INFRARED ABSORPTION SPECTRA OF $Ag_3[PO_4, VO_4]$ MIXED CRYSTALS

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$Ag_3[PO_4, VO_4]$ mixed crystals were prepared in the whole concentration region. For $0-40$ mol % vanadate, the mixed crystals are isostructural with the low-temperature modification of Ag_3PO_4 (T_d^4, $Z = 2$); the site group and factor group analysis was performed for this space group. Mixed crystals containing 60% vanadate and more are tetragonal with the structure of Ag_3VO_4. From the analysis of the infrared spectra it follows that in the cubic mixed crystal with 40 mol % Ag_3VO_4, the site symmetry T is additionally lowered to the effective site symmetry C_3 due to the effect of the lattice vibrations of the types $T(F)$ and $R(F)$.

Ag_3PO_4 crystallizes in two modifications. The structure of the low-temperature modification was determined first by Wyckoff[1], later by Masse, Tordjman and Durif[2]. The space group $T_d^4 - P\bar{4}3n$ was found, $Z = 2$, $a = 602\cdot6$ pm, $\varrho_{\text{X-ray}} = 6\cdot35$ g/cm³, Ag in the site symmetry S_4, P in T, O in C_3. The high-temperature modification is isostructural with the high-temperature form of γ-Na_3PO_4 (ref.[2]). For Ag_3VO_4 the structure has not been determined, only its d-values are known[3].

The infrared spectrum of Ag_3PO_4 has been studied by Bergmann and coworkers[4] and Corbridge and Love[5], and — in relations to the structure — by Steger and Schmidt[6]. The infrared spectrum of Ag_3VO_4 has only been shown pictorially[7]. The $Sr_3[PO_4, VO_4]_2$ and $Ba_3[PO_4, VO_4]_2$ mixed crystals have been studied, with respect to the $\nu_1(VO_4^{3-})$ vibration, by Baran and Aymonino[8].

Studying the infrared spectra of solids we are often not able to discriminate between the site symmetry effect (the so-called first approximation) and the factor symmetry effect (the so-called second approximation). The multiplication of the vibrations in the primitive elementary cell with $Z > 1$ appears only in a broadening of the vibrational bands. For a study of these effects separately it is convenient to investigate the spectrum of the pure substance and that of the substance highly diluted with another isostructural substance, the structure parameters of the components having to permit the formation of mixed crystals. Cubic mixed crystals possessing the structure of Ag_3PO_4 make possible the study of these effects and with regard to the site symmetry of the anions ($G_s \equiv T$) also the study of its additional lowering to the effective site symmetry $G_{s-\text{eff}}$. The correlation $G_s \rightarrow G_{s-\text{eff}}$ has not been studied

yet for any of the theoretically admissible G'_ss. The study of these correlations is the objective of this work.

The size of the anions PO_4^{3-} and VO_4^- is suitable for the formation of the Ag_3 $[PO_4, VO_4]$ mixed crystals. With low Ag_3VO_4 concentrations, the mixed crystals will possess the known structure of Ag_3PO_4, after exceeding a concentration limit they will probably possess the structure of Ag_3VO_4, which has not been so far identified.

EXPERIMENTAL

The samples were prepared by annealing the starting components Ag_2O, $(NH_4)_2HPO_4$, and V_2O_5 in the corresponding stoichiometric ratios at 400°C for 24 h. The density of Ag_3VO_4 and Ag_3PO_4 was determined pycnometrically with toluene. The technique of study of the mixed crystals employed in this work also served to confirm their composition. This composition follows from the absence of the diffraction lines of Ag_2O and from the absence of the absorption bands of polyanions from the spectra of all samples.

The X-ray diffraction analysis of the powder samples was performed on a diffractograph Geigerflex (Rigaku Denki, Japan), Cu anode, Ni filter, Geiger–Müller detector. For the cubic mixed crystals (0—40 mol % Ag_3VO_4), the d value indexing, calculation of the parameter, and selection of the acceptable space groups of the cubic system were carried out by employing an own program on a computer Tesla 200. The indexing of the other samples containing 50—100 mol % Ag_3VO_4 was performed in the tetragonal system by using the reciprocal lattice graphical method according to Gattow[9]. The lattice parameters were calculated by the least squares method.

The infrared spectra were measured on a grating spectrophotometer Perkin–Elmer 325 in KBr disks (13 mm diam.) in the region 4000—200 cm^{-1}.

RESULTS AND DISCUSSION

X-Ray Diffraction Analysis

The results of the X-ray diffraction analysis of the pure components as well as of the mixed crystals $Ag_3[PO_4, VO_4]$ are given in Tables I and II. The samples up to 40 mol% Ag_3VO_4 can be indexed in the cubic system, for the sample with 50 mol%, eleven diffraction lines could be indexed in the cubic system with $a = 600$ pm and nine lines in the tetragonal system with $a = 841$ pm, $c = 643$ pm. The samples with 60—100 mol% can be indexed in the tetragonal system. The Ag_3PO_4 lattice parameter $a = 601$ pm, $\varrho_{exp} = 6\cdot35$ g cm^{-3}, and $Z_{exp} = 1\cdot98$ found by us are in agreement with the published values[1,2].

