VIBRATION SPECTRA OF MIXED CRYSTALS Sc(PO$_4$, VO$_4$) AND Y(PO$_4$, VO$_4$)

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Dedicated to Professor Dr J. Pick on the occasion of his 60th birthday.

Infrared spectra of mixed crystals Sc(PO$_4$, VO$_4$) and Y(PO$_4$, VO$_4$) have been studied from the point of view of group analysis. These systems form substitution mixed crystals in tetragonal space group D_{4h}^{19}. The anions having proper symmetry T_d or D_{2d} in site symmetry D_{2d} exhibit in spectra lowering of the *site* symmetry to effective C_2 as a result of lattice vibrations of the type $T(B_2)$.

Theoretically possible splitting of degenerated vibrations in 12 *site* groups, *i.e.* lowering of *site* symmetry to effective *site* symmetry[1], due to lattice vibrations has been followed so far only in mixed crystals T_d^4 for *site* symmetry T of tetrahedral phosphate, arsenate and vanadate anions[2−4]. In our study[5] of infrared spectra of mixed crystals Y(PO$_4$, VO$_4$) no agreement was found between theoretical spectrum for *site* symmetry D_{2d} and experimental spectrum of PO$_4$ and VO$_4$ anions of suitable concentration, which could indicate[1] limited validity of standard correlation method. Therefore, vibration spectra of this D_{4h}^{19} lattice were followed with samples of Sc(PO$_4$, VO$_4$) and Y(PO$_4$, VO$_4$) within whole concentration range and within whole region of internal vibrations of the anions. The spectra were analyzed from the point of view of further possible lowering of *site* symmetry to effective *site* symmetry and with respect to proper geometry of the anions.

EXPERIMENTAL

Samples of the pure compounds and mixed crystals were prepared by annealing of stoichiometric amounts of Sc$_2$O$_3$ and/or Y$_2$O$_3$, (NH$_4$)$_2$HPO$_4$ and V$_2$O$_5$ at 1 000°C for 2 h. The powdered samples containing scandium were annealed anew at 1 300°C for 3 h., those containing yttrium were annealed at 1 200°C. The said temperatures were necessary for formation of the mixed crystals, which was verified by X-ray analysis of the samples annealed at 1 000, 1 100, 1 200 and 1 300°C. Mixed crystals of substitution type are formed in the whole concentration range.

The X-ray analysis was carried out with polycrystalline sample using a Geigerflex diffracto-graph (Rigaku Denki, Japan), Cu anode, Ni filter.

The infrared spectra were measured with a Perkin–Elmer 325 spectrometer in KBr discs in the range 4 000 to 200 cm^{-1}.

The Raman spectra were measured with a Ramalog 3 apparatus (SPEX), excitation 488 nm with Ar$^+$ laser (RCA), 200 mW output.

RESULTS AND DISCUSSION

The crystallographic data of the starting pure components necessary for structural interpretation of the vibration spectra were taken from literature. Phosphates[6−9] and vanadates[9−11] crystallize in tetragonal space group D_{4h}^{19}-I, $Z = 4$, G_M of the anions is T_d. From these data it is possible to obtain the data of the proper geometry of the anions (Table I). In the Table the value $(O-O)_{XO_4}$ means the distance of two neighbouring oxygen atoms in the anion, the first value is the distance of the atoms in xy plane.

The infrared spectrum of ScPO$_4$ was interpreted[12,13] in the region 4 000 to 450 cm^{-1} from the point of view of *site* symmetry D_{2d} for activation of totally symmetrical vibration A_1. In the region 1 400 to 800 cm^{-1} the splitting of ν_3 vibration of IR spectrum of YPO$_4$ was interpreted[14] as a manifestation of the *site* symmetry D_{2d}. The Raman spectrum of YPO$_4$ in the region 1 100 to 250 cm^{-1} agrees with the *site*-group approach[15]. The IR spectrum of YVO$_4$ agrees[16] with the factor-group approach D_{4h}, the vibration of E_u type being absent in the spectrum in the region of $\nu_4(T_d)$. According to ref.[17] the group analysis of the Raman spectrum of YVO$_4$ fails due to birefringence of the crystal to the polarizability tensor, which changes activities of the vibrations. The spectrum of ScVO$_4$ in the mixed crystal Sc(PO_4, VO_4) was interpreted[18] in the *site*-group approach D_{2d}, and the same is true of the Raman spectra[19] of ScVO$_4$ and YVO$_4$ (the splitting at ν_4 does not agree).

X-Ray Analysis

For verification of formation of the mixed crystals we evaluated the photographs of the powdered samples of the reaction mixtures annealed at various temperatures from 1 000 to 1 300°C. The lattice parameters a and c of tetragonal system were calculated from the line having the indexes 200 and 112, respectively, the accuracy being sufficient for determination of the parameter changes depending on composition. Values of the lattice parameters (Table II) agree with the Vegard law, *i.e.* they are directly proportional to the phosphate and vanadate content in the mixed crystals. The lattice parameters of the pure components agree very well with literature data[9].

