v} symmetry. The ν_3 and ν_4 splitting may be a result of distortion of ClO_4^-, covalent bonding of ClO_4^- to the metal through oxygen or an effect of the water molecules situated around the cation. Other authors[13,14] have attributed the splitting in ClO_4^- spectra to isotopic effects. The increase in the number of active vibrations in the spectra of crystalline BF_4^- does not correspond to T_d symmetry and has been explained[15] by the action of metal ions on BF_4^-. BF_4^- anions in KBr pellets exhibit[16] C_s site symmetry. It is difficult to assign the individual bands because of possible Fermi resonance of ν_3 with overtone $2\nu_4$. It follows from the infrared spectra of additive SeO_4^{2-} and CrO_4^{2-} in the K_2SO_4 lattice[17] that the added ions exhibit "local" C_{2v} symmetry. On the other hand, it follows from other works[18,19] that solid solutions of SO_4^{2-}, CrO_4^{2-} and SeO_4^{2-} yield spectra exhibiting splitting corresponding to C_s site symmetry.

X-*Ray Analysis*

The X-ray recordings for powder samples were evaluated to confirm the formation of mixed crystals in the studied systems. The lattice parameters of the mixed crystals were calculated and the interatomic distances of the anions were calculated from the available crystallographic data for the pure components. The $KClO_4$–$KMnO_4$ and $KClO_4$–KBF_4 systems form mixed crystals over the whole concentration interval. The lattice parameters are in good agreement with the Vegard rule. It follows from the values of the interatomic distances (Table I) in the MnO_4^- anion that the tetrahedron is deformed. This deformation is even more marked for the ClO_4^- and BF_4^- anions. Mixed crystals were confirmed in the K_2SO_4–K_2SeO_4, K_2SO_4–K_2CrO_4 and K_2SO_4–K_2MnO_4 systems only for samples with concentrations of up to 15% of one component. The calculated lattice parameters agreed with those for the pure components. Considering the small concentration range, the change in the lattice parameters in dependence on the concentration was within experimental error.

Infrared Spectra

$KClO_4$, $KMnO_4$, KBF_4, K_2SO_4, K_2SeO_4 and K_2MnO_4 crystallize in orthorhombic space group D_{2h}^{16} – Pnma: $C_1(8)$, $2Ci(4)$, $C_s(4)$. The number of formula units per unit

TABLE I

Interatomic distances of the atoms

	$KMnO_4$	$KClO_4$	KBF_4	K_2SO_4	K_2CrO_4
	156	142	180	153	161
X—Y_4	156	146	146	151	159
pm	154	147	177	146	160
	154	147	177	146	160
	244	232	212	241	259
Y—Y	253	239	225	241	260
pm	255	239	280	241	260
	255	239	280	243	261
	255	241	325	243	262
	255	241	325	251	262

cell is $Z = 4$. It is apparent from theoretical analysis that positions with C_s symmetry are suitable for localization of the XO_4 anions in the D_{2h}^{16} lattice. Nine normal vibrations of the XO_4 anion are realized in point group T_d through irreducible representations $A_1 + E + 2F_2$. Table II lists correlations of proper symmetry $G_M \rightarrow$ site-symmetry $G_S \rightarrow$ factor symmetry G_F with the activity of the vibrations in the infrared spectra. The standard correlation method indicates that a decrease in the symmetry of the T_d anions to C_S site-symmetry or an increase in the site-symmetry C_S to the symmetry of factor group D_{2h} can be expected.

The infrared spectra of the $KClO_4$–$KMnO_4$ and $KClO_4$–KBF_4 system were measured for mixed crystals over the whole concentration range. It follows from the frequency table (Table III) and from the correlation table (Table II) that the spectra of the $KClO_4$–$KMnO_4$ samples with a small content of ClO_4^- anions correspond to a decrease in symmetry to site-symmetry C_S. In agreement with theoretical analysis, vibration ν_1 is activated and vibrations ν_3 and ν_4 are split to triplet $2A' + A''$. Further splitting of vibrations ν_3 (1 080 sh – 1 090) and ν_4 (620 sh – 625; 630 sh – 635) is a result of the presence of isotopes ^{35}Cl and ^{37}Cl in the samples.