The indexing of the cubic samples eliminates fourteen of the seventeen possible sets[10] of the cubic space groups, in the remaining three sets there are a total of nine primitive space groups, among them the space group $T_d^4 - P\bar{4}3n$, i.e. that of Ag_3PO_4. A variation of the elementary cell parameter is not observable, it lies within the limits of error of the parameter determination (Table I). From the spatial arrangement of

TABLE I

Lattice Parameters and Volumes of the Ag₃[PO₄, VO₄] Samples

Ag₃VO₄ mol %	Cubic a pm	Tetragonal a pm	Tetragonal c pm	$V \cdot 10^{-6}$ pm³
0	601 ± 1			217 ± 1
10	600 ± 1			216 ± 1
20	600 ± 2			216 ± 2
30	600 ± 1			216 ± 1
40	600 ± 1			216 ± 1
50	600 ± 1	841 ± 4	643 ± 2	[216 ± 1] [455 ± 6]
60		841 ± 4	651 ± 2	460 ± 6
70		857 ± 5	648 ± 3	476 ± 8
80		913 ± 4	652 ± 3	544 ± 7
90		911 ± 4	653 ± 3	542 ± 7
100		925 ± 5	695 ± 3	595 ± 8

TABLE II

Interplane Distances d, Relative Intensities I, and Indices hkl of the Ag₃[PO₄, VO₄] Samples

Ag₃PO₄, cubic			Ag₃[(PO₄)$_{0.5}$(VO₄)$_{0.5}$]				Ag₃VO₄, tetragonal		
d pm	I	hkl	d pm	I	hkl_{cub}	hkl_{tetrag}	d pm	I	hkl
424·7	20	110	424·7	12	110	(200)	459·5	20	200
301·5	20	200	324·1	6		002	347·7	8	002
268·8	100	210	318·4	6		211	288·2	100	310
245·3	40	211	299·6	18	200		275·3	100	202
212·0	5	220	277·8	6		300	254·7	24	320
190·1	15	310	268·0	100	210	(310)	230·8	20	400; 003
173·2	20	222	245·3	18	211		217·4	8	401
166·5	25	320	203·9	12		401	213·5	12	330
160·6	25	321	189·4	6	310		194·3	4	421
150·4	10	400	173·2	9	222		187·6	4	223
141·8	5	411; 330	166·3	12	320	(501)	177·0	20	501
134·3	7	420	159·4	9	321	(520)	168·8	16	520; 104
131·2	15	421	144·2	6	410	(530)	165·7	8	521
128·1	7	332	131·0	6	421		157·9	4	214
111·6	15	520; 432	123·2	6	422		156·4	4	530
110·0	7	521					154·5	4	423
							148·5	8	601; 304
							143·4	8	540; 503
							138·6	4	005; 541

the elementary cell it is apparent that in the case of the PO_4^{3-}/VO_4^{3-} ratio $1:1$ an arrangement occurs in the mixed crystal such that two PO_4^{3-} anions are no more adjacent and that the mutual neighbourhood of two and gradually also more VO_4^{3-} anions becomes possible. With this ratio, however, the structure converts from the cubic to the tetragonal one, and it can be seen from Table I that in this case a mixture of two mixed crystals (cubic and tetragonal) is present.

Ag_3VO_4 can be indexed in the tetragonal system with $a = 925$ pm, $c = 695$ pm, $\varrho_{exp} = 4.53$ g cm^{-3}, $Z_{exp} = 3.7$. None of the point groups from which the space groups of the tetragonal are derived can be eliminated based on the index extinction, only the 37 diffraction classes[11] of this system can be reduced to 29.

Infrared Spectra

The nine normal vibrations of the PO_4^{3-} or VO_4^{3-} anion are distributed in the point group T_d among the irreducible representations $A_1 + E + 2F_2$. Ag_3PO_4 crystallizes in the primitive cubic space group T_d^4, which can be written as $T_d^4 - P: C_1(24)$, $T(2)$, $D_2(6)$, $2S_4(6)$, $C_3(8)$, $3C_2(12)$, where the numbers of positions are given in parentheses (the T, D_2 and S_4 sites cannot be occupied multiply). For the location of the PO_4^{3-} or VO_4^{3-} possessing the own symmetry $T_d(G_M)$, all sites suit from the point of view of the subgroup, and only the site group $T(2)$ is appropriate from the point of view of the number of positions. The location is thus unique and is consistent with the results of the X-ray diffraction analysis. The factor group (G_F) of the nonsymmorphic space group T_d^4 is isomorphic with the point group T_d. The corresponding correlations, orders of the groups considered (h), and IR activity of vibrations for the symmetry descent $G_M \rightarrow G_S$, $G_S \rightarrow G_{S-eff}$ or ascent $G_S \rightarrow \tilde{G}_F$ are given in Table III. From the correlation table it follows that the increase of symmetry does not manifest itself in the IR spectrum. From the table of the wavenumbers (Table IV) it can be seen that the spectrum of Ag_3PO_4 conforms to the group T and at the same time to T_d. As the PO_4^{3-} ions are diluted in the mixed crystal, in the IR spectrum should appear the G_S or G_{S-eff}, i.e. the effective symmetry to that the