Infrared Spectra

ScPO$_4$, ScVO$_4$, YPO$_4$ and YVO$_4$ crystallize in tetragonal, space-centred non-symmorphous space group D_{4h}^{19}-I: $C_1(32)$, $2D_{2d}(4)$, $2C_{2h}(8)$, $2C_2(16)$, $C_s(16)$. Numbers

of formula units in elementary and primitive cells are $Z = 4$ and $Z_p = 2$, respectively. The experimentally found *site* symmetry D_{2d} of phosphate and vanadate anions agrees unambiguously with frequency of location of the anions and with the group requirements. Nine normal vibrations of the anion are realized in the group T_d in the representations $A_1 + E + 2F_2$. According to the standard correlation method we would expect, in the first approximation, a lowering of molecular symmetry T_d to *site* symmetry D_{2d} (for the anions correspondingly diluted in the mixed crystal) or, in the second approximation, an enhancement of *site* symmetry D_{2d} to the symmetry of the factor group D_{4h}, *i.e.* $A_1 \rightarrow A_{1g} + B_{2u}$, $A_1 + B_1 \rightarrow A_{1g} + B_{2u} +$ $+ A_{1u} + B_{2g}$, $B_2(IR) + E(IR) \rightarrow B_{1g} + A_{2u}(IR) + E_g + E_u(IR)$ (for the pure components).

TABLE I
Geometry of the anions

Compound $MeXO_4$	X—O pm	$(O—O)_{XO4}$ pm	Symmetry XO_4
$ScPO_4$	156	255	T_d
$ScVO_4$	176	271 and 292	D_{2d}
YPO_4	166	245 and 284	D_{2d}
YVO_4	164	270 and 268	T_d

TABLE II
Lattice parameters of the samples

$D_{4h}^{19} - I\,4_1/amd$	mol% PO_4	a, pm	c, pm
	100	687·4	602·7
	80	690·1	605·2
$Y(PO_4, VO_4)$	70	692·7	607·5
	40	700·7	616·0
	20	703·9	623·5
	0	708·9	628·4
	100	656·1	578·1
	80	659·9	583·0
$Sc(PO_4, VO_4)$	50	665·7	592·9
	30	672·1	602·2
	0	676·6	611·4

Table III

Vibration spectra of $Sc(PO_4, VO_4)$ and $Y(PO_4, VO_4)$ mixed crystals

mol%, PO_4	PO_4^{3-}				VO_4^{3-}	
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_3
$Sc(PO_4, VO_4)$						
100	990 sh	320, 365	1 020, 1 080, 1 110 sh	420, 515, 660		—
80		310, 370	1 030, 1 070	460 sh, 510, 655		845, 870, 900 sh
IR 50	990	310, 355	1 020, 1 070, 1 120	460, 520, 650		850, 870
30	985	315, 350	1 020, 1 075, 1 110	460, 535, 650		835, 910 sh
0	—	—	—	—		820, 920 sh
$Y(PO_4, VO_4)$						
100	990 sh	255, 345	1 030, 1 065, 1 095 sh	375 sh?, 525, 645		—
80	975	315, 340	1 025, 1 055, 1 085 sh	450, 525, 640		835, 855, 875
IR 70	975	320, 335	1 015, 1 050, 1 090 sh	460, 525, 640	900 sh	825 sh, 855
20	965	290, 315	1 015, 1 060, 1 085	460, 535, 635	890 sh	760, 835
0	—	—	—	—	885 sh	775, 835, 855 sh
RA $ScPO_4$	1 030	325, 335	1 045, 1 065	410, 475, 595		
YPO_4	1 000	290, 330	1 025, 1 060	480, 580, 660		

