THE INFRARED ABSORPTION SPECTRA OF MIXED $Ag_3[AsO_4, VO_4]$ CRYSTALS

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Mixed $Ag_3[AsO_4, VO_4]$ crystals were prepared over the whole concentration range. In the 0—40% mol. vanadate concentration range the mixed crystals are isostructural with Ag_3AsO_4 (T_d^4, $Z = 2$). Site- and factor-group analyses were carried out for this space group and structure. Above 60 mol% vanadate, the mixed crystals are tetragonal with Ag_3VO_4 structure. It follows from the behaviour of the $\nu_4AsO_4^{3-}$ vibration that, in cubic mixed crystals with 40 mol% Ag_3VO_4, the site-symmetry T is reduced to effective site-symmetry C_3 by the effect of lattice vibrations of the T(F) and R(F) types.

The infrared spectra of pure polycrystalline substances do not permit study of all the effects of crystal symmetry and this it is useful to study the spectra of mixed crystals. The possibility of studying these crystals considering crystal symmetry was mentioned briefly in a previous work[1] dealing with polycrystalline $Ag_3[PO_4, VO_4]$. This work deals with the $Ag_3[AsO_4, VO_4]$ system where the size of the AsO_4^{3-} and VO_4^{3-} anions permits the formation of mixed crystals.

For interpretation of the infrared spectra it is necessary to know the crystallographic data for the initial components. Helmholz and Levin[2] found cubic space group $T_d^4 - P\bar{4}3n$ ($Z = 2$, $a = 612$ pm) for Ag_3AsO_4. The structure of Ag_3VO_4 has not yet been determined, but the interplane distances in polycrystalline samples have been assigned indexes[1] in a tetragonal system ($Z = 4$, $a = 925$, $c = 695$). Differing structures of the initial substances appear as changes in the structure of the mixed crystal at a certain component ratio. The infrared spectrum of Ag_3AsO_4 has not been described in detail[3]; the spectrum of polycrystalline Ag_3VO_4 is given in work[1]. The infrared and Raman spectra of aqueous solutions of vanadates were given by Griffith and Wickins[4] and Griffith and Lesniak[5]. The spectra of mixed $Ag_3[PO_4, AsO_4]$ and $Ag_3[PO_4, VO_4]$ crystals were evaluated from the point of yiew[1,6] of site- and factor-group analysis and considering the effective site-symmetry.

Study of the infrared spectra of the pure substances and mixed crystals considering the effect of crystal symmetry, *i.e.* study of the correlation $G_M \rightarrow G_S \rightarrow G_F$ or $G_S \rightarrow G_{S-eff.}$, is the purpose of this work.

EXPERIMENTAL

Samples of mixed crystals and pure initial components were prepared by precipitation from an aqueous solution of sodium vanadate (V_2O_5 in NaOH solution) and Na_2HAsO_4 with a $AgNO_3$ solution at pH ~ 14. The high alkalinity of the solution is a condition for formation of VO_4^{3-} ions[5]; at lower pH values $V_2O_7^{4-}$ and $(VO_3)_n^{n-}$ ions are formed. The AsO_4^{3-} and VO_4^{3-} ratio changes in 0·1 mol steps over the whole concentration range. The precipitates obtained were dried in the air at laboratory temperature. Analysis of the infrared and X-ray spectra indicated that the samples did not contain polyanions.

X-ray analysis of powder samples was carried out on a Giegerflex difractograph from Rigaku Denki (Japan) with a Cu anode, Ni filter and a Geiger-Müller detector. Samples with 0—40 mol% Ag_3VO_4 were cubic and the *d* value indexing, determination of the lattice parameters and choice of possible space groups was carried out on a Tesla 200 computer using our own program[7]. Indexes were assigned to the other samples graphically by the reciprocal lattice method described by Gattow[8].

Infrared spectra were measured on a Perkin-Elmer 325 grating spectrophotometer using KBr pellets (13 mm in diameter) over the range 4000 — 200 cm^{-1}.