TABLE III

Correlation Table for the Groups T_d, T, and C_3

Vibration	$T_d \longrightarrow T \longrightarrow T_d$			$T \longrightarrow C_3$	
	$h = 24$	$h = 12$	$h = 24$	$h = 12$	$h = 3$
ν_1	A_1	A	$A_1 + A_2$		$A(IR)$
ν_2	E	E	$2E$		$E(IR)$
ν_3, ν_4	$F_2(IR)$	$F(IR)$	$F_1 + F_2(IR)$		$E(IR) + A(IR)$

TABLE IV
Infrared Spectra of the $Ag_3[PO_4, VO_4]$ Samples
Relative band intensity: vs very strong, s strong, m medium, w weak, sh shoulder.

Ag_3VO_4 mol %	PO_4^{3-}				VO_4^{3-}		
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_3	ν_2, ν_4
0	—	420 w?	1 010 vs	550 s	—	—	—
10	—	—	1 115 sh, 1 005 vs, b	560 s, b	830 sh	895—870 s, b, 720 w	415 w
20	980 sh	465 sh	1 025 vs, b	545 s	830 sh	890—850 s, b, 720 w	410 w, 360 sh
30	975 s	455 s	1 110 sh, 1 030 vs, 1 000 vs	625 w, 540 s	820 sh	870 s, b, 710 w	415 m, 380 w, 365 w, b
40	965 vs	465 m	1 105 sh, 1 050 s, 990 s	620 sh, 540 s	810 sh	880—870 s, 710 w	390 sh, 380 sh, 335 m
50	955 vs	460 m	1 050 s, 1 000 sh, 980 sh	620 sh, 540 s	805 s	870 vs, 690 s, b	390 sh, 365 m, 335 m
60	955 sh	450 sh	1 110 sh, 1 075 s, 990 sh	620 sh, 540 s	805 s, b	870 s, 710—670 s, b	400 sh, 365 m, 325 m
70	955 sh	475 sh	1 110 sh, 1 005 sh, 980 sh	615 sh, 545 m	820 sh	860 s, b, 710 m, b	365 m, 330 m
80	960 sh	?	1 110 m, 1 010 sh	615 sh, 550 sh	810 sh	855 vs, b, 745 m, b	365 s, 330 sh
90	965 s	?	1 110 m, 1 060 sh, 1 015 s	620 sh, 550 sh	?	855 s, 740 w, b	365 s, 335 m
100	—	—	—	—	?	850 s, 720 w, b	360 m

original G_S is reduced for some selected groups[12] due to the effect of the lattice vibrations; this can happen in case that the lattice vibrations possess values incomparable with those of the internal vibrations.

For the cubic mixed crystal with the highest content of Ag_3VO_4 (40 mol%), where the multiplication of vibrations in the factor group does not appear any more, the spectrum in the phosphate region corresponds to the symmetry C_3. This is the effective site symmetry, and this symmetry reduction $T \rightarrow C_3$ is due to the influence of the lattice vibrations[12] of the types $T(F)$ and $R(F)$; the degenerate E type vibration is not split, it is only activated, along with the A type vibration (Table III). This appears also in the spectral region of the vanadate. The lattice vibrations could not be identified due to the attempts to obtain reproducible Raman spectra having failed. $A_2(\text{ia}) + E(\text{RA}) + 4F_1(\text{ia}) + 4F_2(\text{IR, RA})$ optical lattice vibrations follow from the theory for an elementary cell of Ag_3PO_4 in T_d^4. However, although the optical lattice vibrations have not been determined, it follows unambiguously from the analysis of the infrared spectra of the cubic mixed crystals that a lowering of symmetry occurs corresponding to the correlation $T \rightarrow C_3$, hence $G_S \rightarrow G_{S-\text{eff}}$. Thus the symmetry lowering was experimentally confirmed for one of the site groups for which it had been predicted theoretically[12].

For the tetragonal mixed crystals, whose space group is not known and whose absorption bands are poorly resolved, a satisfactory analysis cannot be performed, i.e. the G_S or $G_{S-\text{eff}}$ and G_F cannot be determined based on the theory of groups. In the range of the vanadate ν_2 and ν_4 vibrations the individual vibrations cannot be discerned. With other vanadates the situation is alike[13,14].

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