Samples with high ClO_4^- contents exhibit a wide band of degenerate vibrations (Fig. 1). The spectrum of MnO_4^- anions also corresponds to site-symmetry C_S (for small concentrations of MnO_4^-). A decrease in the symmetry appears as splitting of vibrations ν_3 and ν_4 and activation of vibration ν_1. The decrease in the symmetry of samples of $KClO_4$–KBF_4 was confirmed by splitting of the ν_4 vibrations of the ClO_4^- and BF_4^- anions at sufficient dilution (Fig. 2). The greater number of ν_4 bands for the ClO_4^- anion is a result of isotopic effects, as previously. The ν_3 ClO_4^-, ν_3 BF_4^- and sometimes the overtone $2\nu_4$ vibrations appear in the region 1 140 to 1 000 cm^{-1}. All the vibrations are active in the infrared spectra and overlap to form a broad, unresolvable band. A band with wavenumber 1 310 cm^{-1} was also observed in the spectra of mixed crystals of $KClO_4$–KBF_4 with higher BF_4^- contents. This corresponds to combination of frequences $\nu_1 + \nu_4$ for the BF_4^- anion.

TABLE II

Correlation table[a]

T_d ($h = 24$)	C_s ($h = 2$)	D_{2h} ($h = 8$)
A_1	$\underline{A'}$	$A_g + B_{2g} + \underline{B_{1u}} + \underline{B_{3u}}$
E	$\underline{A'} + \underline{A''}$	$A_g + B_{1g} + E_{2g} + B_{3g} + A_u + \underline{B_{1u}} + \underline{B_{2u}} + \underline{B_{3u}}$
$\underline{2F_2}$	$2(2\underline{A'} + \underline{A''})$	$2(2A_g + B_{1g} + 2B_{2g} + B_{3g} + A_u + \underline{2B_{1u}} + \underline{B_{2u}} + \underline{2B_{3u}})$

[a] The underlined symbols are infrared active.

A decrease in symmetry to site-symmetry C_S was also confirmed for small concentrations of the studied anions in K_2SO_4–K_2SeO_4, K_2SO_4–K_2CrO_4 and K_2SO_4–K_2MnO_4 mixed crystals. It is apparent from Table IV that vibration ν_1 is activated