RESULTS AND DISCUSSION

X-*Ray Analysis*

The lattice parameters of the pure substances and mixed $Ag_3[AsO_4, VO_4]$ crystals found by X-ray analysis are given in Table I. Samples containing 0–40 mol% Ag_3VO_4

TABLE I

Lattice Parameters and Wavenumbers of the $\gamma_4AsO_4^{3-}$ Vibrations in $Ag_3[AsO_4, VO_4]$ Mixed Crystals

Ag_3VO_4 mol %	Cubic *a*, pm or tetragonal *a*, *c*, pm		$V \cdot 10^{-6}$ pm^3	Wavenumbers of the $\nu_4AsO_4^{3-}$ vibration, cm^{-1}
0	612 ± 1		229 ± 1	405 vs
10	613 ± 1		230 ± 1	405 vs, 380 sh
20	612 ± 1		229 ± 1	405 vs, 375 sh
30	613 ± 1		230 ± 1	405 vs, 370 vw
40	613 ± 1		230 ± 1	405 s, 385 s
50	612 ± 1		229 ± 1	405 s, 370 m
	692 ± 2	922 ± 3	588 ± 5	
60	693 ± 1	939 ± 2	611 ± 3	400 s, 380 s
70	691 ± 8	915 ± 9	578 ± 17	415 m, 395 m
80	693 ± 5	937 ± 7	608 ± 12	405 m, 385 m
90	687 ± 7	931 ± 9	595 ± 16	415 w, 395 w
100	702 ± 2	935 ± 4	614 ± 6	—

were assigned cubic indexes with lattice parameter $a \sim 612$ pm. Of the 17 possible sets of the cubic space groups[9], index assignment eliminates 14 sets of the cubic space groups; the remaining three sets include only primitive space groups. The 9 possible space groups include the T_d^4-P$\bar{4}$3n group, which is a space group in which the initial pure component Ag_3AsO_4 crystallizes[2]. A change in the lattice parameters of the cubic mixed crystals is not observable and is within experimental error. In samples containing 50 mol% Ag_3VO_4 a structural change from cubic to tetragonal occurs, probably resulting in a mixture of two mixed crystals, cubic with $a = 612$ pm and tetragonal with $a = 922$ and $c = 692$ pm. The lattice parameters of the samples with 60–90 mol% Ag_3VO_4 are listed in Table I. The Ag_3VO_4 sample was assigned tetragonal indexes with $a = 935$ and $c = 702$ pm. It was not possible to determine a single available diffraction class from quenching of indexes alone; only the number could be limited[1].

Infrared Spectra

Because of the coincidence of the $\nu_1VO_4 \sim \nu_3VO_4 \sim \nu_1AsO_4 \sim \nu_3AsO_4 \sim 800\ cm^{-1}$ and $\nu_2VO_4 \sim \nu_4VO_4 \sim \nu_2AsO_4 \sim 350\ cm^{-1}$ vibrations, only the $\nu_4AsO_4 \sim \sim 400\ cm^{-1}$ vibration can be employed for confirming correlation in mixed crystals. In addition to coincidence, strong and broad bands of degenerate vibrations make correlation difficult.

Theoretical analysis of the spectra of the AsO_4^{3-} species in Ag_3AsO_4 and in cubic mixed crystals with space group T_d^4 with site-symmetry T follows from the $G_M(T_d) \rightarrow \rightarrow G_S(T) \rightarrow G_F(T_d)$ or $G_S(T) \rightarrow G_{S\text{-eff}}(C_3)$ correlation. For deformation vibration δOAsO, $F_2(T_d) \rightarrow F(T) \rightarrow F_1 + F_2(T_d)$. The effective site-symmetry appears in splitting of F into two vibration active vibrations in the IR spectrum: $F(T) \rightarrow A + + E(C_3)$.

In cubic mixed crystals containing 40 mol% vanadate, where multiplication of the vibrations in factor group ($Z_p = 2$) does not appear, the deformation vibration band ν_4AsO_4 consists of two bands with maxima at 405 and 385 cm^{-1}. Increasing the content of Ag_3VO_4 increases the splitting of this vibration. In cubic mixed crystals this is a result of symmetry decrease $G_S(T) \rightarrow G_{S\text{-eff}}(C_3)$ as a result of lattice vibrations of the $T(F)$ and $R(F)$ types.* The spectrum of Ag_3AsO_4 in the infrared region (825, 770, 405, 380 sh, 345 sh) is basically in agreement with $G_{S\text{-eff}} \equiv C_3$. The numbers of active vibrations of the symmetry types considered in groups T and C_3 or T_d and C_3 are different and the experimental data favour group C_3.

Group analysis could not be carried out for tetragonal mixed crystals or for Ag_3VO_4 because of lack of knowledge of the space groups and because of coincidence of the VO_4^{3-} and AsO_4^{3-} vibrations.

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* The lattice vibrations could not be found because of the poor quality and irreproducible Raman spectra.

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