TABLE IV
Correlation table of subgroups of the group T_d

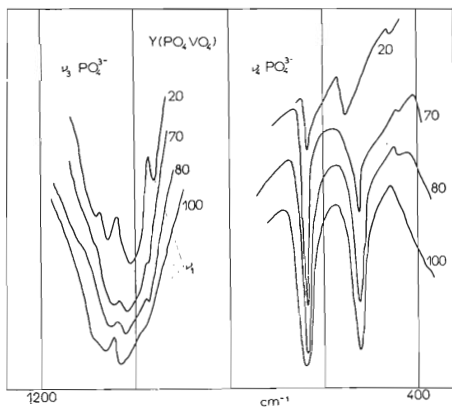| T_d (24)	D_{2d} (8)	S_4 (4)	D_2 (4)	C_{2v} (4)	C_2 (2)	S_1 (2)	C_1 (1)
ν_1, A_1 (RA)	A_1 (RA)	A (RA)	A (RA)	A_1 (IR, RA)	A (IR, RA)	A' (IR, RA)	A (IR, RA)
ν_2, E (RA)	A_1 (RA) B_1 (RA)	A (RA) B (IR, RA)	A (RA) A (RA)	A_1 (IR, RA) A_2 (RA)	A (IR, RA) A (IR, RA)	A' (IR, RA) A'' (IR, RA)	A (IR, RA) A (IR, RA)
$\nu_{3,4}, F_2$ (IR, RA)	B_2 (IR, RA) E (IR, RA)	B (IR, RA) E (IR, RA)	B_1 (IR, RA) B_2 (IR, RA) B_3 (IR, RA)	A_1 (IR, RA) B_1 (IR, RA) B_2 (IR, RA)	A (IR, RA) B (IR, RA) B (IR, RA)	A' (IR, RA) A' (IR, RA) A'' (IR, RA)	A (IR, RA) A (IR, RA) A (IR, RA)
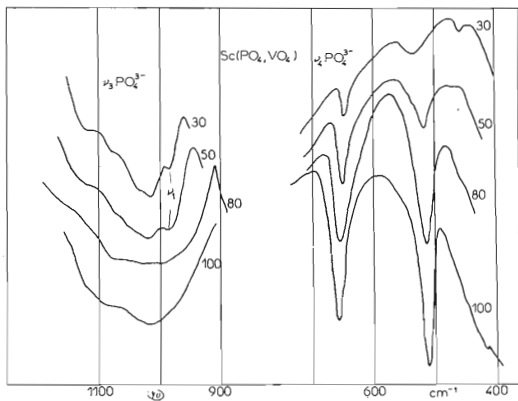
FIG. 1

IR spectra of Sc(PO$_4$, VO$_4$)

FIG. 2

IR spectra of Y(PO$_4$, VO$_4$)

From the table of infrared spectra of the mixed crystals (Table III) it can be seen that the mixed crystals containing 30% ScPO$_4$ and 20% YPO$_4$ (and similarly also the mixed crystals with higher phosphate concentration, *i.e.* 50% and 70% of phosphates, respectively) exhibit activation of ν_1 vibration, splitting and activation of ν_2, and further splitting of the vibrations ν_3 and ν_4. Thus the spectrum does not correspond to the presumed *site* symmetry. This fact was mentioned in our previous paper[5], and it was stated that the activation cannot be explained by standard (simple) way of interpretation of vibration spectra. However, the lowering of *site* symmetry can be accounted for in those groups in which lattice vibrations cause splitting and activation of internal vibrations. If in the symmetrized square of representation of degenerated vibration there exist such a representation to which a rotation or translation coordinate also belongs, then the lattice vibration of this representation can split or activate the respective internal mode. The corresponding separation of internal and lattice modes is, however, a physical prerequisite of this symmetry lowering. In the D_{2d} group the symmetrized square of representation of the degenerated vibration is $(\chi(E))_2 = A_1 + B_1 + B_2$. In the set of these representations there is B_2 which involves the translation T_z, *i.e.* lattice vibration of the type $T(B_2)$ which can split the degenerated vibration type E, and, in this way, lowering of *site* symmetry to effective *site* symmetry can occur. This theoretical possibility is fulfilled in the studied systems of mixed crystals in the case of samples Sc$((PO_4)_{0.5}(VO_4)_{0.5})$, Sc$((PO_4)_{0.3}(VO_4)_{0.7})$, Y$((PO_4)_{0.2}(VO_4)_{0.8})$, *i.e.* for a "diluted" PO$_4$ ion in site D_{2d}. From analysis of the infrared spectra (Table III, Figs 1 and 2) and with respect to the correlation table of subgroups of the group T_d (Table IV) it is thus obvious that the samples of mixed crystals exhibit effective *site* symmetry C_2 in spectrum of PO$_4$ anion. It was impossible to probe this lowering in spectra of VO$_4^{3-}$ anion with all the concentrations of the mixed crystals due to overlapping of absorptions of the vibration ν_3 and/or ν_1 with ν_3. If the not very distinct shoulder in the region of ν_3 is taken into account, then even for CO$_4^{3-}$ anion it is possible to state a *site* symmetry lowering at least to D_2 or C_{2v}.

In the mixed crystals with sufficiently diluted PO$_4$ content the D_{2d} *site* symmetry is lowered to effective C_2 irrespective of proper geometry T_d or D_{2d} of PO$_4^{3-}$ anion (Table I) which is higher than the effective *site* symmetry in the both cases. This finding confirms that a possible symmetry lowering in spectrum of 12 site groups[1] is due to lattice vibrations and not to a symmetry lowering resulting from deformation of the ions in crystal.

The infrared spectra of pure ScPO$_4$ and YPO$_4$ agree with neither the D_{2d} *site* symmetry (splitting and activation of ν_2) nor the D_{4h} factor symmetry, but they exhibit shoulders indicating a *site* symmetry lowering to effective C_2 which is markedly manifested in the corresponding mixed crystals.

The Raman spectra of the pure phosphates (except for the region of ν_3 vibration) also confirm $G_S \rightarrow G_{S\,eff}$.

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