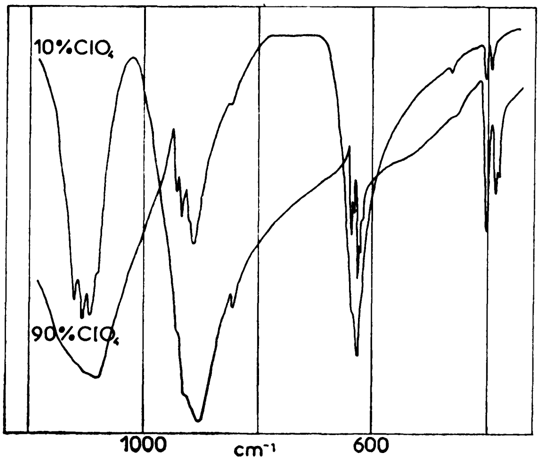

FIG. 1

IR spectra of the sample $KClO_4$–$KMnO_4$

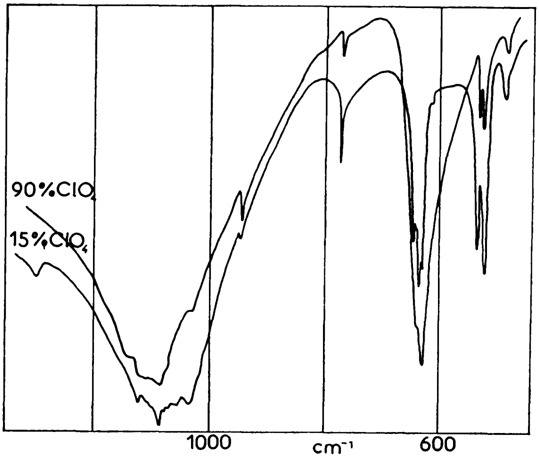

FIG. 2

Vibrations of the ClO_4^- and BF_4^- anions

TABLE III

The vibration spectra of $KClO_4$–$KMnO_4$ and $KClO_4$–KBF_4 mixed crystals

mol% ClO_4^-	ClO_4^-				MnO_4^- or BF_4^-			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_3	ν_4	$\nu_1 + \nu_4$
$KClO_4$–$KMnO_4$								
100	945	455	1 075, 1 085, 1 105, 1 120, 1 140 sh	630, 640				
93	945	460 sh	1 080—1 140 b	625, 635 sh	845	910, 915, 935	385 sh, 395, 405	
90	945	460 sh	1 080—1 140 b	625, 635 sh	845 sh	910, 920 sh, 935	385 sh, 395, 405	
85	940	460 sh	1 080—1 140 b	625, 635 sh	845 sh	910, 915 sh, 930	385 sh, 395, 405	
15	940	455 sh	1 080 sh, 1 090, 1 100, 1 120	615 sh, 620 sh, 625 630 sh, 635	840	900, 925 sh, 930 sh	395 sh, 390, 400	
10	940	455 sh	1 080 sh, 1 090, 1 105, 1 120	620 sh, 625, 630, 635, 640	845	900, 925 sh	385 sh, 390, 400	
7	940	455 sh	1 080 sh, 1 090, 1 110, 1 120	620 sh, 625, 630, 635 sh, 640	835	800, 900 sh, 915 sh	385 sh, 390, 400	
0					845	920, 930	380, 390, 400	
$KClO_4$–KBF_4								
95	945			630, 635 sh, 640	770		490, 525, 535	
90	945			630, 635 sh, 640 sh	770		490, 525, 535	
85	940			625, 630 sh, 635 sh	765		490, 520, 630	
15	945			620 sh, 630 sh, 640 645 sh, 650	775		490, 525, 535	1 305
10	945			630 sh, 635, 640 645	775		490, 525, 535	1 310
5	945			630 sh, 635, 640, 645	775		490, 525, 540	1 310
0					780		525, 540	

TABLE IV

The vibration spectra of K_2SO_4-K_2XO_4 (X = Se, Cr, Mn) mixed crystals

mol% SO_4^{2-}	SO_4^{2-}			XO_4^{2-}			
	ν_1	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
			K_2SO_4-K_2SeO_4				
100		1 115	620				
95	985	1 100 sh, 1 110, 1 145 sh	620, 630 sh	855		885 sh, 890, 895 sh	415, 425 sh, 430 sh
90	985	1 115, 1 130 sh, 1 150 sh	620, 630 sh	845		880 sh, 885, 895 sh	415, 425 sh, 430 sh
10	985 sh	1 100 sh, 1 105 sh, 1 115, 1 140	615, 620, 625	840		880 b	415
5		1 100 sh, 1 110 sh, 1 115, 1 140	615, 620, 625	840		880 b	415
0				845		855, 880, 920 sh	415
			K_2SO_4-K_2CrO_4				
95	985	1 100—1135 b	620	860 sh		900, 905 sh, 925	390, 400, 410
90	985	1 105—1 125 b	620	860 sh		900, 925, 945	390, 400, 415
10	985 sh	1 100 sh, 1 105, 1 115, 1 135	615, 620, 625 sh	860	345	885, 940	390, 400
5		1 100 sh, 1 105, 1 115, 1 135	615, 620, 625	855	345	890, 915, 945 sh	390, 400
0					345	890	390, 400, 410
			K_2SO_4-K_2MnO_4				
97	985	1 100—1 150 b	620, 625 sh	810 sh		830, 855, 880	340 sh, 345, 350 sh
85	985	1 100—1 145 b	615, 620 sh	810		850, 870 sh, 880 sh	340 sh, 345, 350 sh
0				810		835 b,	340

and levels ν_3 and ν_4 are split. No bands were observed for vibration ν_2, except for the K_2SO_4–K_2CrO_4 system. The spectra of the pure substances given in Tables III and IV were taken from the literature.

Analysis of the infrared spectra of the studied polyatomic anions using the correlation method was confirmed by the static crystal field approximation. The anions exhibit C_S site-symmetry in the spectra.

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